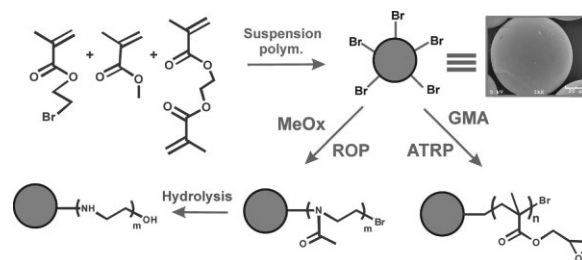


Preparation of Crosslinked Poly(2-bromoethyl methacrylate) Microspheres and Decoration of Their Surfaces with Functional Polymer Brushes

Bunyamin Karagoz, Deniz Gunes, Niyazi Bicak*

Synthesis and crosslinking copolymerization of 2-bromoethylmethacrylate in aqueous suspension is described for preparing bromoalkyl-functional microbeads (125–420 μm). Highly transparent microspheres with a density of accessible bromoethyl groups of $1.55 \text{ mmol} \cdot \text{g}^{-1}$ were prepared in the suspension, stabilized with poly(*N*-vinyl pyrrolidone), by using methyl methacrylate as diluting co-monomer and ethylene glycol dimethacrylate as crosslinker. Bromoalkyl groups on the microparticles were employed as initiation sites for either surface-initiated ATRP of glycidyl methacrylate or ring-opening polymerization of 2-methyl-2-oxazoline to generate epoxy- and *N*-acetyleneimine-functional hairy grafts, tethered to the particle surfaces with hydrolytically stable linkages.



Introduction

Crosslinked polymer beads (CPB) with surface-tethered functional groups have found great interest as scavenging material, catalyst carrier or polymeric reagents.^[1] The reactions on the solid particles have been termed as “solid phase reactions” or “polymer supported reactions”. Extensive works, dealing with synthesis, modification and applications of functional crosslinked polymer beads have been subjected in many papers, review articles^[2] and books.^[3] Ease of their separation from the reaction medium by simple filtration, their recovery and recycling facilities are apparent advantages of the functional bead polymers.

Two general approaches have been employed for preparation of functional crosslinked polymer beads. The first one is modification of pre-polymers (usually in spherical bead form) and the other is polymerization of the monomers having desired functionalities.

The second approach has an advantage of preparing polymers with well-defined constitution. Although some portion of the functional groups remain embedded in the crosslinked structure,^[4] this route is still preferable to attain CPB with desired functional group densities. However, the number of the commercial functional monomers to be chosen is very limited. In this respect, vinylbenzyl chloride (VBC), glycidyl methacrylate (GMA) and acetylated 4-vinylphenol (4-acetoxyvinylbenzene) can be considered as key monomers for functional polymers. VBC is of historical importance and commercially available as a mixture of *meta*- and *para*-isomers.^[5] Pure VBC was also reported^[6] and commercialized some years ago. However, it is very expensive.

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GMA is an epoxy-functional monomer having hydrolytically stable ester linkage. Its crosslinked bead polymers have been used as carrier for chelating ligands^[7] and catalysts. The *t*-butoxycarbonyl derivative of 4-vinylphenol has been used as precursor for poly(4-vinylphenol), which has interesting nucleophilic properties.^[8] Some other monomers, such as 4-vinylpyridine and 2-vinylpyridine can be included in the list due to further functionalization of their polymers by quaternization.^[9]

In this report, we wish to introduce another functional monomer, 2-bromoethyl methacrylate (BEMA). Although synthesis and polymerization of this monomer has been reported^[10] some years ago, it is less common and very expensive probably due to its methacryloyl based manufacturing. Recently, we have developed an alternative method for synthesis of BEMA from relatively cheap sources.^[11] In this method, BEMA was synthesized in acceptable yields (62–78%) by action of methacrylic acid on tris(2-bromoethyl borate). Herein we report suspension polymerization of this monomer yielding crosslinked microspheres possessing bromoalkyl functions.

In the study, formulation and conditions of the suspension polymerization yielding fine microspheres were discussed. The resulting bead polymer was characterized by bromine analysis, Fourier-transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The bromoethyl functions of the bead polymer were then employed as initiation sites for surface initiated polymerization of either ring-opening polymerization (ROP) of 2-methyloxazoline or atom-transfer radical polymerization (ATRP) of glycidyl methacrylate, respectively.

Experimental Part

Materials

Methyl methacrylate (MMA, Aldrich) and ethylene glycol dimethacrylate (EGDMA, Aldrich) were distilled prior to use. 2-methyl-2-oxazoline (MeOx, Aldrich) was purified by distillation over CaH₂. CuBr was freshly prepared by the procedure as described in the literature.^[12] The ATRP ligand 1,1,4,7,10,10-hexakis(hexyl-1,4,7,10-tetraazadecane) (H-TETA) was prepared by alkylation of triethylenetetramine with 1-bromohexane as described before.^[13] All the other chemicals used were analytical grade and used as purchased: 2-bromoethanol (Merck), methacrylic acid (Aldrich), poly(*N*-vinylpyrrolidone) (molecular weight 24.000 g·mol⁻¹, Aldrich), 2,2'-azobisobutyronitrile (AIBN, Fluka) and glycidyl methacrylate (GMA, Aldrich).

