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Studies on Chloroacylation Reaction Process of Crosslinked Polystyrene Microspheres with ω-Chloroacyl Chloride as Reagent

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The Friedel-Crafts acylation reactions of crosslinked polystyrene (CPS) microspheres were conducted in the presence of Lewis acid catalyst at room temperature by using two kinds of ω-chloroacyl chlorides, chloroacetyl chloride and chlorobutyryl chloride, and two kinds of chloroacylated CPS microspheres (CACPS microspheres) were prepared, resulting in the introduction of exchangeable chlorine atoms (chloroacyl groups) onto the surfaces of CPS microspheres. The chemical structure and composition of the product microspheres were characterized by infrared spectroscopy and chemical analysis methods. The effects of various factors on the chloroacylation reactions were mainly investigated. The experimental results show that the chloroacylation process is always attended by Friedel-Crafts alkylation reaction, and it is a problematic side reaction. This side reaction not only decreases the content of the chloroacyl groups on CACPS microspheres, but also leads to additional crosslinking, which causes the property of the microspheres to become poor. This additional crosslinking reaction can be avoided effectively by controlling some reaction conditions, and CACPS microspheres with high chloroacylation degree and few additional crosslinking can be obtained, for example, effectively controlling the reaction time, using $SnCl_4$ as catalyst and $CHCl_3$ as solvent, as well as adopting suitable amounts of the catalyst and solvent.

Keywords: Crosslinked polystyrene microspheres, ω-chloroacyl chloride, Friedel-Crafts acetylation reaction, additional crosslinking

1 Introduction

To introduce exchangeable chlorine atoms onto the surfaces of crosslinked polystyrene (CPS) microspheres is usually the starting step for preparing functional microsphere materials such as ion exchange resin, adsorption resin, chelating resin, chromatography stationary phase, heterogeneous catalyst, support of solid-phase synthesis, polymer-supported reagents and so on (1-7), and so to speak, the most of functional polymeric materials come from the modified crosslinked polystyrene microspheres on which exchangeable chlorine atoms are contained. The traditional method to reach this aim is to make CPS microspheres to be chloromethylated by using chloromethyl ether as chloromethylation reagent. However, chloromethyl ether is highly carcinogenic, and its use has been seriously restricted since the 1970's (8,9). Therefore, researchers have been making an effort to seek the alternative routes to introduce exchangeable chlorine atoms onto CPS microspheres, and until now, there are some possible alternative methods. For example, long chain halomethyl ether can be used as a safe halomethylation agent (10) although the synthesis process is more complicated; monomer *p*-chloromethyl styrene (CMS) can be used for copolymerization with styrene (11) although CMS is expensive and this method is costly. Previously, we prepared 1,4-bis (chloromethoxy) butane (BCMB) and made CPS microspheres to be chloromethylated greenly and high effectively using BCMB as chloromethylation reagent (12). Actually, halogenoacylation of CPS microspheres with ω-halogenoacyl chlorides is also an effective method to introduce exchangeable chlorine atoms onto CPS microspheres and is a green and environment-friendly way. In this halogenoacylation process, the Friedel–Crafts acylation reaction is always accomplished by a side reaction, Friedel–Crafts alkylation reaction, which not only leads to an additional crosslinking and it is disadvantageous to the property of CPS microspheres (13), but also decreases the efficiency of introducing exchangeable chlorine atoms onto CPS microspheres because the side reaction is a process of losing chlorine. Obviously, the halogenoacylation reaction process needs to be researched in depth so as to

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effectively control the reaction conditions to obtain the product microspheres with high quality (higher chlorine content and lower additional crosslinking).Although some researchers have prepared functional CPS microspheres via halogenoacylation reaction with ω-halogenoacyl chlorides as halogenoacylation reagent (14-18), the detail process of the halogenoacylation reaction of CPS microspheres has not been researched, and it has not been reported how the reaction conditions are controlled to obtain the product microspheres with high quality. Along with the development of the functional polymeric materials based on CPS microspheres and the increasing concern for environment, the route of preparing the CPS microspheres containing exchangeable chlorine atoms via halogenoacylation reaction of CPS microspheres will be used more widely, so how to perform this reaction to obtain the modified CPS microspheres with high quality should be researched.

In this paper, two kinds of ω-halogenoacyl chlorides, chloroacetyl chloride and 4-chlorobutyryl chloride were used for the chloroacylation reaction of CPS microspheres, respectively, and effects of different factors on the chlorine content of the chloroacylated microspheres (CACPS microspheres) were mainly examined. The aim of this work is to present valuable references for the effective modifications of CPS microspheres via the chloroacylation reaction with ω-halogenoacyl chlorides as reagent, and to supply important information for obtaining the better precursor (CACPS microspheres) of functional polymeric materials. It was discovered that some factors affect the result of chloroacylation reaction of CPS microspheres greatly, such as the species and the used amount of Lewis catalysts, the polarity and the added amount of the solvents, as well as the species of ω-halogenoacyl chlorides. Only under suitable reaction conditions, the side crosslinking reaction (Friedel–Crafts alkylation reaction) can be avoided as much as possible, and the efficiency of introducing exchangeable chlorine atoms onto CPS microspheres can be obviously enhanced.

