A Comparative Study on Effects of Two Kinds of Polymerization Methods on Grafting of Polymer onto Silica surface

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ABSTRACT: In this article we present the result of a comparative study of two kinds of polymerization methods—solution polymerization (sol. poly.) and dispersion polymerization (dis. poly.) for grafting polymer onto silica. As a model for the grafting polymerization reaction, styrene was chosen as the monomer and azo diisobutyronitrile (AIBN) as the initiator. The study aims at supplying theoretical reference for better selecting polymerization method to graft polymer on the silica particle surface. First, monolayers of 3-methacryloylpropyl trimethoxysilane were chemically bonded onto the surfaces of micrometer-sized silica gel particles, and so double bonds were immobilized onto the silica surface. Second, the copolymerizations between the immobilized double bonds and the monomer styrene were carried out, homopolymerizations of styrene followed, and finally polystyrene was grafted to the silica surfaces. Two kinds of polymerization methods, sol. poly. and dis. poly., were adopted respectively, and the effects of polymerization methods on grafting process were examined mainly. At the same time, the effects of different polymerization conditions on the grafting degree were researched. It was found that in the dis. poly. system the grafting degree is obviously higher than that in the sol. poly. system under the same polymerization conditions, and the grafting degree can go up to 47%, i.e. 47g/100g. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5808–5817, 2006

Key words: grafting polymerization; polystyrene; silica gel; grafting degree; dispersion polymerization; solution polymerization

INTRODUCTION

In recent years, composite materials with various properties are developed rapidly with the advancement of science and technology, and among them the hybrid organic/inorganic composite particle has attracted increasing attention. Through modifying the surface of micrometer- or nano-sized inorganic particles with polymer, the hybrid organic/inorganic composite materials with high performances can be obtained because of combining the advantageous properties of the two kinds of substances. Especially, grafting polymer onto inorganic particle surfaces can give the particles many new specific properties, such as amphiphilic property, photosensitivity, biological activity, dispersibility, adsorption ability, chelating property, and compatibility with organic substance, etc.[1–5] These surface-modified particles (by grafting polymer) have wide applications; for instance, they can be used for reinforcing and toughening of plastic, for stationary phases of the chromatogram, for heterogenous catalysts, for immobilizations of the enzymes, for separations of the biomacromolecules, for novel adsorption materials, for coats and lubricants with high property and so on.[2,6–12] In a word, it has become an important research subject to prepare functional composite particles by grafting polymer onto inorganic particle surfaces.

There are two routes to grafting polymer onto silica gel surfaces: one is "grafting from," i.e., polymerizing of monomer from active compounds (initiators, comonomers, and so on) covalently attached to the inorganic surface,[13] and the other is "grafting onto," i.e., producing a polymer on the inorganic particle surface via reacting of the end-group of the polymer with the functional groups of this surface, for instance, —OH, —NH₃, —COOH, and so on.[14] The first route has the advantage of high grafting degree,[15,16] and has generally become the most attractive way to prepare thick, covalently tethered polymer brushes with a high grafting density. Recent advances in polymer synthesis techniques have given rise to the importance of controlled/living free radical polymerization,[17–19] as it provides a number of advantages over traditional free radical techniques. The main advantages that a controlled/living free radical system provides for polymer brush synthesis are control over the brush thickness, via control of molecular weight and narrow polydispersities. Even so, the traditional free radical techniques still are adopted in grafting polymer onto silica sur-

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faces because of their applicability. Tsubokawa et al. introduced azo groups onto the silica surface, and prepared composite particles of PS/SiO$_2$ by using "grafting from" method in solution polymerization (sol. poly.) systems,[20] whereas Bourgeat-Lami and Lang[21,22] reported the synthesis of PS/SiO$_2$ composite particles by using "grafting from" method in dispersion polymerization systems in the presence of surface-functionalized silica particles using 3-(trimethoxysilyl) propylmethacrylate (MPS) as coupling agent. In the two kinds of grafting polymerization systems, solution grafting polymerization system and dispersion grafting polymerization system, the grafting polymerization reaction occurs directly between solid phase and liquid phase; the grafting polymerization occurs easier than in suspension and emulsion polymerization systems. So the two kinds of polymerization methods are often utilized for grafting polymer on solid surfaces. When "grafting from" is adopted, what effects will be produced on the grafting process by the different polymerization methods? With which of the two methods—dis. poly. and sol. poly.— higher grafting degree can be attained? About these aspects, no in-depth research has been reported in literature.

This article is mainly devoted to the study of the effect of polymerization methods on grafting polymer onto silicon gel particle surface as the way of "grafting from" is adopted. First, micrometer-sized silicon gel particles were modified chemically with coupling agent MPS, double bonds were immobilized on the surfaces, and then the grafting polymerizations of styrene were carried out with two polymerization methods, sol. poly. and dis. poly. While exploring the effect of polymerization methods on the grafting degree, the effects of other factors also were studied, such as the amount of the double bonds immobilized on the silica surfaces, the concentrations of the initiator and monomer, and polymerization time and polymerization temperature, and so on. Through this work, we expected to supply theoretical reference for preparing polymeric/inorganic composite particles using surface-grafting method.

