Colloid Polym Sci (2008) 286:553–561
DOI 10.1007/s00396-007-1800-z

ORIGINAL CONTRIBUTION

Preparation of two kinds of chloromethylated polystyrene particle using 1,4-bis (chloromethoxy) butane as chloromethylation reagent

Chunling Lü · Baojiao Gao · Qing Liu · Changsheng Qi

Received: 23 July 2007 / Revised: 9 October 2007 / Accepted: 8 November 2007 / Published online: 10 December 2007

Abstract By adopting “grafting from” manner, polystyrene was grafted onto the surface of silica gel particles with an average size of 125 μm in a solution polymerization system, and grafted particle PSt/SiO_2 was prepared. Using 1,4-bis (chloromethoxy) butane (BCMB, it is nontoxic.) as chloromethylation reagent, chloromethylation reaction for the grafted particle PSt/SiO_2 was performed in the presence of Lewis acid catalyst $SnCl_4$. At the same time, cross-linked styrene-divinylbenzene copolymer (CPS) microsphere also was chloromethylated with the same reagent as PSt/SiO_2, so that two kinds of chloromethylated polystyrene particles were obtained, and they are chloromethylated grafted particle (CMPS/SiO_2) and chloromethylated cross-linked polystyrene (CMCPS) microsphere, respectively. The chemical structures and compositions of the two particles were characterized using Fourier transform infrared and Volhard method. The effects of various factors on the chloromethylation reactions were mainly investigated. The experimental results show that the process to prepare the two kinds of chloromethylated polystyrene particles not only has the character of environment friendness and low cost but also is convenient to control via adjusting various reaction conditions. The main reaction conditions affecting the chloromethylation reactions are reaction time, the added amount of BCMB, and the used amount of solvent and catalyst. They influence the reaction in two respects: (1) the chloromethylation degrees of polystyrene are different under different conditions; (2) Friedel–Crafts cross-linking reaction between polystyrene macromolecules is accelerated or inhibited under different conditions (for CPS microsphere, this cross-linking reaction also is called the additional cross-linking). Under suitable conditions, the two kinds of chloromethylated polystyrene particles with a high chlorine content (about 17%, this chlorine content was calculated based on polystyrene weight) can be gained using $SnCl_4$ as catalyst and CH_2Cl_2 as solvent at room temperature for 10 h and basically without cross-linking or additional cross-linking.

Keywords Polystyrene · Chloromethylation · Silica gel · 1,4-bis (chloromethoxy) butane · Graft polymerization

Introduction

Chloromethylated cross-linked polystyrene (CMCPS) microsphere is an important precursor of many functional polymer microspheres. Using CMCPS microspheres as starting materials, various functional polymer microspheres can be obtained via further macromolecular reactions due to the high chemical activity of chloromethyl groups ($-CH_2Cl$). Therefore, CMCPS microsphere has wide applications in various fields. For example, it can be used as a support in solid-phase synthesis and combinatorial chemistry [1–3], it can be used to prepare ion-exchanging resin, chelating resin, and adsorption resin [4–7], it can be used as a support of catalysts and reagents in organic synthesis [8–10], and it can be used in the preparation of functional polymer microspheres used in the immobilization, separation, and purification of biomacromolecules, as well as in chromatographic fixed phase [11–13], etc. Apparently, the preparation of CMCPS microsphere should be developed greatly based on its wide applications.

C. Lü · B. Gao (✉) · Q. Liu · C. Qi
Department of Chemical Engineering, North University of China,
Taiyuan 030051, People’ s Republic of China
e-mail: gaobaojiao@126.com

At present, there are mainly two methods to prepare CMCPS microsphere. One is the reaction of cross-linked styrene-divinylbenzene copolymer (CPS) microsphere with chloromethyl ether (CME) or bis-chloromethyl ether (BCME) in the presence of a Lewis acid [14, 15], and another is the copolymerization of p-chloromethyl styrene (CMS), styrene, and divinylbenzene [16, 17]. However, CME and BCME have serious carcinogenic toxicity, and in fact, the first method has been limited for a long time over the world. The second method is expensive because of high price of CMS (400$ per kg [15]), and large-scale preparation of CMCPS microsphere with CMS is therefore unattractive. Considering these drawbacks of the two methods, some new ways to prepare chloromethylted polystyrene microsphere need to be developed. In this work, using 1,4-bis (chloromethoxy) butane (BCMB) as chloromethylation reagent, which is non-carcinogenic and inexpensive [18], two kinds of chloromethylted polystyrene particles were prepared: (1) In the presence of Lewis acid catalyst, CPS microspheres were allowed to be reacted with BCMB, and CMCPS microspheres were obtained; (2) first, styrene was grafted onto the surface of silica gel particles with “grafting from” manner resulting in formation of grafting particles PSt/SiO_2, then, the grafted polystyrene was chloromethylated using BCMB as the chloromethylation reagent, and finally, the composite particles CMPS/SiO_2 were obtained, on which chloromethylated polystyrene (CMPS) was attached chemically. The composite particle CMPS/SiO_2 not only has chemical modificability like as CMCPS microspheres but also has the excellent mechanical property and thermal stability, which are attributed to SiO_2 particles. It can be predicted that the composite particle CMPS/SiO_2 will replace CMCPS microsphere in various application fields, and furthermore, it will display better service performance.

To obtain the two kinds of the chloromethylated particles with high chloromethylation degree and without obvious cross-linking caused by Friedel–Crafts reaction, which is disadvantageous to the application performance of the chloromethylated particles, in this study, a detailed research on the chloromethylation reaction process was carried out. To our knowledge, the new way to obtain chloromethylated polystyrene particles described in this work has not been reported up to now.