The results reported in this work seem to be insignificant and not innovative. However, they are foundational and valuable. The valuable information for chemically modifying CPS microspheres via halogenoacylation reaction, which is a green and environment-friendly route of CPS microsphere modification, is supplied, and some important experimental data are offered for the preparation of CACPS microspheres with high quality. So the results reported in this work are very significant for further preparing various functional microsphere materials with CACPS microspheres as precursor.

2 Experimental

2.1 Materials and Instruments

Crosslinked polystyrene (CPS) microspheres (Tenlong Chemical Ltd, Changchou, Jiangsu Province, China), namely, crosslinked styrene/divinylbenzene copolymer microspheres, with a crosslinking degree of 4% and an average diameter of 0.315–0.45 mm, was received. Chloroacetyl chloride (CAC, Anyang Yonghe Chemical Plant, Henan Province, China) was of reagent grade. Chlorobutyryl chloride (CBC, Jingchun Chemical Ltd., Shanghai, China) was of analytical grade. Anhydrous tin tetrachloride ($SnCl_4$, Yuanli Chemical Ltd., Tianjin, China) was of analytical grade. Anhydrous titanium tetrachloride ($TiCl_4$, Donda Chemical Ltd., Tianjin, China) was of analytical grade. Anhydrous zinc chloride (Wuxi Yuanli Chemical Ltd., Jiangsu Province, China) was of chemical grade. Carbon tetrachloride and other solvents were analytically pure commercial chemicals and purchased from Chinese companies.

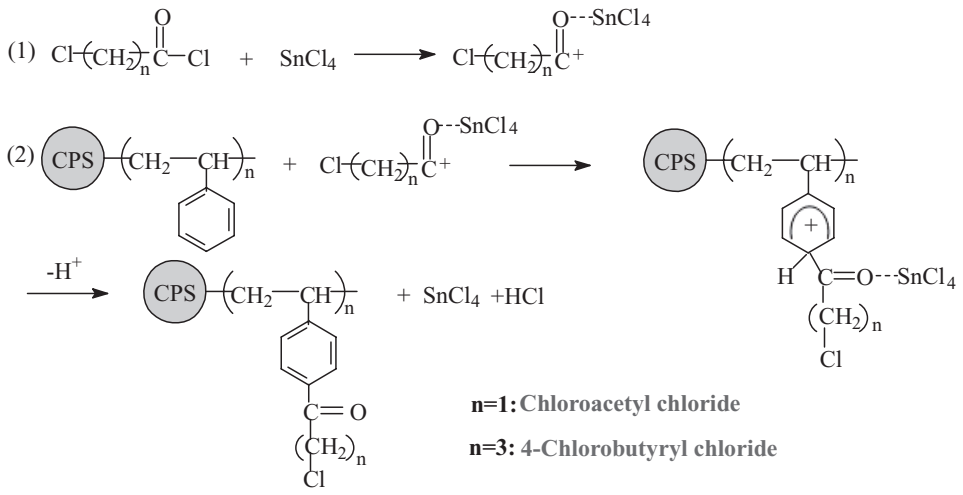
A Perkin-Elmer 1700 infrared spectrometer (Perkin-Elmer, USA) was used for Fourier transform infrared (FTIR) analyses, and a calorimetric meter of oxygen-bomb type made in China was used for analysis of chlorine element with the Volhard method.

2.2 Synthesis and Characterization of Chloroacylated CPS Microspheres

2 g of CPS microspheres was placed into a four-necked flask equipped with a mechanical stirring, a condenser and a thermometer. 20 mL of chloroform as solvent was added, and the microspheres were fully swelled for 12 h. Subsequently, 1.5 mL of chloroacetyl chloride and 2.7 mL of $SnCl_4$(Lewis catalyst) were added. The chloroacylation reaction was carried out at room temperature. After the reaction was finished, the reaction mixture was treated with diluted hydrochloric acid to remove the catalyst physically attaching to the microspheres. After filtering, the resultant microspheres were washed with dioxane to remove residual solvent, washed again with distilled water until free of chloride ions in the cleaning solution, and dried under vacuum, resulting in chloroacylated CPS microspheres, namely, CACPS microspheres. By adopting the same procedures, the chloroacylation reaction was also conducted with chlorobutyryl chloride as a chloroacylation reagent (1.6 mL of chlorobutyryl chloride was added), and another kind of CACPS microspheres was also obtained.