Synthesis of BEMA

Synthesis of BEMA was carried out by a new procedure as described in our previous report.^[11] In this procedure boron ester of 2-bromoethanol was reacted with methacrylic acid in the presence

of pyridine. The procedure is as follows: To a 250 mL volume flask was added 75 g (0.6 mol) 2-bromoethanol, 12.37 g (0.2 mol) H₃BO₃ and 80 mL toluene. The flask was equipped with a Dean-Stark trap and a reflux condenser. The mixture was heated at 150 °C and water removal was completed within 3–4 h under continuous stirring. Then excess of toluene was distilled off and recovered via reservoir of the trap. To the cooled mixture 50.9 mL (0.6 mol) methacrylic acid, 0.1 g hydroquinone and 3 mL pyridine were introduced and the reaction content was heated to 160 °C for 24 h. After cooling, the reaction content was poured into 300 mL water. The organic phase was separated by a separatory funnel and dried with Na₂SO₄. The monomer was isolated by distillation under vacuum (boiling point 112–114 °C at 11 mmHg). The yield was 71.2%.

¹H NMR, (CDCl₃), δ = 6.0 (s, 1H, =CH₂ *cis*), 5.45 (s, 1H, =CH₂ *trans*), 4.3 (broad s, 2H, –COO–CH₂–), 3.4 (broad s, 2H, –CH₂–Br), 1.8 (s, 3H, CH₃–C=C).

In the FT-IR spectrum of the product, the typical C=O stretching vibration of the ester group appears at 1 725 cm⁻¹. The other characteristic peaks associated with C=C, C–O and C–Br stretching vibrations appear at 1 638, 1 160 and 814 cm⁻¹ respectively.

Preparation of Crosslinked Poly(BEMA) Microspheres by Suspension Polymerization

Poly(BEMA) microspheres were obtained by the following procedure: 1 g of commercial poly(*N*-vinylpyrrolidone) and 3 g Na₂SO₄ were dissolved with 300 mL of distilled water in a 1 000 mL three-necked flask equipped with a nitrogen inlet, dropping funnel and a reflux condenser. Then 12.1 g (62.5 mmol) BEMA, 4.95 g (25 mmol) EGDMA, 16.25 g MMA (162.5 mmol), 45 mL toluene (porogen) and 0.160 g (0.098 mmol) AIBN were added successively to the flask under nitrogen flow. The flask was mounted in a thermostatted oil bath and the temperature was adjusted to 60 °C. The nitrogen stream was stopped and the system was closed. The reaction was conducted under constant stirring rate (1 000 rpm) for 12 h. The reaction content was then cooled and poured into 1 L of water and the produced beads were collected by filtration. They were washed with excess of water (5 · 100 mL) and dried at 40 °C for 24 h. The pearl-like bead product weighed 28 g. The product was fractionated by sieving and determined to be mostly (85%) in the 125–420 μ m range.

Determination of Bromide Content of the Microspheres

Half a gram of the bead sample was introduced to 15 mL of methanolic NaOH solution (20%) and the mixture was boiled for 24 h using a reflux condenser. The cooled mixture was filtered and washed with water (3 · 10 mL). The filtrate and washings were combined and made up 50 mL in a volumetric flask. 25 mL of this solution was neutralized with nitric acid solution (65%, \approx 4 mL) and mixed with 4 mL of AgNO₃ solution (1 M). The white precipitate was filtered, washed with water (5 mL) and dried at 40 °C for 16 h under atmospheric pressure. The dry weight of AgBr (0.073 \pm 0.002 g) indicated 1.55 mmol bromide per gram of the crosslinked polymer.

Surface-Initiated ATRP of GMA from the Bromoethyl Groups

To remove soluble impurities in the crosslinked microspheres, 12 g of the sample was placed in a Soxhlet extractor. The extraction was performed using toluene (150 mL), in about 3 h. and dried as described above. Meanwhile to a 100 mL volume three necked flask equipped with a nitrogen inlet and a reflux condenser, 0.22 g CuBr (1.55 mmol), 1 g ligand, H-TETA (1.55 mmol), 7 mL GMA and 7 mL toluene were charged and stirred for 30–40 min to dissolve the copper salt under nitrogen flow. One gram of the bead sample was added to the flask, then the system was closed and reaction mixture was gently stirred (to avoid mechanical disintegration) with a magnetic bar (400 rpm) at 60 °C for 24 h. The mixture was cooled, filtered, washed with toluene (2 · 25 mL), acetone (2 · 25 mL), and ethanol (50 mL) and dried under vacuum at room temperature for 24 h. The dry product weighed 5.2 g. The bead particles were still spherical.