Experimental

Materials and equipment

Cross-linked polystyrene (CPS) microsphere (Tenlong Chemical Ltd, Changchou, China), namely, cross-linked styrene-divinylbenzene copolymer microsphere, with 4% of crosslinking degree and 0.315–0.45 mm in diameter, was received. Silica gel with an average diameter of 125 μm (120–160 mesh) was supplied by Ocean Chemical Ltd (Qingdao, China). Styrene (St, Denfeng Chemical reagent Plant, Tianjing, China) was of analytical grade and was purified by distillation under vacuum before use. Azo-diisobutyronitrile (AIBN, Shanghai Chemical reagent plant), γ-methacryloylpropyl trimethoxysilane (MPS, Chuangshi Chemical Aux Ltd, Nanking, China), and anhydrous tin tetrachloride ($SnCl_4$, Yuanli Chemical Ltd, Tianjin, China) were all of analytical grade. Other reagents were all commercial chemicals with analytical pure grade. BCMB was prepared by us [18].

A Perkin-Elmer 1700 infrared spectrometer (Perkin-Elmer, USA) was used for Fourier transform infrared (FTIR) analyses, A 438VP scanning electron microscope (SEM, LEO, UK) was used for observing the morphology of the grafting particles, a Netzsch STA449 thermogravimetric analyzer (GTA, Netzsch, Germany) was used for GTA analysis, and a calorimetric meter of oxygen-bomb type made in China was used for analysis of chlorine element with Volhard method.

Preparation and characterization of CMCPS microsphere

The chloromethlation reaction of CPS microsphere was carried out in a thermostatic four-necked flask of 100 ml fitted with a reflux condenser, stainless-steel stirrer, and thermometer. Accurately weighted CPS microspheres (about 3 g) and a certain amount of solvent CH_2Cl_2 were added, and the CPS microspheres were allowed to be fully swelled for a period of time. Then, a certain amount of BCMB and catalyst $SnCl_4$ were added (the status of the used amounts of various reagents will be discussed in the “Results and discussion”). The reaction was conducted with stirring at room temperature (25°C) for a certain period of time. After ending the reaction, the product mixture was treated with diluted hydrochloric acid and filtrated to remove the catalyst. The product microspheres were washed adequately with dioxane to remove residual organic solvent and then washed repeatedly with distilled water until without chloride ions. After being dried under vacuum, CMCPS microspheres were obtained. The infrared spectra of CMCPS microspheres and CPS microspheres were measured with KBr pellet method, respectively, to confirm the structure changes. To determined chlorine contents, the sample of CMCPS microspheres was first burned out in an oxygen bomb [19] and chlorine element contained in the sample was fully transformed into chloride ions. Volhard method was adopted to analyze the chlorine contents (wt%).

To explore the effects of various factors on the chloromethylation reaction, the reactions were performed under various conditions, respectively, such as with the different added amounts of chloromethylation reagent BCMB and with the different used amounts of the solvent and catalyst.

Preparation and characterization of CMPS/SiO_2 particle

Preparation and characterization of grafting particle PSt/SiO_2

According to the procedure described in [20], grafted particle PSt/SiO_2 was prepared in the manner of “grafting from” in a solution polymerization system. The typical process is as follows: first, silica gel particles were activated with aqueous solution of methane sulfoacid at 102°C for 4 h; then, activated silica gel particles were allowed to be reacted with coupling agent MPS at 50°C for 24 h using ethanol as solvent, and surface-modified silica gel particles were obtained denoted as MPS–SiO_2; finally, the graft polymerization of styrene onto the surface of MPS–SiO_2 particles was carried out. The grafting polymerization was conducted in a four-necked flask equipped with a reflux condenser, mechanical stirring, thermometer, and N_2 inlet. Solvent toluene, styrene, and MPS–SiO_2 particles were added in turn, and the mixture was stirred and the particles were fully dispersed. As the temperature increased up to 80°C, initiator AIBN was added to this mixture. Under inert gas of N_2, the graft polymerization was carried out at a constant temperature of 80°C for 7 h while being stirred. After finishing the reaction, the product particles were extracted for 20 h in a soxhlet to remove the free polymer physically adsorbed on the surface of the product particles. After drying, grafted particles PSt/SiO_2 were gained. The grafting degree (g/100 g) of PSt/SiO_2 was determined with thermogravimetry. The PSt/SiO_2 particles used in this study have a grafting degree of 17.30/100 g. The infrared spectrum of PSt/SiO_2 particle was measured, and its morphology was observed with scanning electron microscope (SEM).

Chloromethylation of grafting particles PSt/SiO_2 and characterization

Accurately weighted PSt/SiO_2 microspheres (about 3 g) and solvent CH_2Cl_2 were added into a four-necked flaks fitted with a mechanical stirrer, reflux condenser, and thermometer, and the PSt/SiO_2 particles were allowed to be fully swelled for a period of time, followed by the additions of BCMB and $SnCl_4$ (the status of the used amounts of various reagent will be discussed below). The chlorometholation reaction was carried out at room temperature (25°C) for a certain period of time. After finishing the reaction, the product mixture was washed with diluted hydrochloric acid to remove the catalyst. After filtrated, the product particles were washed adequately with dioxane to remove organic solvent and then washed repeatedly with distilled water until in the absence of chloride ions. After being dried under vacuum, CMPS/SiO_2 particles were gained on which chloromethylated polystyrene was attached chemically. The chlorine content of CMPS/SiO_2 particle was determined with the combination of oxygen bomb combustion and Volhard method, and the chlorine content was calculated based on the weight of grafted polystyrene. At the same time, the FTIR of CMPS/SiO_2 particle was measured with KBr pellet method.