2.3 Characterization of CACPS Microspheres

The infrared spectra of CPS microspheres and CACPS microspheres were determined with the KBr pellet method, and via comparing their spectra, the structure changes of CPS microspheres after chloroacylation reaction were confirmed. To determine the chlorine content of the CACPS microspheres, which stands for chloroacyl group content of the CACPS microspheres, the sample of CACPS microspheres was first burned out in an oxygen bomb (19) and chlorine element contained in the sample was fully transformed into chloride ions. Subsequently, the Volhard method was adopted to analyze the chlorine content (wt%).



Sch. 1. Reaction mechanism of chloroacetylation of CPS microspheres with chloroacyl chloride.

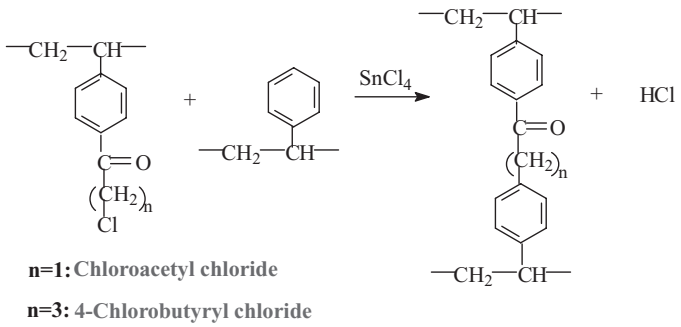
2.4 Examining Effects of Various Factors on Chloroacylation Reaction of CPS Microspheres

By fixing other conditions and changing a certain reaction condition in series, the chloroacylation reactions of CPS microspheres were performed so as to examine effects of various factors on the chloroacylation reaction of CPS microspheres. The changed reaction conditions included the species and the used amount of catalyst, the species and the used amount of solvent, as well as the species of chloroacylation reagent.

3 Results and Discussion

3.1 Mechanism of Chloroacylation Reaction of CPS Microspheres and Side Reaction of Additional Crosslinking

The Friedel–Crafts acrylation reaction between chloroacetyl choloride (or chlorobutyryl chloride) and CPS microspheres, which is in a swelled state, is produced in the presence of a Lewis catalyst, and chloroacylated CPS microspheres (CACPS microspheres) were formed. The reaction mechanism is expressed schematically in Scheme 1. First, the catalyst acts on the chloroacylation reagent, and carbonium ions of chloroacyl groups are formed. The carbonium ion attacks the carbon atom in the para position of the benzene ring of CPS, so the electrophilic substitution reaction, namely, Friedel–Crafts acylation reaction, occurs, resulting in the introducing of chloroacyl groups into the benzene rings of CPS microspheres and the forming of CACPS microspheres.



Sch. 2. Schematic illustration of Friedel-Crafts alkylation crosslinking reaction between PS chains.

Chloroacyl groups are chemically active. Along with the carrying out of the chloroacylation reaction of CPS microspheres, the intermolecular Friedel-Crafts alkylation reaction between polystyrene chains will be produced, leading to the occurrence of additional crosslinking as shown in Scheme 2. HCl is released in the additional crosslinking reaction, so the additional crosslinking reaction is a process of losing chlorine. As the carbon atoms in the para positions of the benzene rings of CPS microspheres are chloroacylated unceasingly, the possibility of the intermolecular Friedel-Crafts crosslinking reaction between polystyrene macromolecules is growing. The additional crosslinking reaction not only reduces the content of the exchangeable chloeine atoms, but also increases the crosslinking degree of CPS microspheres, seriously affecting the mechanical property of CPS microspheres (the microspheres become brittle). Therefore, the reaction conditions need to be controlled during the chloroacylation reaction to avoid the additional crosslinking reaction as much as possible.

Under the same conditions, the chloroacylation reactions were conducted with chloroacetyl chloride (CAC) and chlorobutyryl chloride (CBC) as reagent, respectively, and two kinds of CACPS microspheres were prepared. Figure 1 gives the chlorine contents as a function of reaction time for the two systems.