To inspect free homopolymer formation, the filtrate (before washing) was added into 40 mL methanol. The precipitate was filtered and washed with water (30 mL). The dried product weighed 0.14 g indicating approximately 1.87% of free homopolymer formation in the grafting process.

Kinetics of the surface grafting was performed at the same polymerization conditions. For this purpose in each set of the experiments, 0.2 g of poly(BEMA) sample was employed as macroinitiator. The polymerizations were carried out in degassed tubes using 43 ± 2 mg CuBr (0.31 mmol), 0.2 g (0.31 mmol) H-TETA and 2 g (13.7 mmol) GMA. At the end of predetermined times, the reactions were quenched and the products were isolated as described above. The grafting degree, G (g per gram), monomer conversion in grafting, p were defined as follows:

$$G = \frac{m_G - m_0}{m_0} \quad p = \frac{m_G - m_0}{m_{\text{GMA}}}$$

where m_G is mass of the graft copolymer, m_0 is mass of poly(BEMA), and m_{GMA} is mass of GMA used in the surface grafting process.

Surface-Initiated ROP of MeOx from the Bromoethyl Groups

One gram of the bead sample, 10 mL of acetonitrile and 8.5 mL (0.1 mol) MeOx were introduced to a 100 mL volume flask and flushed with nitrogen for 5 min. Then the system was closed and the reaction was conducted at 110 °C by gentle stirring (400 rpm) for 24 h. The mixture was cooled and poured into water. The bead product was filtered, washed with water (3 · 50 mL), ethanol (20 mL) and dried at 50 °C under vacuum for 24 h. Dry product weighed 1.62 g.

The kinetic experiments were carried out in sealed tubes for each reaction time, using 0.2 g poly(BEMA) sample, 3 mL acetonitrile and 2 mL of MeOx. The grafting was monitored by mass increases of poly(BEMA) samples. The grafting degrees were assigned as described above.

Hydrolysis of the Poly(MeOx) Surface Grafts

A dry sample with poly(MeOx) surface graft (1 g) was mixed with 10 mL HCl solution (4.0 M) and boiled for 48 h. The mixture was

filtered and washed with water several times. Then the solid residue was poured into 20 mL NaOH solution (5 M) and left to stand for 24 h. The product was filtered and washed with water (5 · 100 mL) and dried under vacuum at 50 °C for 18 h. The dry product weighed 0.84 g.

Determination of Amine Content of the Hydrolysis Product

Dry sample of the hydrolysis product (0.2 g) was mixed with 5 mL HCl solution (4.66 M) and left to stand overnight. The mixture was filtered and 2 mL of the filtrate was titrated with 0.1 M NaOH solution. The titer consumption (88.6 mL) revealed an amine content of $5.75 \text{ mmol} \cdot \text{g}^{-1}$.

Synthesis of Model Initiator Bromoethyl Acetate

To a 100 mL flask, there was added 3.6 mL (0.05 mol) bromoethanol and 4.3 mL (0.06 mol) acetyl chloride. The mixture was stirred for 3 h at room temperature and poured into 100 mL water. The organic layer was separated and washed with 100 mL K_2CO_3 solution (1%) and dried with anhydrous MgSO_4 (0.5 g). Distillation of the crude product (boiling point 81 °C at 5 mmHg) gave 7.1 g (84.0%) colorless liquid.

$^1\text{H NMR}$, (CDCl_3), $\delta = 4.30$ (t, 2H, $\text{CH}_2\text{-O}$), 3.50 (t, 2H, $\text{CH}_2\text{-Br}$), 2.05 (s, 3H, CO-CH_3).

Bromoethyl Acetate as Initiator for ATRP of MMA

A typical ATRP mixture containing CuBr (0.067 g, 0.47 mmol), H-TETA (0.31 g, 0.47 mmol), MMA (5 mL, 46.8 mmol) and 5 mL toluene was prepared in a 100 mL round bottom flask under nitrogen atmosphere. The initiator bromoethyl acetate (0.079 g, 0.47 mmol) was added to the flask placed in an oil bath at 70 °C and the reaction was conducted for 5 h. After removal of the copper catalyst via silica column, the polymer was precipitated in hexane 30 mL, filtered and dried at 50 °C for 12 h under vacuum. The yield was 0.7 g (14.8%). The gel permeation chromatography (GPC) trace of the polymer revealed $\bar{M}_n = 18\,500 \text{ g} \cdot \text{mol}^{-1}$ ($\bar{M}_w = 36\,000 \text{ g} \cdot \text{mol}^{-1}$).

