Polystyrene Microspheres Having Epoxy Functional Dangling Chains Linked by Hydrolytically Stable Bonds Via ATRP

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ABSTRACT: We report application of copper-mediated atom transfer radical polymerization in graft copolymerization of glycidyl methacrylate (GMA) from *N*-bromosulfonamide groups on polystyrene-divinyl benzene (PS-DVB) microspheres (210–420 μm). The surface initiator groups were introduced by simple modification of crosslinked PS-DVB (10% mol/mol) beads in three steps: (i) chlorosulfonation, (ii) sulfamidation with propylamine, and (iii) bromination. Initiation from surface-bound *N*-bromosulfonamide groups showed first-order kinetics ($k = 1.04 \times 10^{-4}$ s^{-1} in toluene at 70 °C) and gave poly(GMA) graft chains linked to the surface by hydrolytically stable sulfonamide bonds. High graft yields were attained (up to 294.4% within 21 h) while retaining the epoxy groups. Epoxy content of the resulting product (5.41 mmol g^{-1}) revealed an average 17 GMA repeating units in the graft per initiation site. Taking advantage of the hydrolytic stability of sulfonamide linkages and well-known reactivity of the epoxy groups on dangling chains, "the hair-like structure" of the polymer beads prepared can be considered when devising more efficient functional polymers as catalysts or reagent carriers. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 6708–6716, 2006

Keywords: ATRP; crosslinked resin; glycidyl methacrylate; graft copolymer; surface initiator

INTRODUCTION

Creating surface tethered graft polymer chains on solid substrate is difficult task in practice. The "grafting onto" technique has limited success owing to steric hindrances of the polymer chains approaching the surface. This technique does not allow good control over chain density on the surface.[1] The "grafting from" technique, on the other hand, provides better control of the chain densities and assembled polymer chains on the surface.[2]

However, covalent linking of the initiating sites to any solid surface is difficult. Moreover attachment of classical radical initiator groups to solid surface yields not only surface-bound radical but also a free radical generating a waste amount of ungrafted free homopolymer, beside the desired graft product.

Fortunately formation of free homopolymer is greatly suppressed in controlled/living radical polymerization techniques such as copper-mediated atom transfer radical polymerization (ATRP).[3] It was demonstrated that ATRP is extremely

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versatile technique that is applicable in grafting even from solid particle surfaces.[4] ATRP is superior to other traditional radical initiation techniques, because it avoids homopolymer formation and provides better control of the chain growth in graft copolymerization.[5]

ATRP has been employed also for graft copolymerization of acrylate monomers from solid planar[6] or spherical[7] surfaces. A common approach for graft copolymerization from solid surfaces by ATRP involves two main steps: introduction of ATRP initiators onto the surface and subsequent initiation of the polymerization from surface-bound initiation sites. The first step is crucial for the success of surface initiated graft copolymerization by ATRP. Yu et al. demonstrated controlled grafting of poly(GMA) from 2-bromoester functional surfaces on hydrogen terminated silica substrates.[8] Modification of the silica surface has been one of the most widely studied routes for incorporation of ATRP initiation sites. Common procedure for immobilization of initiator groups onto silica involves chlorination of the surface with chloro-silanes[9] or silane coupling agents[10] and subsequent reaction with appropriate reagents possessing ATRP initiators. However, those materials also carry Si—O—Si linkage that is not so much stable towards hydrolysis. Haddleton's group[11] described the use of Wang resin with benzyl alcohol functionality as solid substrate. Reaction of the methylol groups with 2-bromoisobutyryl bromide followed by grafting from bromoisobutyrate functions was demonstrated to be efficient in graft copolymerization of methacrylate monomers. Stöver's group described two methods for incorporation of initiator groups on densely crosslinked polystyrenes possessing vinyl residues. In the first method, the vinyl residues were transformed into chloroethyl functionalities by hydrochlorination.[12] In the second approach the vinyl residues were converted to hydroxyethyl groups. In either case the following reaction with 2-bromoisobutyryl bromide created the initiator groups on the spherical surface.[13] Both supported initiators were employed successfully in grafting with methacrylate polymers including poly(GMA). Additionally this group demonstrated that lightly crosslinked poly(DVB-*co*-HEMA) can be modified via hydroxyl functions similarly to give 2-bromoisobutyrate groups as initiation sites that allow preparation of graft-block copolymers including poly (MMA-*co*-GMA) poly(MMA-*co*-dimethylaminoethyl methacrylate).