To explore the effects of various factors on the chloromethylation reaction of the grafted particle PSt/SiO_2, the reactions were conducted under various conditions, such as with the different added amounts of chloromethylation reagent BCMB and with the different used amounts of the solvent and catalyst.

Results and discussion

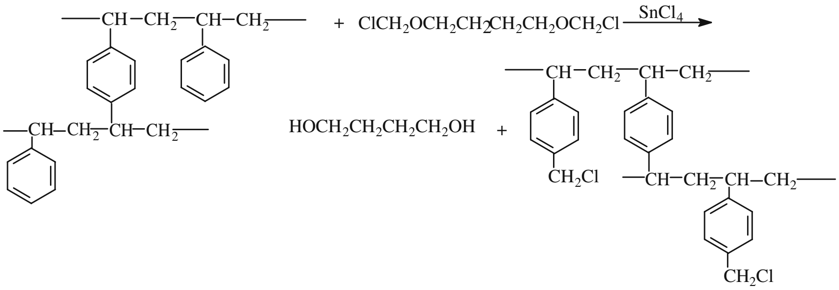
Preparation process and characterization of CMCPS microspheres

Using 1,4-bis(chloromethoxy) butane as chloromethylation reagent and in presence of $SnCl_4$, cross-linked polystyrene (CPS) microspheres were chloromethylated at para-position of benzene ring to form CMCPS microspheres, and the reaction process is expressed schematically in Scheme 1.

Chloromethyl group is a chemically active group. Along with the chloromethylation reaction of CPS microspheres, Friedel–Crafts reaction between polystyrene macromolecules will occur, leading to additional cross-linking, as shown in Scheme 2. This additional cross-linking is a reaction process to lose chlorine due to the deprivation of HCl during the cross-linking reaction. The possibility of the additional cross-linking increases with enhancement of chloromethylation degree of CPS microspheres. The additional cross-linking reaction not only leads to the decrease of chloromethylation degree of CPS microspheres but also increases the cross-linking degree, which will influence the subsequent functional modification reaction for the CMCPS microspheres. Therefore, it is necessary to control reaction conditions to avoid the occurrence of the additional cross-linking as far as possible.

Figure 1 gives the FTIR spectra of CPS and CMCPS microspheres. In the spectrum of CPS, the bands at 3,024, 1,600, 1,492, 1,452, 756, and 700 cm^{-1} are the characteristic absorptions of polystyrene, and the band at 828 cm^{-1} is the vibration absorptions of =C–H bond of benzene ring after binary substituting caused by the incorporation of divinyl benzene. After chloromethylating reaction, some

Scheme 1 Schematic illustration of preparing process of CMCPS microsphere



absorption changes have occurred in the spectrum of CMCPS: (1) Two new bands at 1,421 and 670 cm^{-1} have appeared, and they are the characteristic absorptions of the chloromethyl group $–CH_2Cl$. The band at 670 cm^{-1} corresponds to the stretching vibration of C–Cl bond, and the band at 1,419 cm^{-1} is corresponding to the bending vibration of $–CH_2$ in $–CH_2Cl$. (2) Besides, a new band at 1,263 cm^{-1} have appeared, and the band at 828 cm^{-1} is strengthened, which is attributed to the vibration absorptions of =C–H bond of benzene ring after binary substituting caused by the substitution of hydrogen atoms at the para-position of benzene rings by groups $–CH_2Cl$. These absorption changes indicate that the hydrogen atoms at the para position of benzene ring of polystyrene have been substitutes by chloromethyl groups, fully confirm that CPS microsphers have been chloromethylated, and suggest that CMCPS microsphers have been prepared.

Preparation process and characterization of CMPS/SiO_2 particles

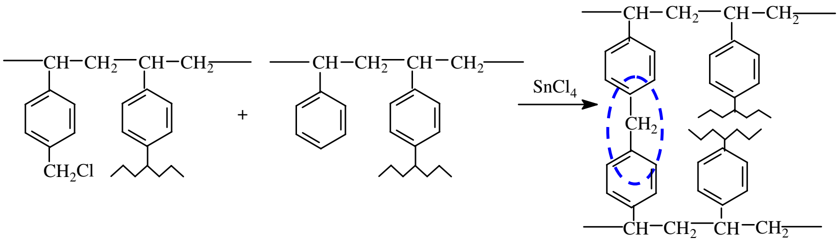
After being activated for silica gel particles, a great quantity of silanol groups is produced on their surfaces, and then MPS reacts with these silanol groups to form modified silica gel, designated as MPS–SiO_2 on which polymerizable double bonds are attached chemically. In the presence of initiator, polystyrene is grafted onto silica gel in the manner of "grafting from" to form grafted particles PSt/SiO_2. By using BCMB without carcinogenic toxicity [18] as chloromethylation reagent and in the presence of Lewis acid catalyst, the chloromethylation reaction of the grafted polystyrene of PSt/SiO_2 is carried out, resulting in the formation of composite particles CMPS/SiO_2. The total process to prepare CMPS/SiO_2 particles is shown in Scheme 3.

As mentioned above, chloromethyl group is an active group. In addition, Lewis acid catalyst also is the catalyst of Friedel–Crafts reactions. Therefore, along with the chloromethylation reaction of particles PSt/SiO_2, the Friedel–Crafts reaction between the grafted polystyrene macromolecules will occur as shown in Scheme 2, leading to the formation of cross-linking (but it is not the additional cross-linking like as in the case of CMCPS). The cross-linking bridge between macromolecules will affect subsequent functional modification of CMPS/SiO_2. Therefore, the Friedel–Crafts reaction also needs to be controlled.