The same polymerization procedure was repeated using bromomethyl propionate and benzylbromide as ATRP initiators instead of bromoethyl acetate. The polymerization yields were determined to be 56.0% and 96.0% for the case of benzylbromide and bromomethyl propionate, respectively. GPC traces of the corresponding polymers indicated $\bar{M}_n = 30\,400$ ($\bar{M}_w = 39\,500$) and $45\,800 \text{ g} \cdot \text{mol}^{-1}$ ($\bar{M}_w = 70\,000 \text{ g} \cdot \text{mol}^{-1}$) for the initiation with benzylbromide and bromomethyl propionate, respectively.

The initiation efficiencies (I_{eff}) were estimated simply from the relationship

$$I_{\text{eff}} = \frac{M_{\text{th}}}{\bar{M}_n} = \frac{([\text{M}]/[\text{I}])pM_0}{\bar{M}_n}$$
 where M_{th} is theoretical molecular weight, \bar{M}_n is the number-average molecular weight determined by GPC, $[\text{M}]$ and $[\text{I}]$ are the concentrations of monomer and initiator, respectively, p denotes the conversion, and M_0 is molecular weight of the monomer (MMA). From these data the initiation efficiencies of bromoethyl acetate, benzylbromide and bromomethyl propionate were calculated as 0.08, 0.12 and 0.33 respectively.

Instrumentation

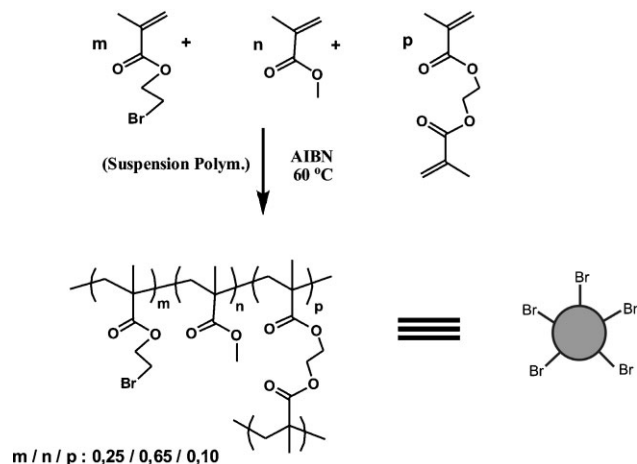
^1H NMR spectra of monomers and polymers were obtained by a Bruker 250 MHz NMR spectrometer, using CDCl_3 as solvent. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. Particle shapes and sizes of the product were determined by optical photography using an image analyzing system consisting of a microscope (XSZ single zoom microscope), a CCD digital camera (TK 1381 EG), and a PC with the data analyzing system, Image-Pro Plus. SEM pictures were taken with a Jeol 1540 instrument at 10 kV, using gold-coated samples. XPS spectra of the samples were taken with a Specs Phoibos-150 electron analyzer equipped with a SPECS XR-50 X-ray source using monochromatized Al K_α radiation (1 486.6 eV) for the excitation. Survey spectra were recorded in 0 to 1 200 eV range with pass energy of 80 eV. All the peaks were referenced to a C1s signal at 285 eV. The pressure of the analyzer chamber was 10^{-8} to 10^{-9} Torr. Molecular weights were determined with a GPC instrument equipped with Waters Styragel column (HR series 2, 3, 5E) with tetrahydrofuran (THF) as the eluent at a flow rate of $0.3 \text{ mL} \cdot \text{min}^{-1}$ and a Waters 410 differential refractive-index detector.

Results and Discussion

The monomer BEMA was prepared in high purity by a new synthetic procedure as described recently by our group.^[11] The procedure involves acidolysis of 2-bromoethyl borate with methacrylic acid. Having bromoethyl function on the monomer offers many transformation possibilities and can be considered as key monomer for preparing various functional polymers. Comparing with the commercially available monomer, vinyl benzyl chloride constituting with a mixture of *meta* and *para* isomers, this monomer has the advantage of purity and higher reactivity of the bromoalkyl function. Although the commercial monomer GMA allows introducing ATRP initiator group by esterification with bromo-functional carboxylic acids such as 2-bromoisobutyric acid, hydrolytic instability of the ester linkage brings an important limitation for further processing of the graft chains in acid-base conditions. Therefore the advantage of BEMA over GMA is that, the graft chains in the former are linked with non-hydrolyzable carbon-carbon bonds. The crosslinked BEMA polymer in spherical bead form was considered as a good alternative to "Merrifield resin".

Preparation of Crosslinked Poly(BEMA) Microspheres

Crosslinked poly(BEMA) microspheres were prepared by suspension polymerization method using MMA as diluting co-monomer to adjust the bromoethyl group density of the resulting polymer. EGDMA was chosen as crosslinker and AIBN was employed as primary radical source. The polymerization and chemical structure of the resulting polymer is depicted in Scheme 1.



Scheme 1. Crosslinking terpolymerization of BEMA-MMA-EGDMA mixture in aqueous suspension, yielding microspheres.

In principle, proper selection of the stabilizer is a critical issue in suspension polymerization to obtain perfect spherical beads. The particle shape may also affect on thickness and homogeneity of the graft layer, when the product is employed as solid macroinitiator in the surface initiated ATRP.