EXPERIMENTAL

Material

3-Methacryloylpropyl trimethoxysilane (MPS) and styrene were distilled under *vacuo* prior to use. Silica gel was purchased from Ocean Chemical engineering Co., Qingdao, China. The particle size was 120–160 mesh (diameter, about 125 μm). Polyvinylpyrrolidone (PVP, chemical purity) was purchased from Beijing chemical reagent company. Toluene, ethanol, and all other chemicals were of analytical or chemical purity grades.

Apparatus

An 8400S Shimadzu FTIR spectrometer was used for IR analyses. A 438VP scanning electron microscope (SEM) from LEO company, UK, was used for observing the morphology of the particles.

Modifying silicon gel particle surface with MPS

Silicon gel (30 g) was placed in 150 mL of aqueous solution of methane sulfoacid with a concentration of 5%, activated for 4 h under stirring at 102°C, and after separation, washed with distilled water repeatedly, and dried under vacuum for 24 h. The activated silicon gel was added into ethanol; certain amount of MPS and a little water was also added. Under nitrogen, the reaction was carried out for 24 h at 50°C. After the reaction was over, the sample was washed with ethanol repeatedly to remove excess MPS, filtrated, dried under vacuum, and finally the surface-modified silicon gel MPS-SiO$_2$ was obtained. The content of double bonds immobilized on the silicon gel surface was determined with KBr-KBrO$_3$ method. By changing the concentration of MPS in the above-described reaction system, MPS-SiO$_2$ particles with varying contents of double bonds were prepared.

Grafting polystyrene by solution polymerization method

Solvent toluene, MPS-SiO$_2$, and styrene were added in turn into a four-necked flask equipped with a thermometer, a mechanical stirrer, an N$_2$ inlet, and a water condenser, and N$_2$ was purged for 30 min so as to eliminate air. In the inert atmosphere of N$_2$, the content of flask was first agitated for 1 h to disperse MPS-SiO$_2$ fully, then the temperature was increased up to the designated value, initiator AIBN was introduced, and the reaction was carried out at a constant temperature for a certain period of time. After the termination of polymerization, the mixture was filtrated, and the product was extracted with toluene in a soxhlet extractor for 20 h to remove the polymer nonattached chemically to the silica gel surfaces. The product was washed with ethanol, dried under vacuum, and finally the grafting degree (wt %) of the composite particles PS/SiO$_2$ was calculated with weighing method according to the following equation:

$$\text{Grafting degree} = \frac{(G_2 - G_1)}{G_1} \times 100\% \qquad (1)$$

where G_1 and G_2 are the weights of MPS-SiO$_2$ before and after grafting, respectively.

To examine the effects of various factors on solution grafting polymerization, the grafting polymerizations were performed under varying conditions, and these varying conditions include contents of the double bonds on the surface of MPS-SiO$_2$, monomer concentrations (the percentage of the solvent weight, wt %), added amounts of initiator (the percentage of the monomer weight, wt %), polymerization time and temperature.

Grafting polystyrene by dispersion polymerization method

The mixed solvent of ethanol and water, dispersant PVP, MPS-SiO$_2$, and styrene were added in turn into a four-necked flask. The grafting polymerization was carried out according to the procedure as mentioned in the grafting method of solution polymerization. The grafting degree of the composite particles PS/SiO$_2$ also was calculated.

Similarly, by varying polymerization conditions, the effects of various factors on dispersion grafting polymerization were researched, and except those conditions mentioned in the grafting method of solution polymerization, the dependences of the dispersion grafting polymerization on the solvent composition (ethanol/water, v/v) and the added amount of dispersant (the percentage of the monomer weight, wt %) were studied.
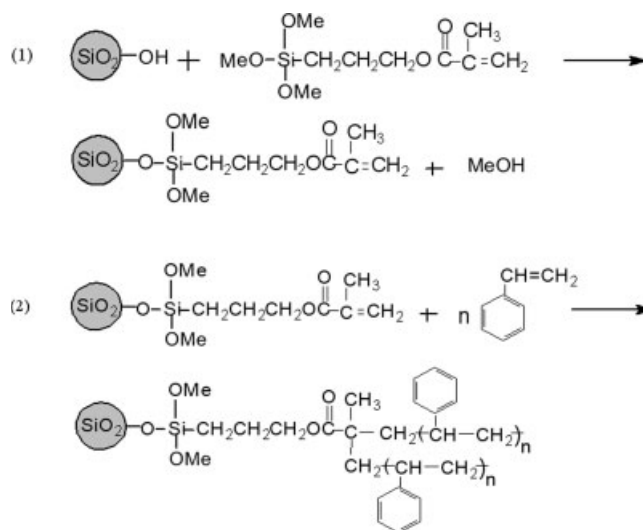
Characterization of the composite particles

The FTIR spectra of these particles, unmodified silica gel, modified silica gel MPS-SiO$_2$, and polystyrene-grafted silica gel PS/SiO$_2$, were measured on a spectrometer with press piece method. The morphologies of the particles before and after grafting polymer were observed, compared on an SEM, and typical samples were photographed.