Previous work mostly involves use of bromoalkyl functional surfaces in which initiator groups are linked to surfaces by hydrolysable ester linkages. Hydrolystability of the ester linkage is useful in harvesting of the graft chains by selective cleavage with acid treatment. Analyses of cleaved linear chains give useful information about chain length distributions and kinetics of chain growths on solid surfaces.

However, hydrolytic instability of the linkage between the surface and graft chains is not desirable, especially when side chains are considered as functional group carriers. Obviously, more stable connection of the graft chains with surface is needed for further functionalization. In a previous study we demonstrated that atom transfer graft copolymerization can be initiated from surface bound *N*-halosulfonamide groups.[14] Also halogenated carbon amides have been demonstrated to be efficient to initiate ATRP.[15] Since the sulfonamide group is considerably stable against acid and base hydrolyzes, in this work this chemistry was employed for preparing crosslinked polystyrene bead particles with epoxy functional graft chains attached to the surface with hydrolytically stable linkages. Therefore, surface-bound *N*-bromosulfonamide initiator groups were formed by three-step modification of crosslinked polystyrene-divinyl benzene (PS-DVB) microspheres. Graft copolymerization of GMA from the bead surfaces was then performed by ATRP at 70 °C. The kinetics of grafting was studied and structure of the graft product was investigated, including determination of the epoxy group content. The hydrolytic stability of the sulfonamide linkage opens many modification avenues via epoxy groups on flexible side chains to obtain more efficient functional polymers.

EXPERIMENTAL

Chemicals

Styrene (E. Merck) and divinyl benzene (E. Merck) were rendered inhibitor free by NaOH solution (3%) prior to use. CuBr was freshly prepared according to the procedure described in the literature.[16] The ATRP ligand, H-TETA (1, 1, 4, 7, 10, 10-hexakis [hexyl1, 4, 7, 10-tetraazadecane]) was prepared by alkylation of triethylene tetramine with 1-bromohexane as described earlier.[17] Styrene (0.8 mol) – divinyl benzene (0.1 mol) – vinyl benzyl chloride (0.1 mol) terpolymer

beads were prepared by suspension polymerization according to procedure given in the literature.[18] Chlorosulfonic acid (Aldrich), propylamine (Aldrich), vinyl benzyl chloride (Aldrich), glycidyl methacrylate (GMA) (Aldrich) and all the other chemicals were analytical grade products. They were used as purchased.

Preparation of PS-DVB Resin Beads

The starting material PS-DVB resin was prepared in spherical bead form by crosslinking copolymerization of styrene-divinyl benzene mixture (with 9/1 M ratio) in aqueous suspension using Gam Arabic as stabilizer, according to literature method.[19] The bead product was dried, sieved and 210–420 μm size of fraction was used in further reactions.

Chlorosulfonation of the PS-DVB Resin

In an efficient fume cupboard, 25 g of PS-DVB resin was placed in a 250 mL-conical flask equipped with a $CaCl_2$ guard tube. 70 mL chlorosulfonic acid was added and the mixture was shaken on a shaker for 2 h at room temperature. The resulting bead product was filtered through a sintered glass funnel and added portion-wise to 1 L ice-water under vigorous stirring. The mixture was rapidly filtered, washed with acetone (2 $\times$ 50 mL) and ether (60 mL). Vacuum dried (24 h at room temperature) product weighed 28.8 g. It was stored in a tightly closed bottle.