In the present work, various polymers; poly(vinyl alcohol), Gum Arabic, poly[styrene-*alt*-(maleic acid)] and poly(*N*-vinylpyrrolidone) (PNVP) were studied for stabilization of the suspension droplets of the monomer mixture in water. Experiments were conducted at various oil/water volume ratios with different stirring rates (500–1 000 rpm). Except for the case of PNVP, the products obtained were amorphous gels or irregular beads in different sizes. Although, poly[styrene-*alt*-(maleic acid)] was successfully employed in our previous works, for preparing fine microbeads of GMA-MMA copolymer,^[7] this stabilizer did not work in the present case, most probably due to its increasing hydrophobicity of the stabilizing polymer by partial condensation of the carboxylate function with bromoethyl groups of BEMA. Changing the stabilizer ratio and stirring rates were not helpful and the resulting solid particles obtained were irregular. The experiments with gum arabic gave similar amorphous products.

The stabilization with PNVP gave colorless microspheres in relatively narrow size distributions (125–420 μm). The recipe for the suspension polymerization procedure with PNVP is given in Table 1. Optical photography of the dry product in Figure 1 shows nearly spherical beads with smooth surfaces.

The fraction in the 210–420 μm size range was employed for the surface initiated polymerizations in the following studies. Bromide content of this product was determined to be $1.55 \text{ mmol} \cdot \text{g}^{-1}$. Considering with the initial molar composition of the monomer mixture in the suspension

Table 1. Recipe for suspension copolymerization of BEMA.

Parameter	Value
BEMA (monomer) amount	12.1 g (62.5 mmol)
EGDMA (cross-linker) amount	4.95 g (25 mmol)
MMA (co-monomer) amount	16.25 g (162.5 mol)
toluene (porogen) amount	45 mL
poly(<i>N</i> -vinylpyrrolidone) (stabilizer) amount	1 g
water (continuous phase) amount	300 mL
AIBN (radical initiator) amount	0.160 g (0.098 mmol)
stirring rate	1 000 rpm
polymerization temperature	60 °C
reaction time	12 h
appearance of the product	colorless microspheres
particle size	125–420 μm
accessible bromine content	1.55 mmol·g ⁻¹

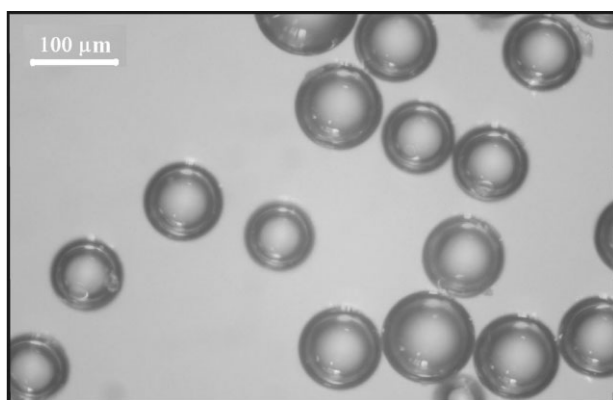


Figure 1. Photograph of crosslinked poly(BEMA) microparticles prepared by suspension polymerization using PNVP (1%) as stabilizer.

polymerization process, the theoretical bromide content must be 1.88 mmol·g⁻¹.

Therefore, the practical bromide content accounts for about 82.5% of the theoretical amount. Obviously, the remainder of the bromide is embedded in the crosslinked matrix and remains inaccessible in further reactions.

Surface-Initiated ATRP from the Bromoethyl Groups

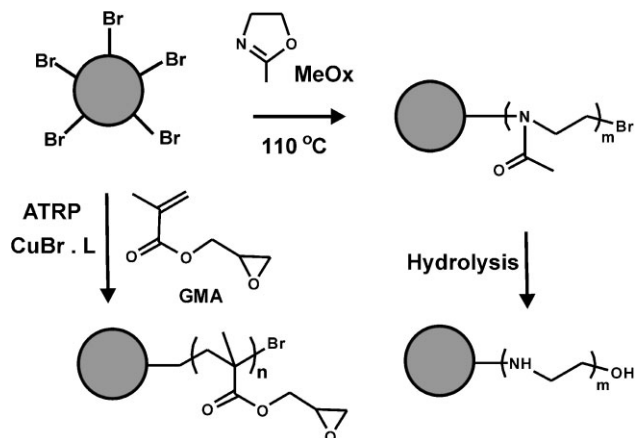
Since alkyl halides are well-known initiators for ATRP of acrylic and styrenic monomers, the bromoethyl groups on the beaded polymer surface were considered useful for creating polymeric surface brushes. Among controlled/living polymerization techniques, ATRP is especially useful for grafting from solid surfaces.^[14] Negligible formation of free homopolymer is the main advantage of surface-

initiated ATRP, in addition to nearly controlled chain growth in the grafting process.^[15]