The following facts can be seen clearly from Figure 1. At the starting stage, the chlorine contents enhance rapidly

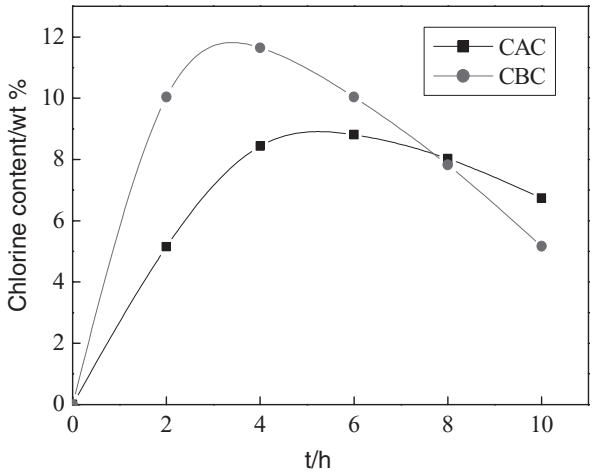


Fig. 1. Variation of chlorine content of CACPS microspheres with reaction time Catalyst $SnCl_4$: 2.7 mL; Solvent $CHCl_3$: 20 mL.

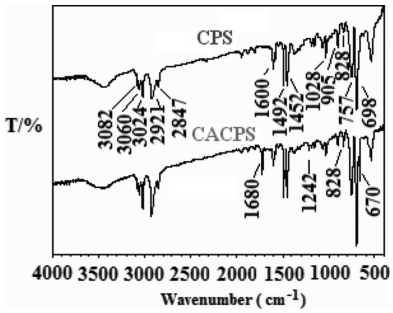


Fig. 2. FTIR spectra of CPS and CACPS microspheres.

with the reaction time, after 3-5 h, the change of the chlorine contents turn slowly, and then the chlorine contents begin to decline. The start of the decrease of chlorine content on the curves is important information, and it reflects that Friedel-Crafts crosslinking reaction between polystyrene chains has clearly occurred. At the starting stage, the Friedel-Crafts acylation reaction is very rapid because of the high concentration of the chloroacylation reagent, chloroacetyl chloride or chlorobutyryl chloride, resulting in the noteworthy enhancement of chlorine content with time. Accompanying the increase of the chloroacylation degree of CACPS microspheres, the Friedel-Crafts acylation reaction between polystyrene chains become easier to occur. This additional crosslinking reaction is a process of losing chlorine as described above, so after a certain time, the change of the chlorine content turns smooth. In comparison with the chloroacylation reaction process, as soon as the Friedel-Crafts crosslinking reaction becomes predominant, the chlorine content will exhibit a decline trend. Therefore, it is inevitable that there is a maximum point on the curve of chlorine content vs. reaction time. The maximum point implies that at the corresponding time, the additional crosslinking reaction has obviously occurred. Therefore, in order to obtain CACPS microspheres with high quality (high chloroacylation degree and little additional crosslinking), the reaction time needs to be effectively controlled. The time corresponding to the maximum point on the curve of the chlorine content vs. time is namely a suitable period of time.

Another important fact can be also found from Figure 1. As chloroacetyl chloride was used as a reagent, the chloroacylation reaction of CPS microspheres is slower, and the chlorine content of CACPS microspheres at the maximum point is lower (about 9%, wt%). However, as chlorobutyryl chloride was used as reagent, the chloroacylation reaction of CPS microspheres is quicker, and the chlorine content of CACPS microspheres at the maximum point is higher (about 12%, wt%), indicating that the CACPS microspheres with chlorobutyryl chloride as reaction reagent have a higher chloroacylation degree. At the same time, the time corresponding to the maximum point is shortened from 5 h to 3 h for the chlorobutyryl chloride system in comparison with the chloroacetyl chloride system. This indicates that for the chlorobutyryl chloride system, the time in which the additional crosslinking reaction is obviously produced has moved up. The possible reason for the above facts can be explained as follows. There is only one methylene group in the molecule of chloroacetyl chloride, whereas there are three methylene groups in the molecule of chlorobutyryl chloride. Multi-methylene groups have a stronger property of providing electrons, enabling the carbonium ions of chloroacyl groups formed during the electrophilic substitution reaction to be more stable, and it is advantageous to the electrophilic substitution reaction. Thus, the rate of chloroacylation reaction is faster for the chlorobutyryl chloride system than that for the chloroacetyl chloride system. For the chlorobutyryl chloride system, higher chloroacylation reaction rate leads to a greater chloroacylation degree of CACPS microspheres in a short period of time, and at the same time, it makes the Friedel-Crafts crosslinking reaction between polystyrene chains occur in a shorter period of time, resulting in the moving up of the time in which the additional crosslinking reaction is obviously produced.