Figure 2a and b shows the SEM images of SiO_2 particles and the grafted particles PSt/SiO_2, respectively. It can be seen from Fig. 2a that, before graft polymerization, the surface of the bare SiO_2 particles is rough and irregular, whereas after graft polymerization, the surface of particle PSt/SiO_2 becomes smooth because of the effect of filling up and covering of the grafted polymer layer as Fig. 2b shown.

Figure 3 displays the FTIR spectra of PSt/SiO_2 and CMPS/SiO_2 particles. In the spectrum of PSt/SiO_2, in addition to the absorption bands of SiO_2, there are the characteristic absorptions of polystyrene, such as the bands at 3,028, 1,580, 1,499, 1,450 and 710 cm^{-1}. Only because the strong background of the absorption bands of SiO_2 exists, all the characteristic absorptions of polystyrene become weaker, and so much as some bands cannot be displayed. As compared with the spectrum of PSt/SiO_2, in the spectrum of CMPS/SiO_2, there are two new bands to be

Scheme 2 Schematic illustration of Friedel–Crafts cross-linking reaction between PSt chains



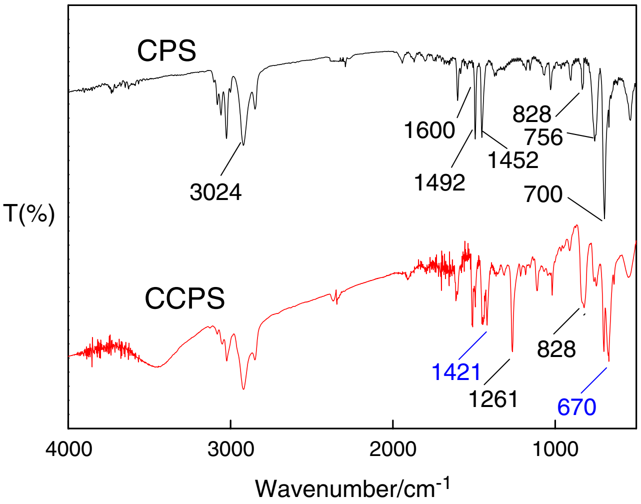


Fig. 1 FTIR spectra of CPS and CMCPS microsphere

produced, and they are at 1,423 and 818 cm^{-1}. The former is ascribed to the characteristic absorptions of chloromethyl group –CH_2Cl, and the later is attributed to the vibration absorptions of =C–H bond of benzene ring after binary substituting caused by the substitution of hydrogen atoms at the para-position of benzene rings by groups –CH_2Cl. The above changes of the absorptions reveal that the grafted polystyrene on PSt/SiO_2 has been chloromrthylated and the composite particles CMPS/SiO_2 have been obtained.

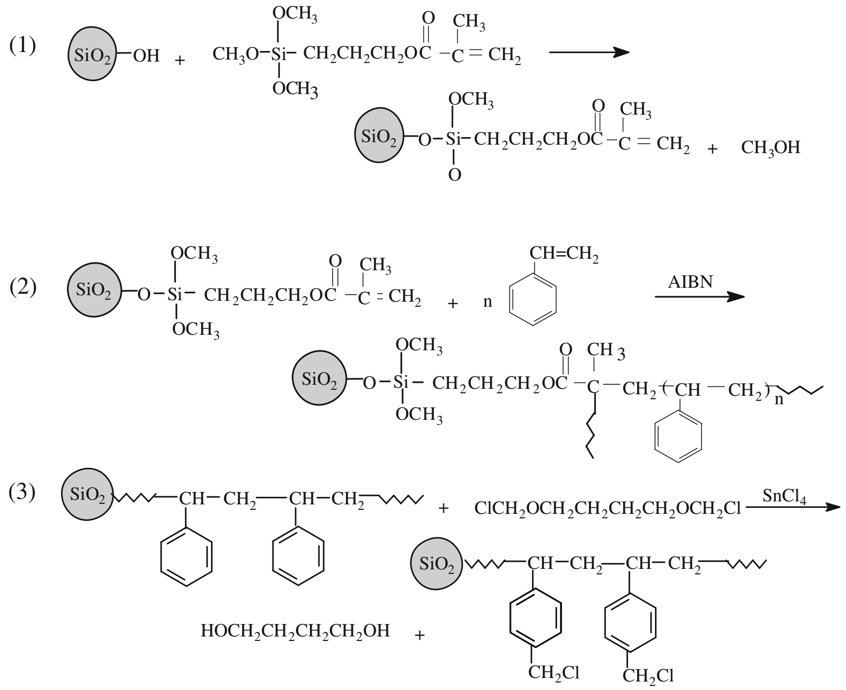
Effect of various factors on chloromethylation reaction of CPS microsphere

Effect of the used amount of BCMB

By varying the used amount of the chloromethylation reagent BCMB, chloromethylation reactions of CPS microspheres were carried out, and Fig. 4 shows the dependence of chlorine content of CMCPS microspheres on time as different amounts of BCMB are used.