Chlorosulfone content of the product was determined as follows: The polymer sample (0.2 g) was introduced to 10 mL of NaOH solution (5%) and the mixture was refluxed for 2 h. The mixture was filtered, neutralized with HNO_3 (3 M), and diluted to 100 mL in a volumetric flask. The chloride content of the solution was assayed colorimetrically by mercuric thiocyanate method.[20] Thus, 2.68×10^{-3} M concentration of the solution corresponds to a chlorosulfone density of 1.34 mmol g^{-1}.

Sulfamidation with Propyl Amine

The chlorosulfonated polymer (28 g) was added portion-wise to a stirred solution of propylamine (36 mL, 0.435 mol) in 40 mL of 2-methyl pyrrolidinone at 0 °C. The reaction mixture was shaken for 6 h at room temperature. Then it was filtered washed with water and alcohol (2 $\times$ 40 mL). The yield of vacuum (at 40 °C for 6 h) dried product was 28.24 g.

Estimation of sulfonamide content of this product was carried out based on salt forming ability of this group with concentrated KOH as follows: 20 mL methanolic solution of 0.84 g KOH was divided into two parts and 10 mL of this solution was interacted with 0.1 g of the sulfonamidated bead polymer and left to stand overnight. The mixture was filtered and 7 mL of the filtrate was titrated with 0.1 M HCl solution in presence of phenolphtalein as color indicator. Thus 0.9 mL of less titer consumption (in comparison to 7 mL of the original solution) indicated a 1.29 mmol of sulfonamide content per gram of polymer.

Bromination of the Sulfonamide Group

The sulfamidated polymer (28 g) was added to 100 mL of distilled water in a 250 mL flask. To the stirred mixture there was added 4 mL Br_2 (7.76×10^{-2} mol). The mixture was shaken for 90 min. Then a solution of 3.1 g NaOH (7.76×10^{-2} mol) in 10 mL water was added while stirring. Shaking was continued for another additional 90 min at room temperature. The mixture was filtered, washed with water (500 mL), alcohol (50 mL), and ether (50 mL), successively. The product was dried under vacuum at room temperature for 30 h. Yield (30.8 g).

Bromine content of this product was estimated by iodometric method as follows: In a 50 mL of Erlenmeyer flask 0.21 g polymer sample, 5 mL chloroform, 5 mL acetic acid, 0.8 g KI, and 15 mL water were added, the flask was tightly closed and the mixture was stirred for 24 h at room temperature. The iodine formed was titrated with 0.05 M $Na_2S_2O_3$ solution. 5.3 mL titer indicated a bromine content of 1.26 mmol g^{-1}.

Graft Copolymerization of GMA from Supported Bromosulfonamide Groups

A 250 mL three necked flask equipped with a nitrogen inlet and a reflux condenser was placed in an oil bath at 70 °C. The bromosulfonamide polymer (7.0 g), GMA monomer (30 mL, 0.21 mol), and toluene (30 mL) were charged to the flask. Meanwhile the cuprous complex was prepared in a separate bottle by mixing 0.662 g CuBr (4.61 mmol), 3.0 g ligand, H-TETA (4.61 mmol), and 10 mL toluene. The bottle was closed and

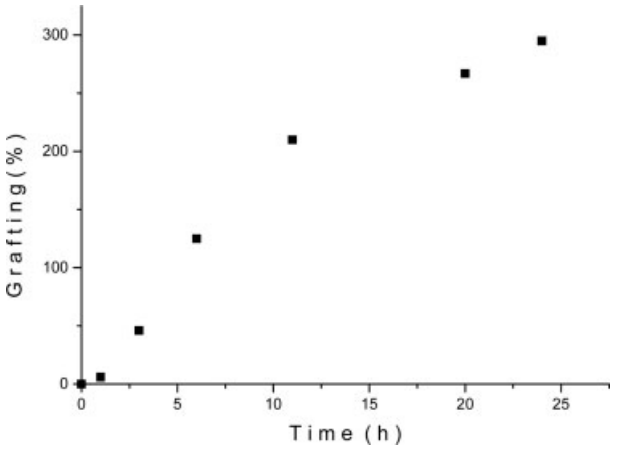


Figure 1. Percentage grafting of poly(GMA) *versus* time plot.