RESULTS AND DISCUSSION

Reaction process to prepare composite particles PS/SiO$_2$

After activation, a great number of silanol groups are produced on the silica gel particle surfaces. These silanol groups react with MPS, and the surface-modified silica gel particles MPS-SiO$_2$ are formed. In this step, double bonds are introduced chemically onto the surfaces of silica gel particles. This enables it possible to graft polymer onto the surfaces of silicon gel particles by the way of ''grafting from,'' and finally the composite particles PS/SiO$_2$ are obtained. The reaction process to prepare composite particles PS/SiO$_2$ can be expressed as follows:

Characterization of composite particles PS/SiO$_2$

FTIR spectrum of PS/SiO$_2$

Figure 1 shows the spectra of three kinds of particles—unmodified silicon gel, modified silica gel MPS-SiO$_2$, and polystyrene-grafted silica gel PS/SiO$_2$. For the unmodified silica gel particles, the wide absorption band at 3433 cm^{-1} is correlative to silanol groups and adsorbed water. After surface modification of silica gel particles, the absorption at 3433 cm^{-1} is weakened, the absorption of the asymmetry stretching vibration of C—H bond appears at 2960 cm^{-1}, and the stretching vibration absorption of C=O bond of the carbonyl group at 1730 cm^{-1} and the stretching vibration absorption of C—O—C bond of the ester group at 1297 cm^{-1} appear, respectively. The appearances of these bands indicate that the reaction between MPS and silanol groups on silica gel particles has occurred, namely the chemical modification of the silicon gel surface has been realized, and particles MPS-SiO$_2$ have been obtained. After grafting polymerization, the framework vibration absorptions of the benzene ring at 1498 and 1452 cm^{-1} appeared. The band at 3100 cm^{-1} is the stretching vibration absorption of C—H bond of the benzene ring, and the band at 698 cm^{-1} is the characteristic absorption of the single substitution of the benzene ring. These results indicate that polystyrene has been grafted onto the surface of the silica gel particles, and the composite particles PS/SiO$_2$ have been obtained.

Morphology of particles PS/SiO$_2$

Figure 2(A and B) are the SEM photomicrographs of SiO$_2$ particles and the composite particles (PS/SiO$_2$) respectively. It is seen from Figure 2(A) that before
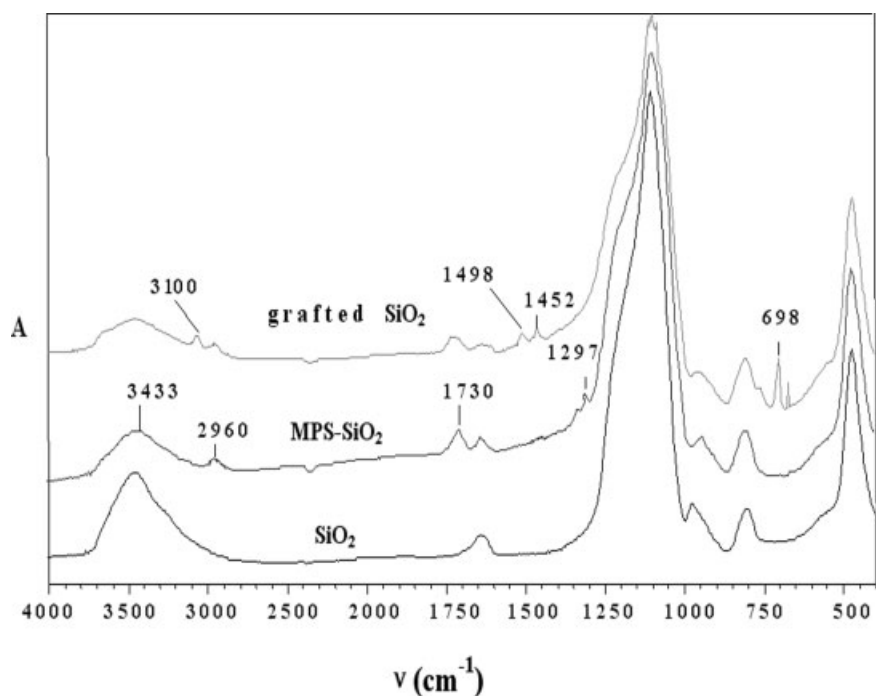
Figure 1 IR spectra of SiO$_2$, MPS-SiO$_2$, and PS/SiO$_2$.

grafting polymer, the surface of SiO$_2$ particle is rough and irregular, whereas Figure 2(B) shows that after grafting polymer, the surface of particle PS/SiO$_2$ becomes slippery because of the effect of filling up and covering of the grafted polymer layer.