It can be found that, at the initial stage, the chlorine content increase rapidly with reaction time; then, the increase becomes smooth as after a certain time; finally, the chlorine content turn to decrease. A vertex appears on the curve, and this is a signal that indicates that the additional cross-linking reaction between polystyrene macromolecules has been occurred obviously. At the initial stage, because the concentration of BCMB is very high, the chloromethylation reaction at para-position of benzene ring for CPS microspheres is carried out with a high rate, resulting in rapid enhancement of the chlorine content. However, along with the increase of the chlorine content, Friedel–Crafts cross-linking reaction between macromolecules turns to be easy to occur. As described before, the Friedel–Crafts cross-linking reaction is a process to loss chlorine. Therefore, after a certain reaction time, the increase of the chlorine content tends to be smooth because of the neutralization of chlorine loss. When the process to

Scheme 3 Schematic illustration of preparing process of CMPS/SiO_2 particles



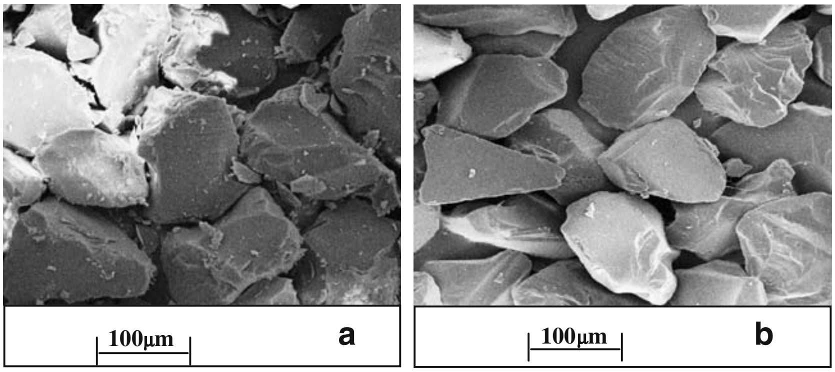


Fig. 2 TEM photographs of SiO_2 and PSt/SiO_2 particles

loss chlorine turns to be predominant over the chloromethylation process, the chlorine content will began to decrease. This above reason leads to the character with a maximum for the curve of chlorine content vs time. The vertex occurrence implies that Friedel–Crafts cross-linking reaction has occurred obviously. Therefore, to obtain the CMCPS microspheres with high chloromethylation degree and without obvious additional cross-linking, the reaction time needs to be control effectively.

By comparing the three curves in Fig. 4, it can be observed that on the left side of the vertex, in the same period of time, the chlorine content of the product is higher as the concentration of BCMB is greater. This fact accords with general kinetics rule, namely, the higher the reactant concentration, the rapider the reaction rate. It still can be found that the higher BCMB concentration, the shorter the time when the vertex occurs. This is caused by rapid Friedel–Crafts cross-linking reaction. Therefore, to obtain the CMCPS microspheres with high chloromethylation degree and without obvious additional cross-linking, the used amount of BCMB should be controlled. Basing on experimental results, we consider that the suitable added amount of BCMB should be 1.5 times more than theoretic amount (i.e., expected chlorine content) or lower. In this study, with the suitable amount of BCMB, the CMCPS macrospheres with about 16 wt% of chlorine content can be obtained in 10 h as displayed in Fig. 4 (13 ml of BCMB).

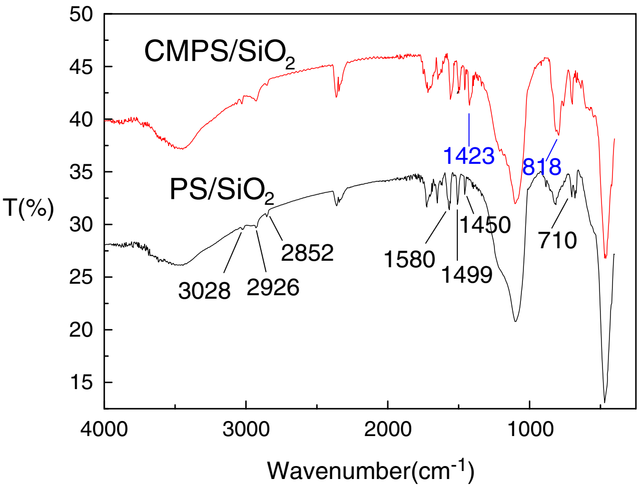


Fig. 3 FTIR spectra of PSt/SiO_2 and CMPS/SiO_2 particles

Effect of the used amount of solvent

By varying the used amount of CH_2Cl_2 and fixing other reaction conditions, chloromethylation reactions of CPS microspheres were carried out, and Fig. 5 gives the dependence of chlorine content of CMCPS microspheres on time as different amounts of CH_2Cl_2 are used.

It can be seen clearly that for 3 g of CPS microspheres, the chlorine content of the product in the same period and the time when the maximum appears are different for the different used amounts of solvent CH_2Cl_2: (1) the chlorine content of the product is the highest as 30 ml of solvent CH_2Cl_2 is used, and the chlorine content maximum appears in 8–12 h; (2) whereas as 20 ml of CH_2Cl_2 is used, the chlorine content is lower; (3) the chlorine content of the product is the lowest as 40 ml of CH_2Cl_2 is used, and the chlorine content maximum appears in 15–18 h.

As the used amount of solvent is lower (20 ml), the cross-linking networks of CPS microspheres cannot be

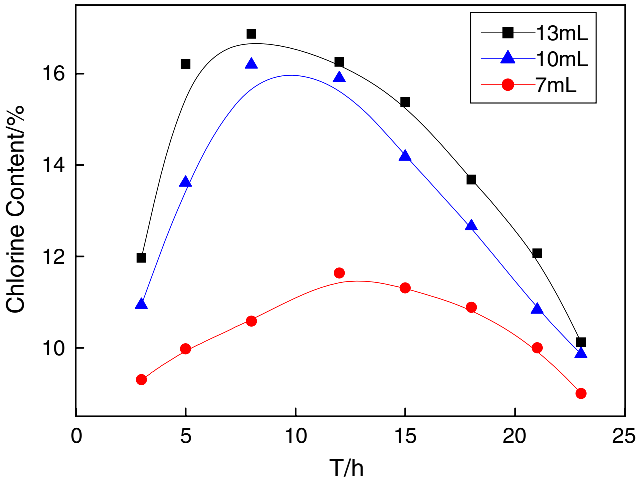


Fig. 4 Plot of chlorine content of CMCPS microsphere vs time with different BCMB amounts. CPS microsphere, 3 g; temperature, 25°C; CH_2Cl_2, 30 ml; $SnCl_4$, 1.5 ml (0.013 mmol)