shaken until the copper salt was dissolved completely. The resulting homogeneous solution was added to the flask while stirring with magnetic bar, under nitrogen flow. Nitrogen was flushed through the mixture for 5 min, and then stopped. The system was closed and reaction mixture was gently stirred (to avoid mechanical disintegration) with magnetic bar (250–300 rpm) at this temperature for 21 h. At the end, the mixture was cooled, filtered, washed with ethanol (50 mL) and diethyl ether (50 mL), and dried under vacuum at room temperature for 24 h. Dry product weighed 26.9 g. The bead particles were still in spherical form and significantly bigger than the initial size.

To inspect homopolymer formation 5 mL of the above filtrate was added to 40 mL acetone. Slightly turbid solution was transferred into a closed bottle and left to stand overnight in the fridge. No precipitate was detected at the end of this time, nor GPC analysis of the solution evidenced formation of homopolymer.

Epoxy content of this product was determined by pyridine-HCl method[21] as follows: 1 mL concentrated hydrochloric acid was added to 50 mL dry pyridine while stirring. 10 mL of this solution was mixed with 0.155 g polymer sample and the mixture was boiled for 3 h. After cooling it was filtered and excess of pyridinium chloride was determined by back-titration of 8 mL of the filtrate with methanolic KOH solution (0.079 M). Thus 20.5 mL of titer consumption, in comparison to 29 mL for 8 mL of pristine pyridine-HCl solution revealed 5.41 mmol epoxy group per gram of the graft copolymer.

Kinetics of the Grafting Polymerization

The progress of the grafting was followed by a series of small scale experiments using mixtures of 0.2 g bromosulfonamide polymer, 0.6 g GMA, 3 mL toluene with 22 mg CuBr (1.53×10^{-4} mol), and 0.1 g H-TETA (1.53×10^{-4} mol). The reactions were carried out for different times (0–21 h) similarly to the preparative reaction. Extent of the grafting was assayed by monitoring mass increases of the bead samples with time. Percentage grafting was calculated simply by the following relationship:

$$\% \text{ Grafting} = \frac{W_t - W_0}{W_0} \times 100$$

where W_0 is initial weight and W_t is weight of graft product obtained at any given time (Fig. 1). The data were used to build Figure 2. For the kinetics plot (Fig. 2) unreacted monomer contents were estimated by differences of initial monomer contents from the mass increases of bead samples.

Modification with Morpholine

To inspect unchanged epoxy groups on graft chains, 1 g of the graft copolymer sample was introduced to 10 mL morpholine while stirring at 0 °C. The mixture was stirred for 2 h at room temperature and heated at 80 °C for 10 min. The beads were filtered, washed with water (50 mL), alcohol (2×10 mL) and ether (10 mL).

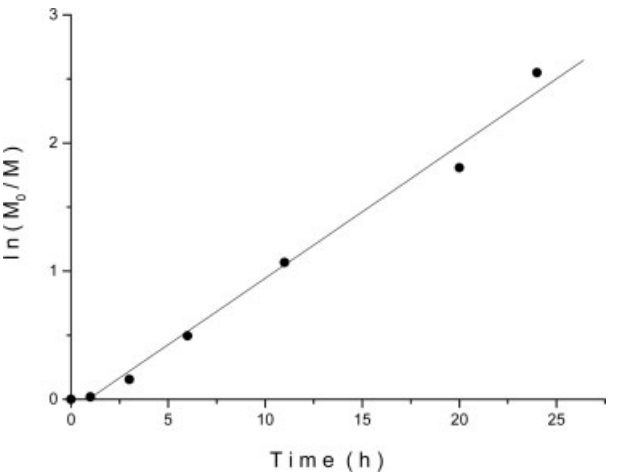
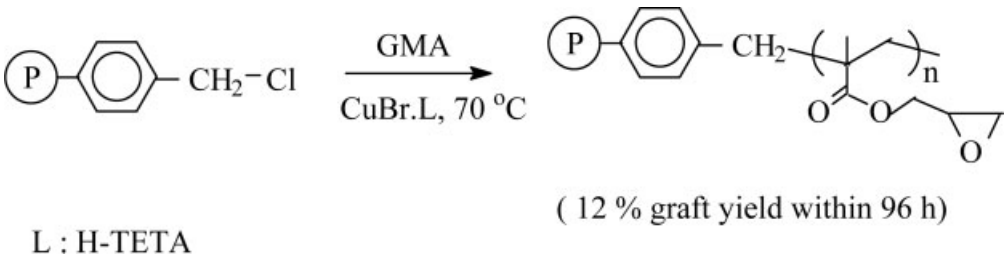