This strategy has been employed successfully to generate surface grafts on solid PS or on inorganic pigment particles in μm or nanometer sizes.^[16–17] In the reported procedures, the surface grafts have been generated by ATRP from haloalkyl functions onto the surfaces. Common approach for incorporation of ATRP initiator groups onto solid particles involves esterification of surface hydroxy groups with 2-bromo isobutyryl bromide.^[18–19] Selective hydrolysis of the ester linkages after ATRP is useful for harvesting and analyses of the graft chains. However, hydrolytic instability of this linkage is not desirable, especially when the graft chains are considered as functional group carriers. In this respect, utilization of a suitable co-monomer bearing haloalkyl function in preparing spherical bead polymer might be useful to generate surface brushes linked to the surface by non-hydrolyzable covalent bonds. Perhaps vinyl benzyl chloride is the only haloalkyl functional monomer commercially available. Its crosslinked polymer has been reported as solid initiator for ATRP of dimethyl amino ethyl methacrylate.^[20] However, crosslinked copolymer of this monomer (Merrifield resin) has been demonstrated to be too slow in surface-initiated ATRP (SI-ATRP), due to less initiation efficiency of the chloromethyl group.^[14,21]

It was concluded that, bromoethyl groups on poly(BEMA) microspheres could be used as efficient initiating sites for grafting by SI-ATRP, without necessity of surface modification.

Starting from the beaded polymer with known density of surface initiator groups is an apparent advantage of this approach. And also non-hydrolyzability of the linkages



Scheme 2. Decoration of crosslinked poly(BEMA) microspheres with functional polymer brushes, by ATRP and ROP using bromoethyl surface groups as initiation sites.

between the graft chains and microspheres is an additional advantage of this material.

In conjunction with this, ATRP of GMA was studied in order to test radical initiation efficiency of the supported bromoethyl groups. The reaction was carried out with CuBr catalyst at 60 °C as depicted in Scheme 2. This procedure resulted in 420% graft yields within 24 h (see Table 2), indicating efficiency of those groups in initiation of ATRP. GMA was chosen for grafting monomer, due to numerous chemical transformation possibilities of the epoxy group on the graft chains.^[14]

In order to test radical generating ability of the bromoethyl function, bromoethyl acetate was synthesized as a model compound by reacting bromoethanol with acetyl chloride (see experimental part). This compound was employed as initiator for ATRP of MMA at 70 °C in toluene (using constant $[\text{monomer}]/[\text{initiator}]/[\text{CuBr.L}] = 100/1/1$ ratios) (where L denotes the ligand, H-TETA). For comparison of its initiation efficiency with those of the well known ATRP initiators, the polymerization was repeated with bromomethyl propionate and benzyl bromide in the same conditions. After 5 h of the polymerization, the resulting polymers were isolated. The initiation efficiencies were assigned simply by ratio of the theoretical to the

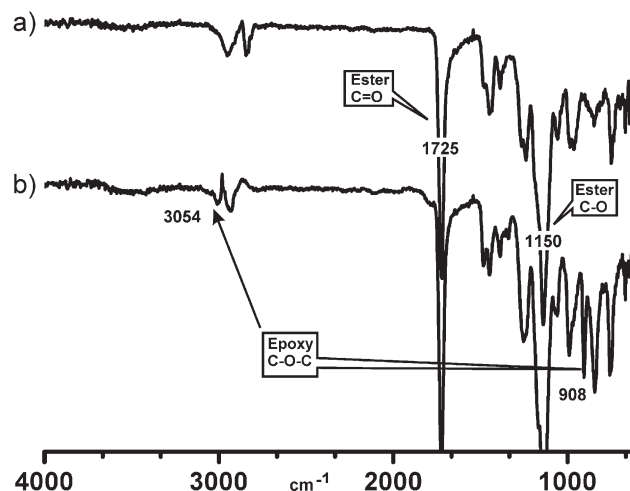


Figure 2. FT-IR spectrum of poly(BEMA) microspheres (a) before and (b) after surface grafting with GMA.

practical molecular weights inferred from the GPC traces. These experiments revealed initiation efficiencies 0.08, 0.12 and 0.33 for bromoethyl acetate, benzylbromide and bromomethyl propionate respectively. These results showed that the initiation efficiency of bromoethyl acetate is less than that of bromomethyl propionate, but comparable with that of benzylbromide.

The FT-IR spectrum of the GMA-grafted resin (Figure 2b) exhibits methacrylate ester vibrations at 1725, 1255 and 1150 cm^{-1} associated with stretching vibrations of carbonyl, CO–O and COO–C bonds respectively. These bands appear also in the IR spectrum of the starting microspheres (Figure 2a), but their intensities are significantly higher in the spectrum of grafted resin. The specific oxirane bands of the poly(GMA) brushes, which are different from those of the base material, appear at 3054 (shoulder) and 908 cm^{-1} and these represent C–H and C–O stretching vibrations of the epoxy ring respectively.