Effect of polymerization method on grafting process

Under the same conditions, the grafting polymerizations of polystyrene on the surfaces of silica gel particles were carried out by adopting two kinds of poly-merization methods, sol. poly. and dis. poly., and Figure 3 shows the varying curves of the grafting degree with reaction time. First, it is seen that what-ever kind of the polymerization methods adopted, at the beginning stage of polymerization the grafting degree increases with time; when the polymeriza-tions are carried out to a certain time, about 5 h for dis. poly. and about 7 h for sol. poly., the grafting degrees nearly no longer change with time. How-ever, in fact there still are a lot of initiator and monomers in the reaction system and the polymer-ization reaction still continues.[8] How can this behav-
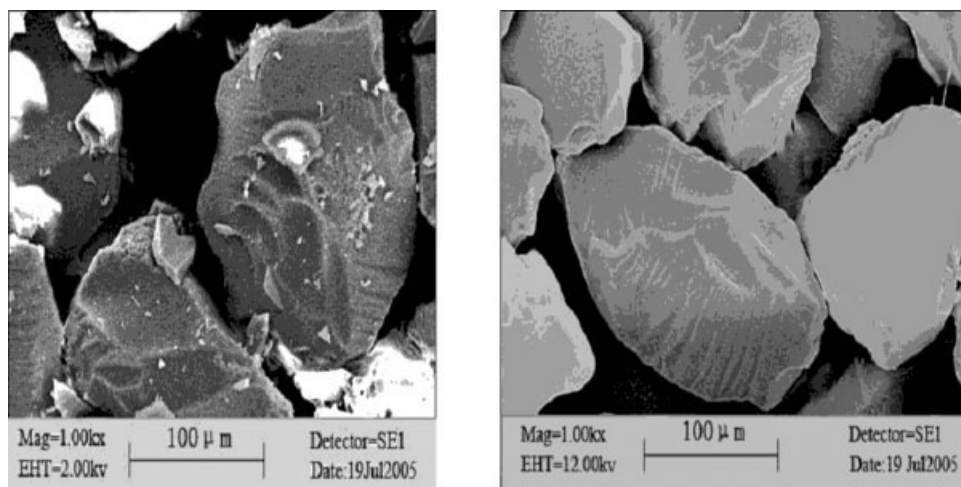
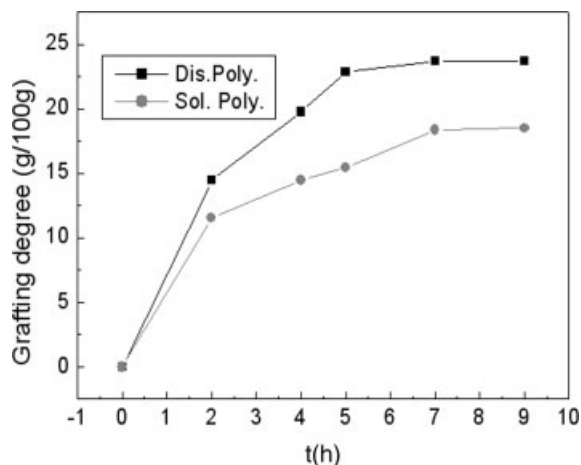**Figure 2** SEM photographs of SiO$_2$ and PS/SiO$_2$.

Figure 3 Varying of grafting degree with time of grafting reaction. Amount of double bond, 2.13 mol/g; amount of initiator, 2%; concentration of monomer, 10%; temperature, 70°C; in addition, for dispersion polymerization – the amount of dispersant, 3%; composition of solvent, ethanol/water = 6 : 1 (v/v).

ior of the grafting polymerization appear? Some scholars have given a reasonable explanation.[8,23,24] The grafting reaction may be separated into two steps. At first, growing chains or monomer molecules have to diffuse to the surface to react with the double bonds of the MPS monolayer. After this, the new attached chain continues to grow by adding further monomer molecules, and grafted polymer is formed. However, a kinetic barrier will be built up as soon as the density of the attached macromolecules reaches a value at which the polymer coils start to overlap. Further molecules of monomers or growing chains that will be attached to the surface have to diffuse through this layer. The diffusion process becomes more and more unfavorable, and after a certain point no more polymer molecules are added to the layer. So it can be assumed that as soon as grafted polymer chains start to overlap, a ''kinetic hindrance'' will be formed and will block the accessibility of monomers and growing chains toward the surface initiating site and propagating end, so that the grafting degree becomes constant at the middle and last stages of the polymerization reaction and part of the double bond sites are covered by the dense layer of grafted polymer. To increase the grafting degree further, Tsubokawa et al. put forward a new mode of ''grafting from'' reaction:[20] first the monomers having pendant azo groups are grafted onto silica surface; then vinyl monomers are post-grafted by initiating the azo groups of polymer chains grafted onto the silica surface, and hyper-branched polymers grafted onto the silica surface are obtained and the grafting degree reaches 120%. The mechanism of kinetic barrier formation by grafted polymer is shown in Figure 4.

It still can be seen from Figure 3 that under the same reaction conditions, the grafting degree in the dis. poly. system is higher than that in the sol. poly. system, and this should be attributed to the special mechanism of the dis. poly. During the grafting polymerization process, the hindrance for grafting reaction not only is from the overlapping and entwisting polymer layer grafted onto the silica gel surfaces, but also is from the polymers adsorbed physically into the layer. In other words, the polymers (homopolystyrene) independent of silica particles in the solution also participate in the building of kinetic barrier by physical adsorptions between solid phase (silica gel) and liquid phase (solution), and this makes the overlapping polymer layer denser. In the sol. poly. system, the macromolecules (homopolystyrene) independent of silica particles always are dissolved in the solvent no matter how long the macromolecule chains are; these macromolecules with longer chains are very easy to be adsorbed into the overlapping polymer layer on the silica surface, so that the kinetic hindrance is strengthened. But in the dis. poly. system, at the beginning stage of the polymerization reaction the status is analogous to the sol. poly. system, however, when the polymers reach the critical chain length, the polymers (homopolystyrene) separate at once from the medium, and are suspended in the system by the aid of the effect of the dispersant. Obviously, although there also is the physical adsorption of polymer at the interface of solid/liquid, it is not possible that the macromolecules with the chain longer than the critical chain length are adsorbed, so that in the dis. poly. system, the kinetic hindrance caused by the physical adsorp-
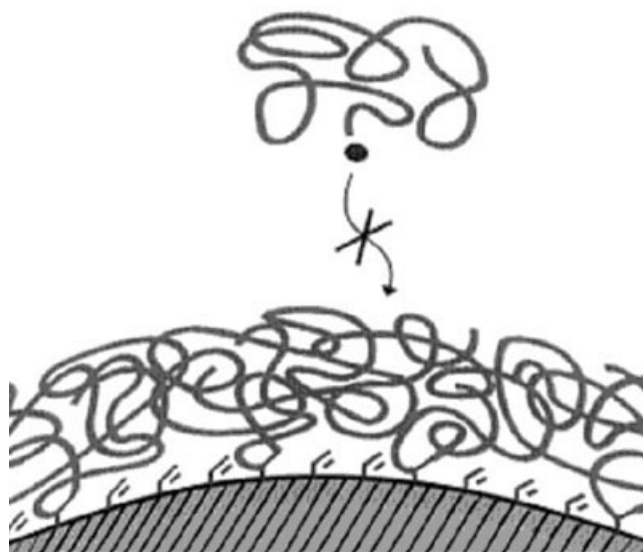