3.2 Infrared Spectrum of CACPS Microspheres

The infrared spectra of CPS microspheres and CACPS microspheres are shown in Figure 2. The characteristic absorptions of CPS microspheres are as follows: the bands at 3082, 3060 and 3024 cm^{-1} are attributed to the stretching vibration absorptions of the C-H bond of the benzene ring; the bands at 2847 cm^{-1} and 2921 cm^{-1} should be ascribed to the stretching vibration absorptions of C-H bond of the main chain of polystyrene; the bands at 1600 cm^{-1} is the vibration absorption of skeletal vibration of the benzene ring; the bands at 1492 cm^{-1} and 1452 cm^{-1} correspond to the bending vibration absorptions of C-H bonds of

benzene ring; the bands at 756 cm^{-1} and 698 cm^{-1} correspond to bending vibration absorptions of C-H bonds of benzene rings after unitary substitution; the bands at 1242 cm^{-1} and 828 cm^{-1} are ascribed to the vibration absorptions of C-H bonds of the benzene ring after binary substitution at 1 and 4 positions. After chloroacylation reaction, there are greater changes in the spectrum of CACPS microspheres in comparison with that of CPS microspheres. On the one hand, the bands at 1242 cm^{-1} and 828 cm^{-1} which are the characteristic absorptions of the benzene ring after binary substitution are strengthened greatly, and on the other hand, two new bands have appeared at 1680 cm^{-1} and 670 cm^{-1}. The band at 1680 cm^{-1} should be attributed to the characteristic absorption of carbonyl group in acyl group, and the band at 670 cm^{-1} should be ascribed to the stretching vibration absorption of C-Cl bond in chloroacyl group. The above infrared spectrum data fully confirms that the hydrogen atoms at 4 position of the benzene rings of CPS microspheres have been substituted partly by chloroacyl groups, and chloroacylated CPS microspheres, CACPS microspheres, have been formed.

3.3 Effects of Various Factors on Chloroacylation Reaction

3.3.1. *Effect of Solvent Species*

Three kinds of solvents, dichloromethane, chloroform and carbon tetrachloride, were used in the chloroacylation reaction of CPS microspheres. Figure 3 (A) gives the relationship curves between the chlorine content of CACPS microspheres and reaction time as different solvents were used for the chloroacetyl chloride system, whereas Figure 3 (B) presents the relationship curves between the chlorine content of CACPS microspheres and reaction time as different solvents were used for the chlorobutyryl chloride system. Similar experimental facts are displayed in Figure 3 (A) and (B), and under the same reaction conditions, the chloroacylation reaction results in the three solvents are in the order: $CHCl_3$ > CCl_4 > CH_2Cl_2. There are greater differences of chloroacylation degree for the CACPS microspheres prepared in the three solvents.

The experimental results showed that in all the three solvents, CPS microspheres can be swelled well (20), namely, the three solvents are all good solvents of polystyrene. It is obvious that the above facts cannot be explained by swelling abilities of the three solvents towards CPS microspheres. A reasonable explanation can be given by comparing the effect of the solvent polarity on the chloroacylation reaction. The greater differences of chloroacylation degree of CACPS microspheres prepared in the three solvents originate from their polarity differences probably. The data of dielectric constant and polarity constant for the three solvents are presented in Table 1. Obviously, the polarities of the three solvents are in the order: CH_2Cl_2 > $CHCl_3$ > CCl_4.

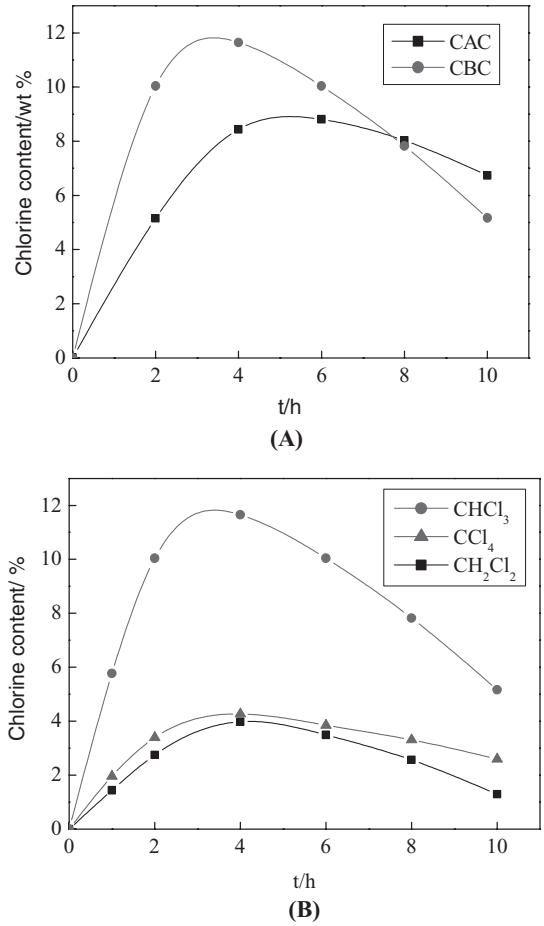


Fig. 3. Variation of chlorine content of CACPS microspheres with time with different solvents. (A) Using chloroacetyl chloride; (B) Using chlorobutyryl chloride. Catalyst $SnCl_4$: 2.7 mL; Solvent: 20 mL.