The semi-logarithmic plot of the conversion/time data of the grafting with GMA (Figure 3) implies nearly first order kinetics (regression factor, $R = 0.98$) with a rate constant of $k = (6.6 \pm 0.04) \times 10^{-6} \text{ s}^{-1}$. The graphic reveals a constant radical concentration in the graft copolymerization of GMA in these conditions. The slope of the curve however,

Table 2. Graft copolymerization characteristics of the monomers initiated from bromoethyl surface groups of crosslinked poly(BEMA) microspheres.

Grafted monomer	Polymerization method	Catalyst	Temperature	Time	Grafting ratio
			°C	h	
GMA	ATRP	CuBr/H-TETA	60	24	4.20 ^{a)}
MeOx	ROP	–	110	24	0.62 ^{a)} , 0.65 ^{b)}

^{a)}Estimated from the mass increase (g per g); ^{b)}Calculated from the amine content.

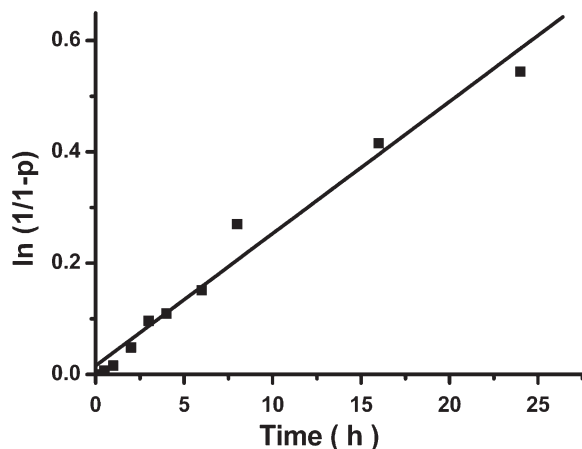


Figure 3. First-order kinetic plot for the surface-initiated graft copolymerization of GMA on poly(BEMA) microspheres by ATRP.

increases beyond 24 h indicating somewhat greater rate constant at high conversions. This must be due to heterogeneity of the grafting at the earlier stage of the reaction.

Increasing lengths of the graft chains at higher conversions provide quasi-homogeneous conditions and slightly higher polymerization rates. Since the grafts are not detachable from the surface, we are unable to make a precise estimation for the rates of the chain growths and polydispersities.

Considering the heterogeneity of the reaction, the surface grafting of GMA is not expected to proceed in thoroughly controlled fashion. Nevertheless, it is fact that initiation of ATRP of GMA from the bromoethyl groups on the solid microspheres is possible and provides reasonable graft yields.

XPS was also employed in order to follow the changes in surface characteristics of the microspheres by the grafting process. Figure 4a clearly shows core levels of the elements in poly(BEMA) microspheres. Thus, the main elements, carbon and oxygen, exhibit binding energies for C1s and O1s core levels at 285 and 534 eV, respectively. These elements show also Auger KLL peaks at 1000 and 979 eV respectively. The typical bromine peaks in poly(BEMA) are observed at 73 and 186 eV for Br3d and Br3p core levels (see inset in Figure 4). However, after grafting with poly(GMA), these peaks become almost invisible (Figure 4b). Considering with livingness of ATRP process, the chain ends of poly(GMA) brushes must carry bromine atoms. Absence of the two peaks in the XPS must be due to dilution of the bromine atoms by increasing volume of the microspheres in the grafting.

Surface-Initiated ROP from the Bromoethyl Groups

In the last part of the study, the bromoethyl groups of the poly(BEMA) microspheres were also employed as initiator

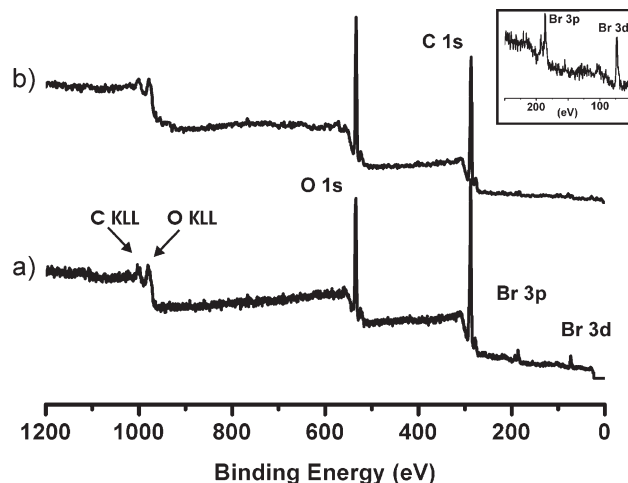


Figure 4. Full-scale XPS of poly(BEMA) microspheres (a) before and (b) after surface-initiated grafting with GMA. The inset shows Br3p and 3d core levels on the poly(BEMA) microspheres.

for the ROP of MeOx. Alkyl halides are known to polymerize also oxazoline monomers.^[22] Since polymer of MeOx is the precursor for linear polyethyleneimine, its grafting from the surface of poly(BEMA) microspheres allows preparing amine-functional surface grafts. The grafting in this study was simply achieved by heating crosslinked poly(BEMA) sample with MeOx in the presence acetonitrile as solvent at 110 °C. The mass increase in the reaction product indicated 62% of grafting yield. The FT-IR spectrum of the product in Figure 5b clearly shows a carbonyl stretching vibration band of the *N*-acetyl group at 1630 cm⁻¹, indicating the presence of poly(*N*-acetyleneimine) grafts in the resulting product.