Figure 4 Schematic representation of the kinetic barrier attached polymers for polymer radicals to reach the immobilized double bonds.
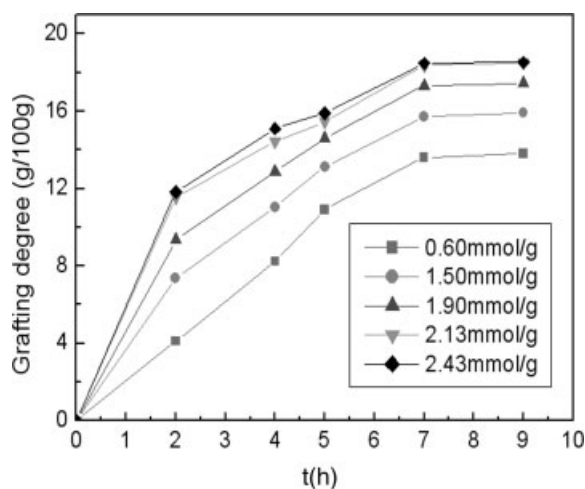
Figure 5 Varying of grafting degree with reaction time as used modified silica with different amount of double bond in solution polymerization system. Amount of initiator, 2%; concentration of monomer, 10%; temperature, 70°C.
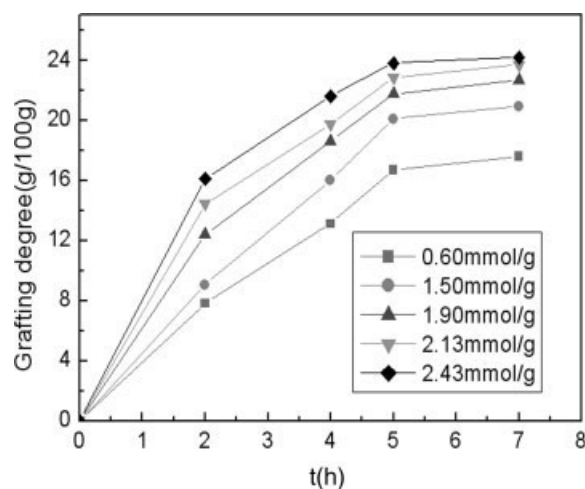

Figure 6 Varying of grafting degree with reaction time as used modified silica with different amount of double bond in dispersion polymerization system. Amount of initiator, 2%; concentration of monomer, 10%; temperature, 70°C; amount of dispersant, 3%; composition of solvent, ethanol/water = 6 : 1 (v/v).

tion is much weaker than that in the sol. poly. system. It was also found that in the dis. poly. system the polymers extracted out with toluene in the soxhlet extractor were much fewer than that in the sol. poly. system. Besides, in the sol. poly. system the macromolecular dissolving causes increasing viscosity of the reaction medium, and this caused the difficulty for the monomers to diffuse toward the silica surface. Based on the above description, this article puts forward the following viewpoint or conclusion: the kinetic hindrance for grafting polymerization onto solid surfaces in the dis. poly. system is weaker than that in sol. poly. system, and so the rate of the grafting reaction in the dis. poly. system is faster than that in the sol. poly. system and the former has higher grafting degree than the latter under the same reaction conditions.

period of time, the grafting degree in the dis. poly. system is higher than that in the sol. poly. system. To display the these rules more clearly, by taking the same time, the curves of the grafting degree data from Figures 5 and 6 versus the contents of the bonds on the surface of MPS-SiO$_2$ particles are plotted, and Figure 7 is obtained. The explanation for the rules can be given as follows.