As CCl_4 with the weakest polarity among the three solvents is used, the dipole-dipole interaction between the solvent and chloroacylation reagent is too weak, and it is disadvantageous to the moving off of chlorine atom (actually, chloride ion) from chloroacylation reagent molecule, namely, it is not beneficial to the production of the carbonium ions of chloroacyl groups, so the chloroacylation reaction is affected negatively. As CH_2Cl_2 with the strongest polarity among the three solvents is used, the carbonium ion is liable to be produced via a strong dipole-dipole interaction between the solvent and chloroacylation reagent. However, on the other hand, the dipole-ion interaction

Table 1. Data of delectric constant and polarity constants of three solvents

Substance	*CCl_4*	*$CHCl_3$*	*CH_2Cl_2*
$E_T(30)$/(kcal/mol)	32.5	39.1	41.1
ε	2.24	4.81	9.08

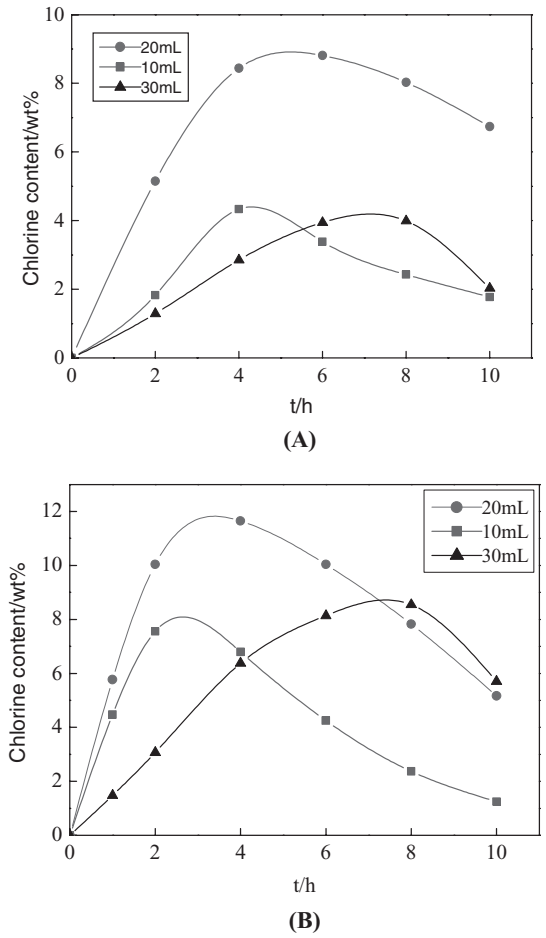


Fig. 4. Variation of chlorine content of CACPS microspheres with time with different used amount of solvent. (A) Using chloroacetyl chloride; (B) Using chlorobutyryl chloride. Catalyst $SnCl_4$: 2.7 mL; Solvent: $CHCl_3$.

between solvent and carbonium ion is probably excessively strong for the CH_2Cl_2 system, and the strong solvation action restrains the carbonium ion to attack benzene ring, resulting in the slowing of the chloroacylation reaction rate. Consequently, the integration of the two effects of solvent polarity on the chloroacylation reaction leads to the following result: as the chloroacylation reaction is performed in $CHCl_3$ with a centered polarity, there is the best reaction result and the resultant microspheres have the highest chlorine content. Therefore, $CHCl_3$ can be considered as the suitable solvent for the chloroacylation reaction of CPS microspheres.

3.3.2. *Effect of Used Amount of Solvent*

By fixing other conditions and changing the used amount of the solvent $CHCl_3$ in series, the chloroacylation reactions were conducted, and Figure 4 (A) and (B) show the results as used chloroacetyl chlorideand chlorobutyryl chloride as chloroacylation reagent, respectively.

In Figure 4 (A) and (B), some similar facts can also be found, and these facts are discussed by using the chloroacetyl chloride system as an example. As 10 mL of $CHCl_3$ was used for 2 g of CPS microspheres, the chlorine content of CACPS microspheres is lower, and the time in which the chlorine content of CACPS microspheres reaches the maximum value is shorter and is about 4 h; As the used amount of solvent is increased to 20 mL, the chlorine content of CACPS microspheres is enhanced remarkably, and the maximum value of chlorine content appears after 5 h. As the used amount of the solvent is continuously increased to 30 mL, the chlorine content of CACPS microspheres again declines, and after 7 h, the maximum value appears.