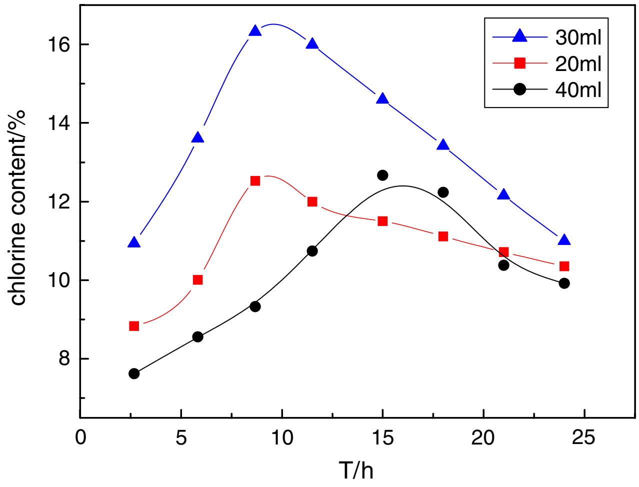


Fig. 5 Plot of chlorine content of CMCPS vs time with different solvent amounts. CPS microsphere: 3 g; Temperature: 25 °C; BCMB: 13 ml; $SnCl_4$: 1.5 ml (0.013 mmol)

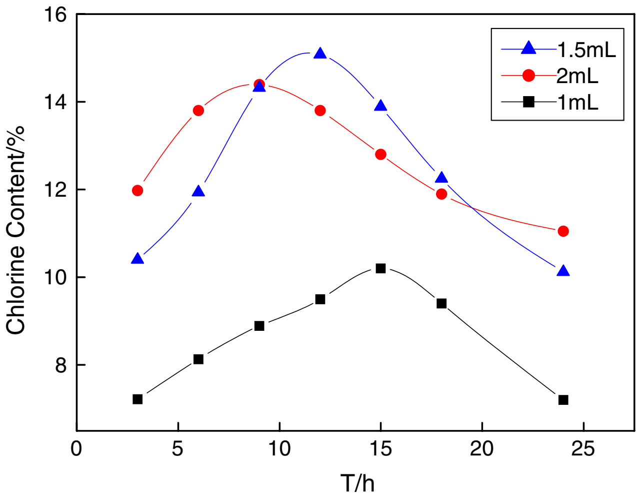


Fig. 6 Plot of chlorine content of CMCPS vs time with different catalyst amounts. CPS microsphere, 3 g; temperature, 25°C; BCMB, 13 ml; CH_2Cl_2, 30 ml

fully swelled; the chloromethalation reaction is nor easy to be carried out, resulting in the lower chlorine content in the same period. As the used amount of solvent is greater (30 ml), the cross-linking networks of CPS microspheresthe can be fully swelled, and they become adequately extended. This enables the active reaction sites to be fully exposed, and it is greatly advantageous to the chloromethylation reaction, resulting in the highest chlorine content in the same period. Whereas as the used amount of solvent is increased further (40 ml), the chlorine content in the same period turns to decrease because of diluted effect for the reactant BCMB. The above described reason leads to the interlacing up and down for the three curves as shown in Fig. 4. It also can be found that the greater the used amount of solvent is, the longer the period in which the maximum chlorine content is attained, namely, the time when Friedel–Crafts cross-linking reaction obviously occur is prolonged. This is another display of the diluted effect. As the solvent amount is very great, the networks of CPS are swelled enough and become quite extended so that the space between chains becomes greater, and it makes the additional cross-linking reaction difficult to occur, resulting in the longer time when vertex appears. By this token, to obtain the CMCPS microsphere with high chloromethylation degree and without obvious additional cross-linking, the used amount of the solvent also needs to be selected rightly. Apparently, for the studied system, the suitable used amount of CH_2Cl_2 is 30 ml.

Effect of catalyst amount

By varying the used amount of catalyst (1, 1.5, and 2 ml) and fixing other reaction conditions, chloromethylation reactions of CPS microspheres were performed, and Fig. 6 gives the dependence of chlorine content of CMCPS microspheres on time as different amounts of catalyst were used. By comparing the three curves in Fig. 6, it can be observed that on the left side of the vertex, the chlorine content in the same period is higher as the catalyst amount is greater. This accords with the general kinetics rule, namely, the greater the catalyst concentration is, the rapider the reaction rate. It still can be found from Fig. 6 that the greater the catalyst amount is, the shorter the time corresponding to the maximum, namely, the time when Friedel–Crafts cross-linking reaction has occurred obviously. The reason for this is that the catalysis action of $SnCl_4$ for Friedel–Crafts cross-linking reaction is stronger as more catalyst is used. Interleaving up ad down for the curves also happened in Fig. 6. Obviously, for the studied system, the suitable used amount of $SnCl_4$ is 1.5 ml, as displayed in Fig. 6. Therefore, to obtain the CMCPS microsphere with high quality, the catalyst amount also needs to be selected suitably.

Effect of various factors on chloromethylation reaction of PSt/SiO_2 particles

Effect of the used amount of BCMB

The chloromethylation reactions for the grafted particles PSt/SiO_2 were conducted with the different used amount of BCMB and with fixed other conditions. Figure 7 displays the dependence of the chlorine content of the product particles CMPS/SiO_2 on time.