Figure 2. First-order kinetic plot for graft copolymerization from *N*-bromosulfonamide groups on PS-DVB micro spheres.



Scheme 1. Graft copolymerization of GMA from Merrified Resin by ATP.

Dried sample weighed 1.47 g. For analysis of the morpholine content, 0.2 g of the sample was soaked into 5 mL of 1 M HCl solution and left to stand overnight. The mixture was filtered and 3 mL of this filtrate was titrated with 0.1 M NaOH solution. 25.6 mL of titer indicated a morpholine content of 3.66 mmol g^{-1}.

Characterization

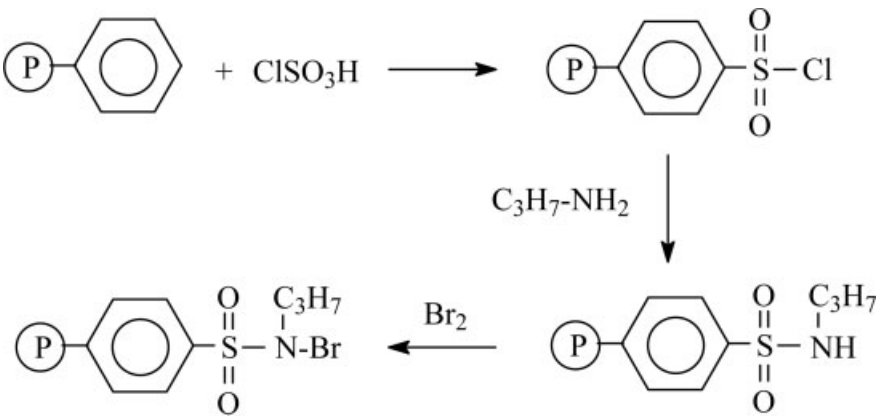
^{1}H-NMR measurements were performed in $CDCl_3$ solution, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. Scanning Electron Microscopy (SEM) pictures were taken with a Jeol 1540 instrument at 10 kV, using gold coated samples.

RESULTS AND DISCUSSION

Poly(GMA) was grafted on PS-DVB (10% mol/mol) bead resin containing *N*-bromosulfonamide groups by copper-mediated ATRP. This procedure gave "hair like" polymers in which graft chains are linked to resin surface with hydrolytically stable sulfonamide bonds.

Before doing so, initiation from chloromethyl groups on crosslinked PS was explored as a more direct way of obtaining nonhydrolysable linkage between graft chains and the bead core. For this purpose crosslinked styrene (0.8 mol) – vinylbenzyl chloride (0.1 mol) – divinylbenzene (0.1 mol) terpolymer was prepared in bead form by suspension polymerization of the mixture, as described in the literature.[18] The resulting product (Merrifield Resin) was used as solid macroinitiator for graft copolymerization of GMA by ATRP using H-TETA-CuBr as the catalyst complex. (Scheme 1). However, all attempts were only partially successful with 12% of graft yield being attained within 96 h in toluene at 70 °C.