As the used amount of the solvent is less (10 mL), the crosslinked networks of CPS microspheres cannot be swelled sufficiently, and the chloroacylation reaction cannot be carried out favorably, leading to lower chlorine content. Furthermore, because the distance between the chains of the polystyrene networks is shorter, the additional crosslinking reaction is easy to occur, resulting in a very short time in which the chlorine content of CACPS microspheres rises to the maximum value. As the used amount of the solvent is increased to 20 mL, the crosslinked networks of CPS microspheres are swelled sufficiently and turn to extending, and the active sites can be exposed fully. It will be advantageous to the chloroacylation reaction, leading to a notable enhancement of the chlorine content of CACPS microspheres. On the other hand, the distance between the chains of the polystyrene network is longer because of the sufficiently swelling of CPS microspheres, and it will slow down the additional crosslinking reaction, resulting in delaying the time in which the chlorine content maximum appears. However, as the used amount of the solvent is continuously increased to 30 mL, it is possible that the concentration of the chloroacylation reagent becomes obviously lower, and the dilution effect makes the reaction rate slower, resulting in a repeated declining of the chlorine content of CACPS microspheres. Furthermore, the time corresponding to the maximum value of the chlorine content is also delayed greatly because of the suppression of the additional crosslinking reaction, and this is another display of the dilution effect. By this token, in order to prepare the CACPS microspheres with high chlorine content and without obvious additional crosslinking, the used amount of the solvent needs to be controlled. For 2 g of CPS microspheres, 20 mL of $CHCl_3$ is appropriate.

3.3.3. *Effect of Catalyst Species*

Three kinds of Lewis catalysts with the same used amount (2.3×10^{-2} mol), $SnCl_4$, $TiCl_4$ and $ZnCl_2$, were used in the chloroacylation reaction of CPS microspheres, respectively. Figure 5 (A) and (B) gives the relationship curves between chlorine content of CACPS microspheres and reaction time as different catalysts were used for the chloroacetyl chloride system and for the chlorobutyryl chloride system, respectively. The similar experimental facts are displayed in

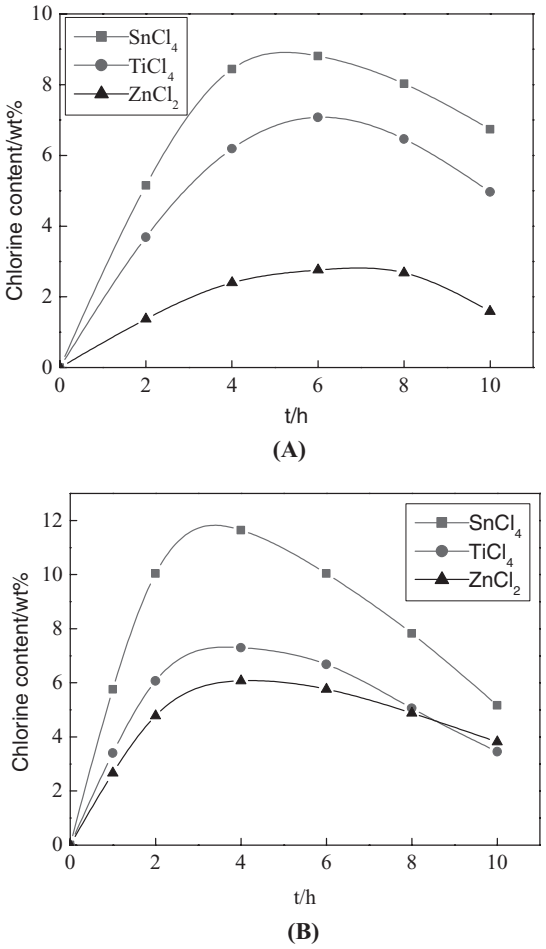


Fig. 5. Variation of chlorine content of CACPS microspheres with time with different catalysts. (A) Using chloroacetyl chloride; (B) Using chlorobutyryl chloride. Catalyst: 2.3×10^{-2}mol; Solvent $CHCl_3$: 20 mL.