The status in Fig. 7 is the same as in the case in Fig. 4. The chlorine content exhibits the variation trend of first a rising and then a declining with reaction time. The reason for this is similar to that described in section Effect of the

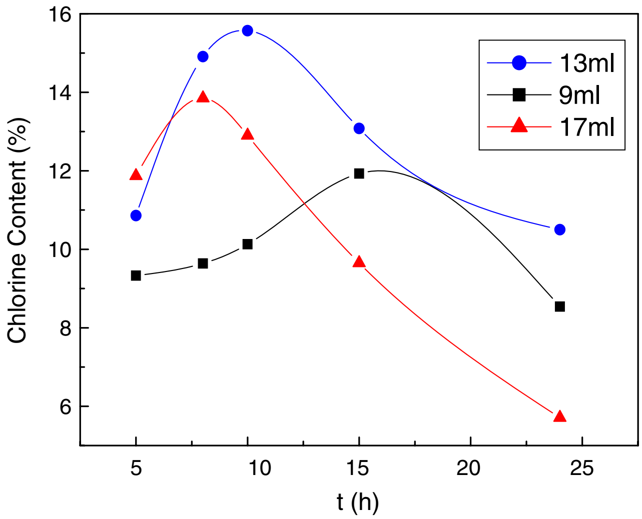


Fig. 7 Plot of chlorine content of CMPS/SiO$_2$ particle vs time with different BCMB amounts. PSt/SiO$_2$ particle, 3 g; temperature, 25°C; CH$_2$Cl$_2$, 40 ml; SnCl$_4$, 1.5 ml (0.013 mmol)

used amount of BCMB "Effect of the used amount of BCMB." In comparison with the chloromethylation systems of CPS, the only difference is that the Friedel–Crafts cross-linking reaction along with the chloromethylation reaction is the cross-linking reaction between grafted polystyrene macromolecules in the chloromethylation system of PSt/SiO$_2$, and it cannot be called "additional cross-linking reaction." The appearance of the maximum means that the Friedel–Crafts cross-linking reaction between grafted macromolecules has been produced obviously.

As three amounts of BCMB, 9, 13 and 17 ml, were used, the cholromethylation results are distinctly different, although the relationship between the reaction rate and the amounts of BCMB as well as the relationship between the time corresponding to the maximum and the amounts of BCMB are the same as in the chloromethylation system of CPS. There appears curve interleaving as shown in Fig. 7. For the studied system, 13 ml of BCMB is an appropriate amount. Therefore, for the chloromethylation system of PSt/SiO$_2$, the used amount of BCMB also should be choice correctely.

Effect of the used amount of solvent

By varying the used amount of CH$_2$Cl$_2$ and fixing other reaction conditions, the chloromethylation reactions for PSt/SiO$_2$ particles were performed. Figure 8 displays the dependence of the chlorine content of grafted polystyrene on time.

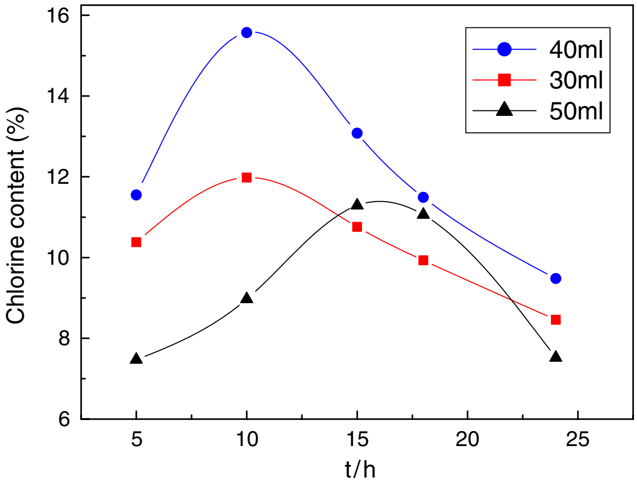


Fig. 8 Plot of chlorine content of CMPS/SiO$_2$ particle vs time with different solvent amounts. PSt/SiO$_2$ particle, 3 g; temperature, 25°C; BCMB, 13 ml; SnCl$_4$, 1.5 ml (0.013 mmol)

It is seen from Fig. 8 that, for 3 g of PSt/SiO$_2$ particles, the chlorine content is the highest as 40 ml of CH$_2$Cl$_2$ is used, compared with 30 ml and 50 ml of CH$_2$Cl$_2$, and the maximum appears after 10 h. This fact indicates that, in 40 ml of CH$_2$Cl$_2$, the grafted polystyrene macromolecules can be well swelled and extended so that the active reaction sites can be adequately exposed and the chloromethylation reaction can be carried out favorably. The less and more solvent than 40 ml are disadvantageous for preparing CMPS/SiO$_2$ with high quality. As 30 ml of CH$_2$Cl$_2$ is used, the rate of the chloromethylation reaction is slower due to un-enough swelling of grafted polystyrene, and the cross-linking reaction occurs prematurely owing to a shorter distance between the grafted macromolecules. As 50 ml of CH$_2$Cl$_2$ is used, the rate of the chloromethylation reaction is also slower due to the diluted effect, and the cross-linking reaction occurs lingeringly owing to a distant interval between the grafted macromolecules.

