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Atom transfer radical polymerization of glycidyl methacrylate followed by amination on the surface of monodispersed highly crosslinked polymer microspheres and the study of cation adsorption

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ABSTRACT

The introduction of reactive groups on the surface of monodispersed highly crosslinked poly(styrene–divinylbenzene) (PSDVB) microspheres was accomplished in two steps. The first step requires immobilizing the initiating groups by a Friedel–Craft acylation between 2-chloropropionyl chlorides and the phenyl groups on the spheres. The second step requires the atom transfer radical polymerization (ATRP) of glycidyl methacrylate (GMA) to obtain spheres (PSDVB-g-PGMA) with epoxy groups on the surface. To demonstrate the feasibility of introducing functionality, the epoxy groups were ring-opened by ethylenediamines, resulting in spheres with amino functionality (PSDVB-g-PGMAEDA). The final spheres were found to have an adsorption capacity of 0.66 mmol/g in the Cu^{2+} adsorption experiments, as a preliminary application study.

1. Introduction

Polymer microspheres with various functionalities have been widely used in many fields, such as chromatography, electronics and information, cosmetics, biological medicine, sensing and many other areas [1–7], due to their many outstanding characteristics, such as large surface-to-volume ratio, stable dispersibility, good reusability as well as the ease in tuning surface functionality, composition, texture and morphology [8–17]. Surface modification and functionalization of conventional polymer microspheres is important for extending their applications as well as increasing the added value of the products because the surface properties of the microspheres are very important to their function in these applications. In addition, there are several basic requirements for microspheres according to the specific application in addition to the desired functionality [1–7]. One requirement is that the spheres should have good mechanical properties as well as thermal, pressure and chemical stability. Size uniformity of the microspheres is also a determining factor in improving functional performance, such as separation efficiency in chromatography.

To meet the diverse industrial demands for these functional microspheres, developing a platform to prepare spheres with all of the above-mentioned merits would be very useful. There have been numerous reports about preparing functional microspheres, as already mentioned above; however, none of the microspheres meet all of the above-mentioned merits at the same time. For example, SiO_2 spheres are less stable in alkaline environment, and lightly crosslinked polystyrene spheres demonstrate relatively weak mechanical performance; the ability to control monodispersity is always a challenge. Several advantages can be envisioned if employing commercially available monodispersed polystyrene–divinylbenzene (PSDVB) microspheres with a high degree of crosslinking as the core. PSDVB microspheres provide good mechanical properties as well as thermal and chemical stability, which have been proven in our previous studies for other applications [18,19]. However, the introduction of reaction sites on the surface of highly crosslinked PSDVB microspheres is more challenging than other spheres.

In this study, we utilized a strategy (Fig. 1) to introduce reactive groups on the surface of monodispersed highly crosslinked PSDVB microspheres that can be easily converted into different functionalities according to the application requirements. After the introduction of an initiator, the surface-initiated atom transfer radical polymerization (ATRP) of glycidyl methacrylate (GMA) was conducted. The resulting polymer (PGMA) with a reactive epoxy group in each repeating unit is expected to be ideal for further high-density surface functionalization. Thus, different surface

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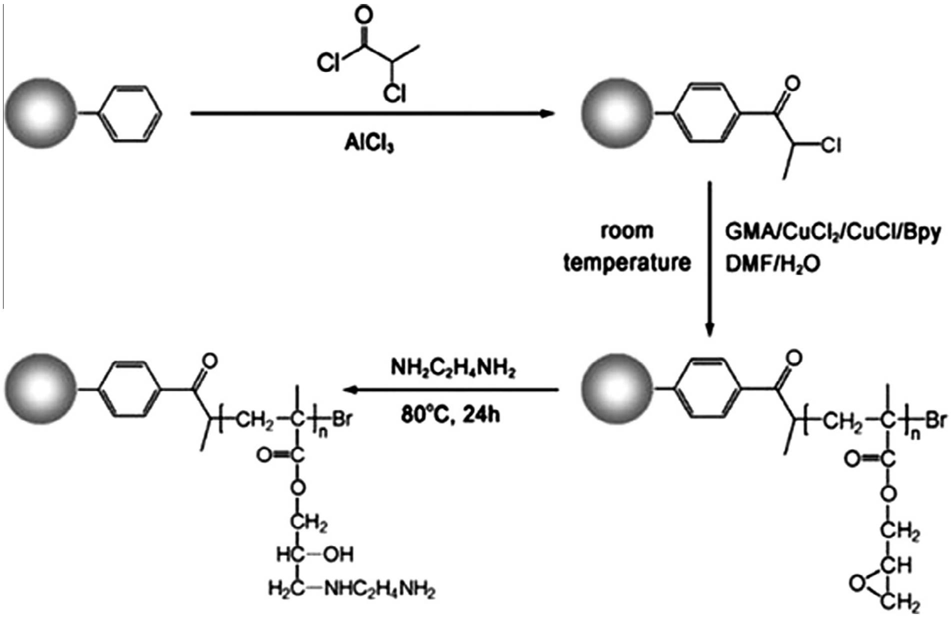