When MPS-SiO$_2$ particles with the low content of the double bonds are used, the rate of the grafting reaction will speed up with the increase of the double bonds on the silica surface, and so the grafting degree augments observably with the increase of the double bond contents. When the content of the double bonds on MPS-SiO$_2$ reaches a bigger value, the
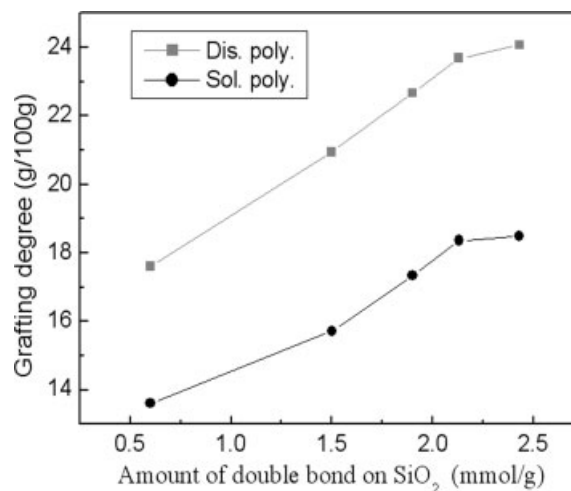
Effect of other factors on grafting process

Effect of double bond content

Figures 5 and 6 show the varying curves of grafting degree with time as MPS-SiO$_2$ particles with different double bond contents are used in the two kinds of polymerization systems, dis. poly. system and sol. poly. system, respectively. Three rules can be seen from Figures 5 and 6: when MPS-SiO$_2$ particles with the low content of the double bonds are used, in the same period of time the grafting degree augments remarkably with the increase of the double bonds; when the content of the double bonds on MPS-SiO$_2$ reaches a bigger value, the grafting degree augmentation with the increase of the double bonds becomes gentle; when MPS-SiO$_2$ particles with the same content of the double bonds are used and in the same

Figure 7 Varying of grafting degree with amount of double bond on MPS-SiO$_2$. Reaction time, 7 h.
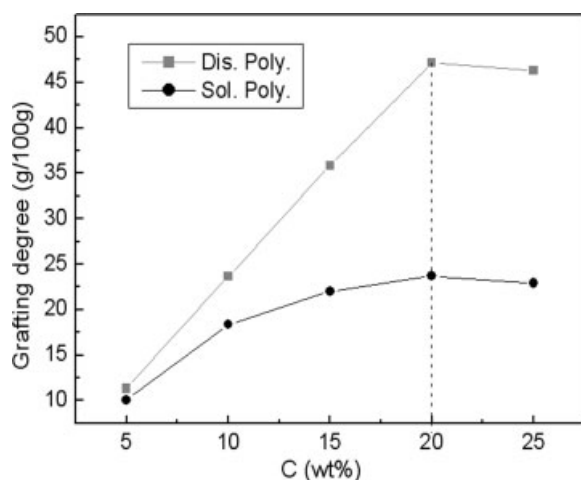
Figure 8 Effect of concentration of monomer on grafting degree. Amount of double bond, 2.13 mol/g; amount of initiator, 2%; temperature, 70°C; reaction time, 7 h.

overlapping and enwinding polymer layer will form in a shorter period of time because of faster grafting reaction rate, and so the grafting degree augmentation turns gentle with the increase of the double bonds. From the conclusion deduced in the section of effect of polymerization method on grafting process that the rate of the grafting polymerization reaction in the dis. poly. system is faster than that in the sol. poly. system, it can be understood completely that when MPS-SiO$_2$ particles with the same content of the double bonds are used and in the same period of time (5 h), the grafting degree in the dis. poly. system is higher than that in the sol. poly. system.

Effect of monomer concentration

Figure 8 shows the varying curves of grafting degree with the monomer concentrations in the two kinds of polymerization systems, dis. poly. system and sol. poly. system, respectively. Three rules can be seen clearly from Figure 8: when the concentrations of the monomer are lower, the grafting degree enhances remarkably with the increase of the monomer concentrations in the same period of time (7 h); when the concentrations of the monomer go up to a certain value, the grafting degree trend toward decreasing; as the same monomer concentrations are used, the grafting degree in the dis. poly. system is much higher than that in the sol. poly. system. The corresponding interpretations for these experimental facts can be given as follows. When the monomer concentrations are lower, the increase of the monomer concentrations will result in obvious acceleration of the grafting reaction, and the increase of the monomer concentrations also is advantageous to forming the grafting polymer with high molecular weight, and so in the same period of time (7 h), the higher the

monomer concentration, the greater the grafting degree is. When the concentration of the monomer goes up to a certain value (about 20%), the grafting degrees reach a tiptop (47% for the dis. poly. system and 24% for the sol. poly. system). Thereafter, further increase in the concentration of the monomer will result in too fast a rate of grafting reaction, and will lead to rapid formation of the dense overlapping and enwinding polymer layer, so that the grafting degrees trend to decrease in the same period of time. According to the conclusion drawn in the section of effect of polymerization method on grafting process that the rate of the grafting reaction in the dis. poly. system is faster than that in the sol. poly. system, it can be comprehended entirely that as the same monomer concentrations are used, the grafting degree in the dis. poly. system is much higher than that in the sol. poly. system in the same period of time.

Effect of initiator concentration

Figure 9 displays the varying curves of grafting degree with the initiator concentrations in the two kinds of polymerization systems respectively. There also are three rules in Figure 9: when the concentrations of the initiator are lower, the grafting degrees in the same period of time (7 h) enhance sharply with the increase of the initiator concentrations; when the initiator concentrations are over a certain value (1.5% for the dis. poly., 2.5% for the sol. poly.), contrarily, the grafting degree decreases obviously, and a maximum value appears on the grafting degree curves; when the same initiator concentrations are used, the grafting degree in the dis. poly.
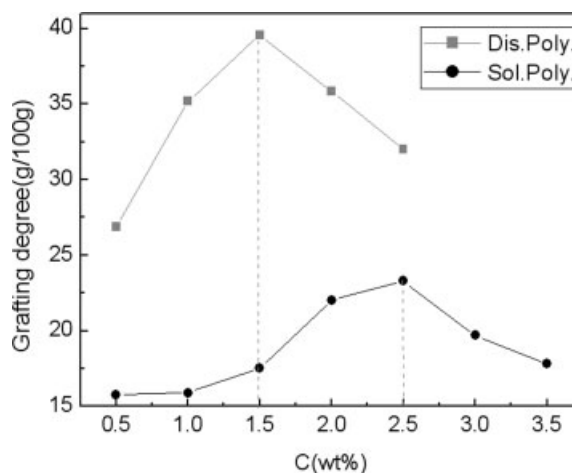