Changing initiator to the copper complex ratios did not result in any significant improvement. Also no detectable grafting was attained in dimethoxy ethane or 1, 4-dioxane solvents in the same reaction conditions. This must be largely due to low initiation efficiency of the chloromethyl groups at this temperature. We have not studied polymerization at higher temperatures to avoid ring opening of the oxirane function in GMA. Because of these drawbacks, we addressed an alternative pathway for the surface initiation.



Scheme 2. Introducing initiator groups on PS-DVB resin beads.

Incorporation of Initiator Sites on PS Bead Surfaces

N-bromosulfonamide group seemed to be ideally suited for initiation of the graft copolymerization by ATRP. Incorporation of this group onto PS-DVB (10%) resin beads (220–410 μm) was performed in three steps: (i) chlorosulfonation, (ii) reaction with propylamine, and (iii) bromination, as depicted in Scheme 2.

The first step was achieved by direct soaking of the resin beads into chlorosulfonic acid, without solvent. Two hours-contact with chlorosulfonic acid at room temperature led to a weight gain of 15.2%. Since incorporation of one mole chlorosulfone group yields 98.5 g mass increase, this indicated a chlorosulfone group content of

$$\frac{15.2/98.5}{100+15.2} = 1.33 \times 10^{-3} \text{ mol g}^{-1}$$

$$= 1.33 \text{ mmol g}^{-1}.$$

This amount is consistent with the value obtained from chlorine analysis (1.316 mmol g^{-1}). Reaction period in this step is crucial to adjust density of initiation sites on the surface.

Less chlorosulfone group contents might be desirable for some applications of final graft copolymer. However we have not dealt with optimization of this step.

The amidation with excess propyl amine (second step) was almost quantitative as inferred from titrimetric analysis of the sulfonamide group (1.32 mmol g^{-1}). N_2 sorption isotherms showed very small surface area (0.67 m^2 g^{-1}) and pore volume (5.1×10^{-3} cm^3 g^{-1}) in dry state. This result can be ascribed to small percentage of invariant pore volume of the product. In other words the sulfonamide groups should be located mostly at outer surface regions of the microspheres.

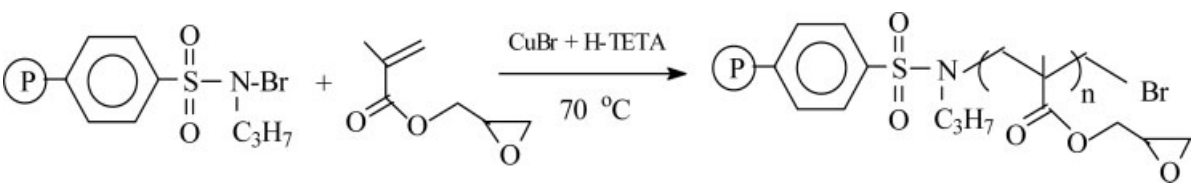
The bromination in the third step was performed in aqueous mixture of sulfamidated polymer. Water was preferred as the reaction medium. CCl_4 and $CHCl_3$ were also studied as swelling solvents for the bromination reaction. However, those procedures resulted in highly swollen particles from which physically absorbed bromine could not be removed under vacuum. Due this fact water was chosen as the reaction medium. Physically absorbed bromine, in this case, was removed under vacuum, as followed visually by disappearance of light brown color of the brominated product. The different behavior is because of the fact, that hydrophobic polymer does not swell in water and the micropores in the crosslinked matrix remain closed. So, excess bromine cannot penetrate into the micropores in aqueous medium. Accordingly, removal of excess bromine adsorbed on the surfaces of macro pores is relatively easy.

Poly(GMA) Grafts on PS-DVB Microspheres

Graft copolymerization of GMA from *N*-bromosulfonamide groups on PS-DVB resin beads was performed at 70 °C in toluene using freshly prepared CuBr and hexylated triethylenetetramine (H-TETA) as ligand (Scheme 3). This ligand forms entirely soluble copper complex in organic media as demonstrated earlier.[14]

Evaluation of those data indicated a linear first-order kinetic plot (Fig. 2), implying constant active radical concentration during the process.