Fig. 1. Schematic diagram of the three-step synthetic strategy of the surface functionalization of PSDVB microspheres: introducing the initiator, ATRP and amination.

functionalities could be realized by using the same starting spheres, such as the introduction of a chelating group for adsorbing metal cations or a hydrophilic group for the separation of biomolecules [1,6]. The monodispersity of the spheres, combined with the surface functionality, will meet the requirement for some practical applications, such as for chromatographic column fillers. Amination was chosen as an example of the type of functionalization that can be accomplished. It should be noted that there is another advantage of using the ATRP surface modification: much denser functionality may be introduced compared to conventional surface modifications because each repeating unit on the resulting polymer can have one functional group, as shown in the schematic shown in Fig. 2.

Atom transfer radical polymerization (ATRP) [20] has been demonstrated as a good technique for the surface modification of microspheres and nanospheres due to well-controlled chain growth [5–11,21–25]. ATRP usually involves two steps: the introduction of an ATRP initiator onto the surface and the subsequent polymerization. Significantly fewer silica-based microsphere systems were found in the literature [11,24,25] compared to reports about polymer-based microspheres [5–10,21–23]. This lack of reports may be due to the instability of silica-based materials in alkaline environments, although it is relatively easier to introduce functionality on a silica substrate. For polymer-based spheres, there are generally two ways to introduce the initiating groups. In some reports, the reaction site was directly introduced during the preparation of the spheres by using specific monomers [5,6,9]. Those methods provided a high-density of reactive sites while sacrificing mechanical performance because the interior portion of the material is reactive instead of being solid and stable. Thus, the relatively stable crosslinked poly(styrene–divinylbenzene) is more commonly used as the material of the core spheres. However, in the literature, bromoalkyl-initiating groups were linked to the surface by hydrolysable esters or other linkages [7,10,22,23]. Hydrolysable linkage can be advantageous by allowing one to selectively cleave the grafted chains from the spheres for characterization but are not desirable in grafted chains with functional group carriers. Moreover, the introduction of the initiators onto the PSDVB-based cores in the literature usually requires three or more steps, which is unfavorable for future scale-up production. There was also one report using a one-step hydrochlorination of residual vinyl groups on the polymer sphere followed by ATRP of the styrene and methylstyrene, but no further functionalization was carried out [21]. In our system, the initiating group was successfully introduced in one-step (first step in Fig. 1) through a Friedel–Crafts reaction.

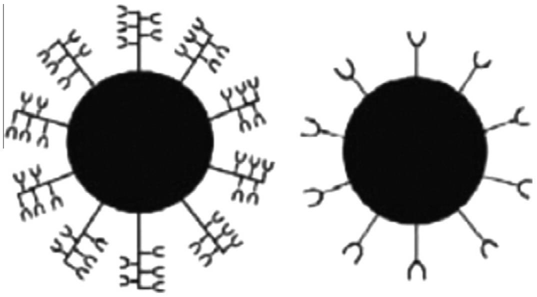

Fig. 2. Expected structures of the microspheres after surface functionalization by ATRP (left) and by the conventional method (right). The semicircle denotes the functional group.

Poly(glycidyl methacrylate) (PGMA) is a good material for surface modification due to the ease in converting epoxy groups into various functional groups, such as alcohol, amine and acid functional groups. The ATRP of GMA in solution or on film surfaces has been well studied [26–32]. One problem for GMA polymerization is the possible crosslinking among PGMA chains due to the existence of highly reactive epoxy groups, which could be circumvented by using a dilute solution in the solution polymerization reaction. As for the film, the small degree of PGMA crosslinking would not have much influence on the film surface properties. However, the crosslinking among the grafted chains in our system may cause the agglomeration of the spheres, thus generating spheres that are inappropriate for further applications. Therefore, the ATRP of GMA on the surface of microspheres is more challenging. This difficulty might be the reason why there were few reports about using GMA polymerization to modify sphere surfaces [6,9,23]. There are reports about the surface-grafting of GMA onto lightly crosslinked PSDVB surfaces using three steps to immobilize