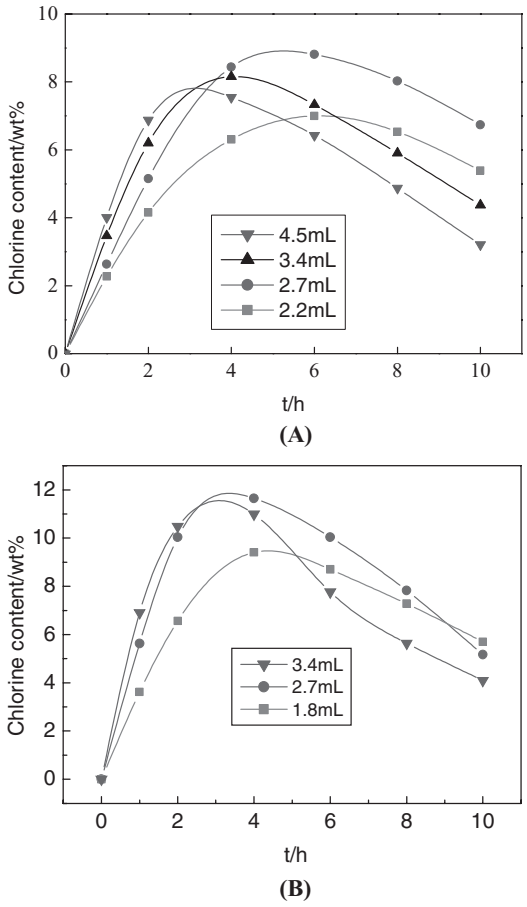


Fig. 6. Variation of chlorine content of CACPS microspheres with time with different used amount of catalyst. (A) Using chloroacetyl chloride; (B) Using with chlorobutyryl chloride. Solvent $CHCl_3$: 20 mL; Catalyst: $SnCl_4$.

Figure 5 (A) and (B), and under the same reaction conditions, the chloroacylation reaction results for the three catalysts are in the order: $SnCl_4 > TiCl_4 > ZnCl_2$.

The results displayed in Figure 5 (A) and (B) are closely related to the catalytic activity of the three catalysts. It is well known that the acidity of the three Lewis catalysts is in the order: $SnCl_4 > TiCl_4 > ZnCl_2$. Obviously, this is consistent with the above order. Among the three catalysts, the ability to accept electron for $SnCl_4$ is the strongest. $SnCl_4$ is easer to act on chloroacyl chloride, leading to the easy formation of carbonium ions of chloroacyl groups, and the chloroacylation reaction of CPS microspheres will be effectively accelerated. Therefore, the reaction result with $SnCl_4$ as Lewis catalyst is the best. $AlCl_3$ is a Lewis catalyst with stronger acidity than that of $SnClB_4$, and it was also used in the experiment. However, it was found that the serious fragmentation of the microspheres occurred during the reaction process as $AlCl_3$ was used. Therefore, the authors consider that $SnCl_4$ is a suitable Lewis catalyst for the chloroacylation reaction of CPS microspheres.

3.3.4. *Effect of Used Amount of Catalyst*

By fixing other conditions and changing the used amount of the catalyst $SnCl_4$ in series, the chloroacylation reactions of CPS microspheres were conducted, and Figure 6 (A) and (B) show the results as used chloroacetyl chloride and chlorobutyryl chloride as reagent, respectively.

Some facts can be found from Figure 6 (A). On the left side of the maximum point on the curve, the chlorine content in the same period of time is increased with increasing the used amount of the catalyst, i.e., the Friedel-Crafts acylation reaction speeds up, and it agrees with the general kinetics rules. It can be also found in Figure 6 (A) that the greater the used amount of the catalyst, the shorter the time corresponding to the maximum value of the chlorine content, namely, the time in which the additional crosslinking reaction occurs noticeably, moves up more markedly. The reason for this is as follows: Lewis catalyst, $SnCl_4$, is also the catalyst of the Friedel-Crafts alkylation reaction (additional crosslinking reaction), and to use more $SnCl_4$ will also accelerate the additional crosslinking reaction, resulting in the moving up of the time corresponding to the

maximum value of the chlorine content. Consequently, in order to prepare the CACPS microspheres with high chlorine content and low additional crosslinking, the used amount of the catalyst needs to be effectively controlled. It can be observed that for 2 g of CPS microspheres, 2.7 mL of $SnCl_4$ is adequate, as chloroacetyl chloride is used as a reagent. Here, the rate of the chloroacylation reaction is moderate, and the chlorine content of CACPS microspheres at the maximum point is higher (about 9%, wt%), namely, CACPS microspheres have a higher chloroacylation degree. For the chlorobutyryl chloride system, the facts similar to the above status can also be found, and 2.7 mL of $SnCl_4$ is still an adequate used amount of the catalyst.

4 Conclusions

In this work, the chloroacylation reaction of CPS microspheres with two kinds of ω-chloroacyl chlorides, chloroacetyl chloride and chlorobutyryl chloride, as the reagent was investigated in depth. Some important facts were found. There is always additional crosslinking reaction following the chloroacylation reaction, and this side reaction not only reduces the content of the exchangeable chlorine atoms, but also makes the property of the product microspheres become poor. In order to prepare the chloroacylated CPS microspheres, (CACPS microspheres) with high chloroacylation degree, the additional crosslinking reaction should be avoided as much as possible. By effectively controlling various reaction conditions, such as the reaction time, the species and used amount of Lewis catalyst, and the species and used amount of solvent, this goal can be realized. The suitable solvent is chloroform, and the adequate catalyst is $SnCl_4$. Furthermore, the used amount of the catalyst should not be excessive, and the used amount of the solvent should also be moderate.

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