The grafting in these conditions proceeded smoothly without formation of free homopolymer as by-product. Homopolymer formation was checked by GPC analysis of the solution filtrates of the polymerization mixtures and by adding them into a large excess of acetone. Indeed, no homopolymer formation was detected in either preparative or kinetic studies. It is important to note that, the residual toluene in PS beads is responsible for the homopolymer formation. Because toluene is also chlorosulfonated and forms *N*-bromo *p*-toluene sulfonamide in the following



Scheme 3. Graft copolymerization of GMA from *N*-bromosulfonamid groups on crosslinked PS-DVB microspheres.

modification steps. This material acts as initiator to give free-homopolymers. We have observed that no homopolymer forms when PS bead product is well dried under vacuum.

Progress of the grafting was followed by monitoring mass increases of the separate resin samples (Fig. 1).

Figure 2 reveals a rate constant of 2.88 $\times$ 10^{-4} s^{-1} (correlation factor: 0.9942). The kinetics plot shows also 30 min of induction period in grafting. This can be ascribed to the heterogeneity of the initiation process at the beginning.

As the grafting proceeds the reaction becomes more homogenous due to increasing flexibility of growing chains carrying radical centers.

Significant weight gain (284.3%) attained within 21 h (for the preparative sample) implies

$$\frac{2.843/142}{1+2.843} = 5.2 \times 10^{-3}$$
$$= 5.2 \text{ mmol GMA units per gram of the starting microsphere}$$

where 2.843 is loaded poly(GMA) per gram of the starting resin and 142 is molar mass of GMA.

If mass of replaced bromine (1.26 mmol g^{-1}) is taken into consideration, true weight gain will be 2.843 + 80 $\times$ 1.26 $\times$ 10^{-3} = 2.9438 g. This means 294.4% of grafting which corresponds to 5.39 mmol of GMA units per gram. This quantity is consistent with the epoxy content found by pyridine-HCl method (5.41 mmol g^{-1}).

Then, average degree of the polymerization per initiation site would be

$$\frac{5.41(1+2.9438)}{1.26} = 17$$

Obviously this structure does not allow cleavage of the graft chains for further analyses of their molecular weight distributions. Nevertheless, a uniform chain length distribution is likely in this process in agreement with previous report on ATRP of GMA.

Comparison of FT-IR spectra (Fig. 3) of the grafted resin and initial solid initiator resin clearly proves incorporation of GMA units into the structure.

Thus, N—H stretching vibration band of the sulfonamide resin [Fig. 3(a)] at 3270 cm^{-1} disappears almost completely in the IR spectrum of the brominated product in [Fig. 3(b)]. The peak at 1600 cm^{-1} is associated with N—H plane bending and phenyl ring vibrations. Reduced intensity of this peak [Fig. 3(b)] implies the bromine substitution. IR spectrum of grafted resin [Fig. 3(c)] exhibits typical methacrylate ester vibrations of GMA units. The strong carbonyl vibration band at 1725 cm^{-1} and two C—O stretching vibrations at 1255 and 1150 cm^{-1} indicate ester functionality of the repeating units in the side chains.

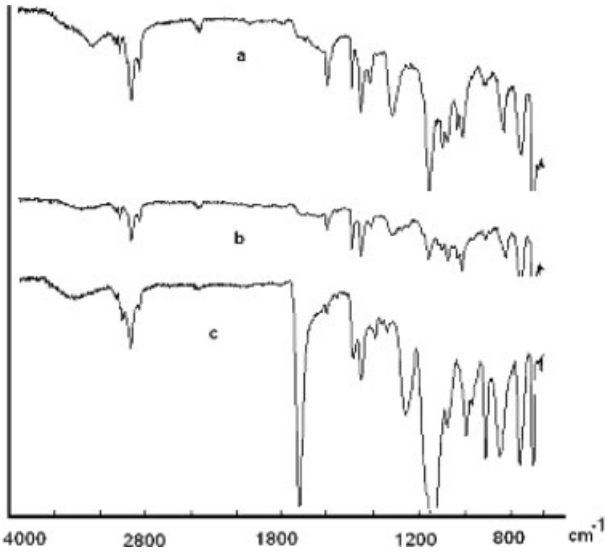


Figure 3. FT-IR spectra of the microspheres (a) with sulfonamide groups, (b) bromosulfonamide groups, and (c) with poly(GMA) grafts.