Figure 9 Effect of concentration of initiator on grafting degree. Amount of double bond, 2.13 mol/g; concentration of monomer, 15%; reaction time, 7 h; temperature, 70°C; in addition, for dispersion polymerization, amount of dispersant, 3%; composition of solvent, ethanol/water = 6 : 1 (v/v).
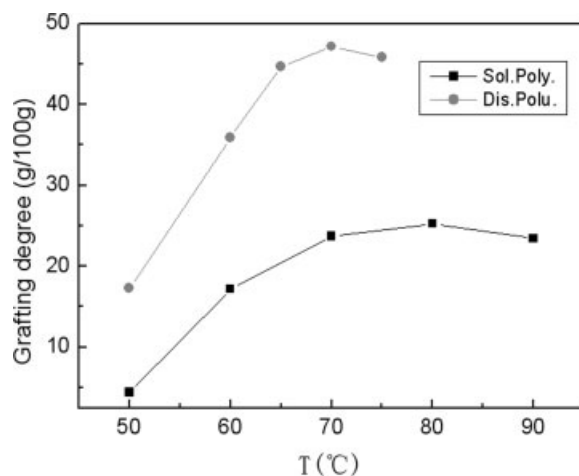
Figure 10 Effect of temperature on grafting degree. Amount of double bond, 2.13 mol/g; concentration of monomer, 15%; reaction time, 7 h; amount of initiator, 2%; composition of solvent, ethanol/water = 6 : 1 (v/v); amount of dispersant, 3%.

system is much higher than that in the sol. poly. system. The above-mentioned experiment results can be analyzed as follows. When the used amounts of the initiator are small, the increase in the initiator amount will be conducive to the increase in the number of the radical, and the grafting reaction will speed up remarkably; so in the same period of time (7 h) the grafting degrees enhance rapidly with the increase of the initiator concentrations. When the used amounts of the initiator are very great, the grafting reaction occurs too rapidly, so that in a very short time the dense overlapping and enwinding polymer layer will form on the silica surface. Besides, the greater the used amount of the initiator, the lower the molecular weight of the polymer, and the production of the grafted polymers with low molecular weight will lead to the formation of more dense overlapping polymer layer.[8] The dense ''kinetic wall'' formed prematurely will block the grafting polymerization reaction badly. In addition, as the used amounts of the initiator are very great, the chain transfer reaction of active chain toward the initiator is easy to occur, and the grafting polymer chains will rupture and terminate easily. So several reasons lead to that the grafting degree decreses obviously with the increase of the initator concentrations as the used amounts of the initiator are very great. By utilizing the conclusion drawn in the section of effect of polymerization method on grafting process that the rate of the grafting reaction in the dis. poly. system is faster than that in the sol. poly. system, it can be explained fully that as the same initiator concentrations are used, the grafting degree in the dis. poly. system is much higher than that in the sol. poly. system in the same period of time.

Effect of temperature

Figure 10 displays the varying curves of grafting degree with the reaction temperature in the two kinds of polymerization systems respectively. It is indicated clearly that at the beginning, the grafting degree increased rapidly with the rising of the temperature because of the fast grafting reaction caused by the acceleration of the decomposing reaction of the initiator. When the temperatures are over a certain value (70°C for the dis. poly., 80°C for the sol. poly.), further rising of the temperature leads to the decrease of the grafting degree; the reason for this is partly similar to the analysis in the section of effect of initiator concentration. In addition, as the temperatures are too high, the chain transfer reaction will speed up, leading to chain rupture of the grafted polymer,[25] and these are all disadvantageous to the increase of grafting degree. Analogously, in Figure 9 it is also shown that at the same temperature and in the same period of time, the grafting degree in the dis. poly. system is much higher than that in the sol. poly. system because of the faster grafting reaction in the former system.

Further discussion on dispersion polymerization

Effect of solvent polarity

The compositions of the solvent were varied in series by changing the volume ratio of ethanol to water. Figure 11 shows the varying curve of the grafting degree with the composition of the solvent. When the volume ratio of ethanol to water increases, initially the grafting degree increases sharply and then decreases, and when the ratio is equal to 6 : 1, a maximum value (47.5%) appears on the grafting
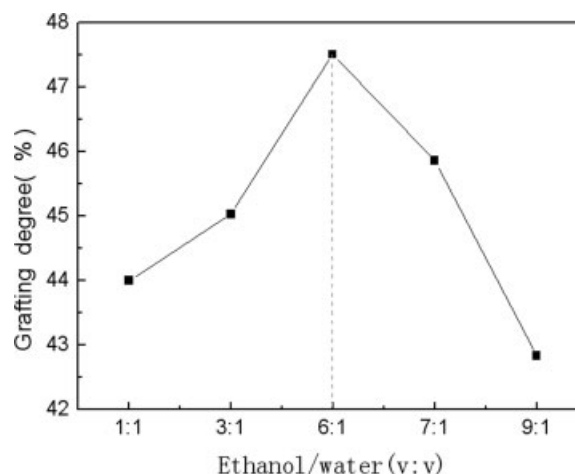