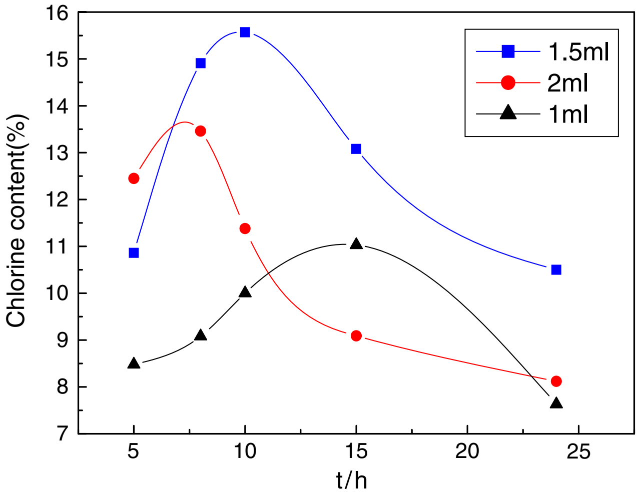


Fig. 9 Plot of chlorine content of CMPS/SiO$_2$ particle vs time with different catalyst amounts. PSt/SiO$_2$ particle, 3 g; temperature, 25°C; BCMB, 13 ml; CH$_2$Cl$_2$, 40 ml

Effect of the used amount of catalyst

By varying the used amount of $SnClB_4$ (1, 1.5, and 2 ml) and fixing other reaction conditions, the chloromethylation reactions for PSt/SiO_2 particles were performed. Figure 9 displays the dependence of the chlorine content of grafted polystyrene on time. The curve interleaving status also can be found in Fig. 9. For 3 g of PSt/SiO_2 particles, 1.5 ml of $SnClB_4$ is optimal as compared with 1 and 2 ml of $SnCl_4$ as displayed in Fig. 9. The less catalyst will lead to slower chloromethylation reaction rate, whereas the more catalyst will result in prematurely occurring of the cross-linking reaction and lower chlorine content.

About reaction temperature

The reaction temperature is an important factor for nearly all chemical reactions. The effect of temperature on the chloromethylation reaction of polystyrene was examined. It was found that Friedel–Crafts cross-linking reaction is very sensitive to temperature. If the temperature goes up to above 20°C, the rate of the cross-linking reaction will be enhanced distinctly. Hence, higher temperature is not suitable to chloromethylation reaction. In this study, the reaction was conducted at room temperature (25°C) to avoid Friedel–Crafts cross-linking reaction as far as possible.

Conclusion

In this work, the chloromethylation reaction of cross-linking styrene-divinyl styrene copolymer microspheres was realized in the presence of Lewis acid catalyst by using BCMB as chloromethylation reagent, and chloromethylated cross-linking polystyrene (CMCPS) microspheres were prepared. This method is environmentally friendly because of no cancerogenic toxicity of BCMB. Besides, this method is also more economical because of the low cost of BCMB. The chloromethylation reaction of the grafted particles PSt/SiO_2 also was performed and the composite particles CMPS/SiO_2 were obtained. The composite particle CMPS/SiO_2 well combine the chemical modificability of chloromethylated polystyrene with the excellent mechanical property and thermal stability of silica gel, so it is a kind of chloromethylated polystyrene particles with high performance. During the process in preparing CMCPS microspheres and CMPS/SiO_2 particles, along with the increase of chlorine content, Friedel–Crafts cross-linking reaction will occur. To prepare the chloromethylated particles with high chlorine content and without obvious cross-linking, the suitable reaction conditions need to be controlled, such as reaction time and the used amount of BCMB, solvent, and catalyst. The reaction should be carried out at lower temperatures (about 20°C) because of the sensitivity of Friedel–Crafts reaction to temperature.

References

1. Wang Y, Zhang G-H-, Yan H-S et al (2006) Tetrahedron 62:4948–4953
2. Arunan C, Nagaraj R, Rajasekharan Pillai VN (2000) Peptides 21:773–777
3. Xu M-C, Ou Zh-Z, Shi Z-Q et al (2001) React Funct Polym 48:85–95
4. Masuda T, Kitahara K-I, Aikawa Y, Arai S (2002) J Chromatogr A 961:89–96
5. Jain VK, Pandya RA, Pillai SG, Shrivastav PS (2006) Talanta 70:257–266
6. Mondal BC, Das AK (2002) React Funct Polym 53:45–52
7. Marquès G, Bourdelande JL, Valiente M (1999) React Funct Polym 41:77–89
8. Maurya MR, Kumar M, Sikarwar S (2006) React Funct Polym 66:808–818
9. Moghadam M, Tangestaninejad S, Mirkhani V et al (2005) Bioorganic Med Chem 13:2901–2905
10. Sophiamma PN, Sreekumar K (1997) React Funct Polym 35:169–177
11. Kedem M, Margel S (2002) J Polym Sci A Polym Chem 40:1342–1352
12. Khan AA, Abdelaal MY, Ali MM, Abdel-Latiff EH (1998) Polymer 40:233–241
13. Jang BB, Lee K, Kwon WJ, Suh J (1999) J Polym Sci A Polym Chem 37:3169–3177
14. Jang BB, Lee K, Kwon WJ, Suh J (1999) J Polym Sci A Polym Chem 37:3169–3177
15. Carre EL, Lewis N, Ribas C, Wells A (2000) Org Process Res Dev 4:606–610
16. Kavaklı C, Özvatan N, Tuncel SA, Salih B (2002) Anal Chim Acta 464:313–322
17. Unsal E, Bahar T, Tuncel M, Tuncel A (2000) J Chromatogr A 898:167–177
18. Shen Y-L, Yang Y-F, Gao B-J, Zhu Y (2007) Acta Polymerica Sinica 6:531–537 (in Chinese)
19. Shen Y-L, Yang Y-F, Gao B-J, Li G (2007) Chem J Chin Univ 28 (3):559–565 (in Chinese)
20. Gao B-J, Wang R-X, Jiu H-F, Kong D-L (2006) J Appl Polym Sci 102:5808–5817