The grafted resin was also characterized by SEM showing marked increase in diameter of the microspheres (Fig. 4). The spherical shape of the beads was retained after the grafting.

The 210–420 μm initial size range was almost doubled after grafting and became 400–600 μm in average. Indeed diameter of 93% graft sample was found to be larger than 420 μm by sieving.

Modification of the Epoxy Groups

To test reactivity of the epoxy groups on the micro spheres, the graft sample was further modified with morpholine. Two hours interaction at room temperature and subsequent heating at 80 °C resulted in 47.0% weight gain based on dry product. Having one N—H group for ring opening of the oxirane functions morpholine was chosen as suitable reagent. The result reveals that grafting was performed without damaging

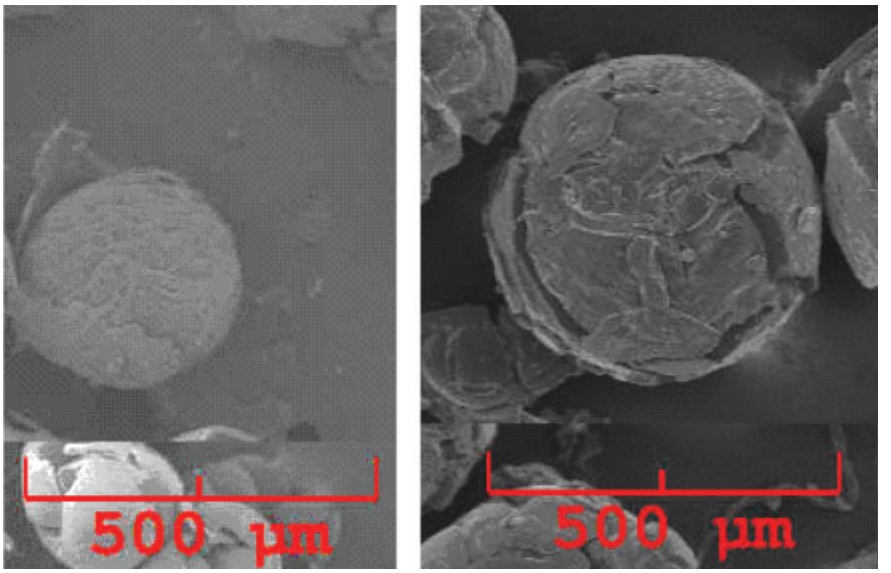


Figure 4. SEM pictures of PS-DVB micro spheres with bromosulfonamide function (left) and with poly(GMA) surface grafts (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

epoxy rings of GMA units and almost all of the epoxy groups are accessible by morpholine as reagent. The 47.0% of weight gain indicated an epoxy content of 5.4 mmol g^{-1} which was almost equal to the one found by pyridine-HCl method (5.41 mmol g^{-1}).

CONCLUSIONS

N-bromosulfonamide groups supported on solid PS-DVB microspheres were demonstrated as efficient ATRP initiators in graft copolymerization of GMA in high yields. Since graft chains are attached to the microspheres with hydrolytically stable sulfonamide linkages, the resulting materials can be further modified via epoxy groups to impart any desired functionality. Flexibility of the side chains is expected to provide pseudohomogeneous reaction conditions and easy accessibility of the functional groups involved. Therefore, such a macromolecular architecture would offer an excellent combination of insolubility of the bead core and fast reactivity of the dangling chains to be considered as catalyst or reagent carriers.

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