Figure 11 Effect of solvent polarity on grafting degree. Amount of double bond, 2.13 mol/g; concentration of monomer, 15%; reaction time, 7 h; amount of initiator, 2%; amount of dispersant, 3%.

degree curve. Why will the rule appear? As the content of ethanol in the solvent increases, the solvent polarity weakens, and its dissolving ability for polystyrene is strengthened. The strengthened dissolution ability of the solvent for polystyrene will produce two opposite actions for the grafting degree. Because the dissolving property of the solvent for polystyrene is strengthened, the grafted polystyrene is easy to swell and the active chains become more stretched, so that it becomes easier for the monomers to approach the grafted active chains, which will lead to the increase of the grafting degree. On the other hand, the strengthened dissolution property of the solvent for polystyrene increases the critical length of polymer dissolved, so that the physical adsorption of macromolecules on the silica surface is strengthened and the resistance of the grafting reaction is increased, and this will lead to the decrease of the grafting degree. It can be considered that when the volume ratio of ethanol to water is less than 6 : 1, the first action is dominant, and so the grafting degree enhances with the increase of the volume ratio of ethanol to water, whereas when the volume ratio of ethanol to water is more than 6 : 1, the second action is predominant, and so the grafting degree decreases with the increase of the volume ratio of ethanol to water. The experiment results show that the suitable volume ratio of ethanol to water is 6 : 1 when polystyrene is grafted onto the silica surface with dis. poly. method and by using the mixture of ethanol and water as the solvent.

Effect of used amount of dispersant

The added amounts of the dispersant were varied in series, and Figure 12 shows the varying curve of the grafting degree with the used amount of the dispersant PVP. It is also seen that initially the grafting degree increases and then decreases with the increase of the used amount of the dispersant, and a maximum point appears on the grafting degree curve at 3%. Why will the rule appear? There also are two opposite factors for the grafting degree. When the added amount of the dispersant increases, the protective action of the dispersant for the polymers separated from the medium is strengthened, the polymers can be suspended fully in the medium, the depositing of the separated polymers onto silica surface is avoided, and this is advantageous to the grafting polymer. On the other hand, the viscosity of the solution will be enhanced with the increase of the added amount of the dispersant, the resistance for the monomer to diffuse toward the silica surface will be increased, and this is disadvantageous to the grafting reaction. It can be assumed that when the added amount of the dispersant is less than 3%, the
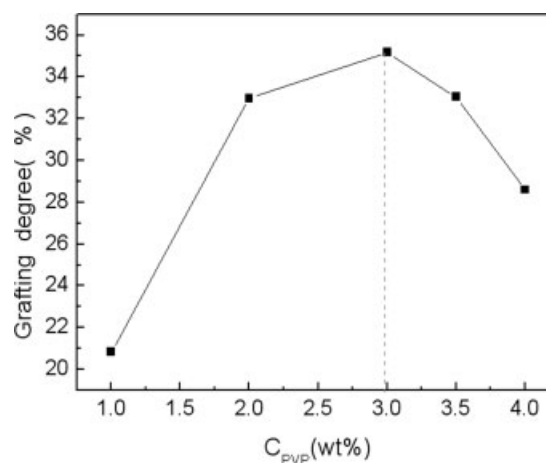

Figure 12 Effect of dispersant content on grafting degree. Amount of double bond, 2.13 mol/g; concentration of monomer, 15%; reaction time, 7 h; amount of initiator, 2%; composition of solvent, ethanol/water = 6 : 1 (v/v).

first action is predominant, and so the grafting degree enhances with the increase of the added amount of the dispersant, whereas when the added amount of the dispersant is more than 3%, the second action is regnant, so the grafting degree decrease with the increase of the added amount of the dispersant.

CONCLUSIONS

In this article, grafting of polystyrene onto the surface of silica gel particles is performed by adopting the way of ''grafting from'' and by using two kinds of polymerization methods, sol. poly. and dis. poly. Whatever kind of polymerization method is utilized, the grafting degree becomes constant at the middle stage of the polymerization because of the blocking of the initiating sites and propagation ends on the surface by grafted polymer chains. However, in the dis. poly. system the kinetic barrier formed by the overlapping and enwinding layer of the grafted polymer is much smaller than that in the sol. poly. system owing to lack of physical adsorption of longer macromolecules into the layer, which is homopolystyrene forming in the medium of sol. poly., so that the rate of the dispersion grafting polymerization is faster than that of the solution grafting polymerization, and under the same conditions, the former has greater grafting degree than the latter. Besides, regarding the effects of other factors on the grafting degree, such as concentrations of the monomer, concentrations of the initiator, and polymerization temperature, all of them have the positive influence on the grafting degree only to a certain extent because of the formation of the kinetic barrier. In the dis. poly. system, the solvent polarity and the used

amount of the dispersant also have great influences on the grafting degree, and their effects on the grafting degree can be divided into two types, positive effect and negative effect. When the two factors are taken to be suitable, they will play an active role in the enhancing of grafting degree.

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