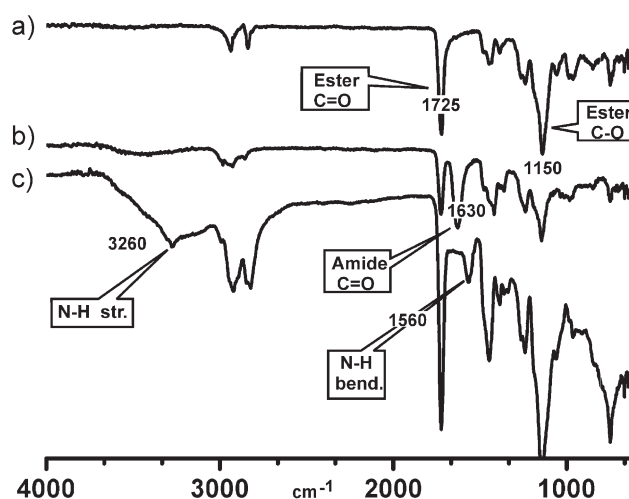


Figure 5. FT-IR spectrum of poly(BEMA) microspheres (a) before and (b) after surface grafting with MeOx, and (c) its hydrolysis product with poly(ethyleneimine) brushes.

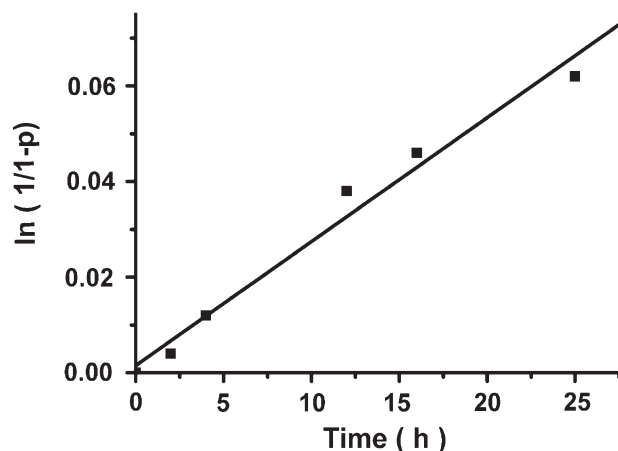


Figure 6. First-order kinetic plot for the surface-initiated ROP of MeOx at 110 °C.

Comparing with the FT-IR spectrum of the starting bead product in Figure 5a, the characteristic bands originating from C=O and C–O vibrations of the methacrylate ester groups remain unchanged at the same positions.

Kinetics of the ring opening polymerization of MeOx is first order with a rate constant of $k = (7.2 \pm 0.01) \times 10^{-7} \text{ s}^{-1}$ as inferred from slope of the straight line (regression factor, $R = 0.993$) in Figure 6. As a result, the successful grafting in both cases implies sufficient reactivity of the bromoethyl groups of poly(BEMA) microspheres for surface initiated ATRP of GMA and ROP of MeOx.

The microspherical product with poly(MeOx) surface grafts were then subjected to acid hydrolysis. However, the original procedure of Jeong et al.^[23] given for hydrolysis of linear poly(MeOx) did not result in complete hydrolysis. The complete hydrolysis of the poly(MeOx) grafts however was achieved by boiling with HCl solution (4.0 M) for 48 h and following neutralization with NaOH solution. FT-IR spectrum of the hydrolysis product in Figure 5c does not show the carbonyl vibration at 1630 cm^{-1} that indicates removal of the acetyl groups by hydrolysis. New peaks originating from stretching and plane bending vibrations of the amino groups appear respectively at 3250 and 1560 cm^{-1} . The unchanged C=O and C–O vibrations of the methacrylate ester groups in this spectrum implies selective hydrolysis of the acetamido groups in the poly(MeOx) grafts to give a poly(BEMA)-graft-poly(ethyleneimine) structure. Acid titration of this product revealed an amino group density of $5.75 \text{ mmol} \cdot \text{g}^{-1}$. By assuming full hydrolysis of the *N*-acetyleneimine groups of the graft chains, this corresponds to a 65% of the grafting, in the ROP of MeOx which is slightly greater than the one estimated by the mass increase (62%).

Moreover, transformation of poly(MeOx) surface grafts was also evidenced by XPS using Al K α as excitation source. The sample possessing poly(MeOx) surface brushes exhibits

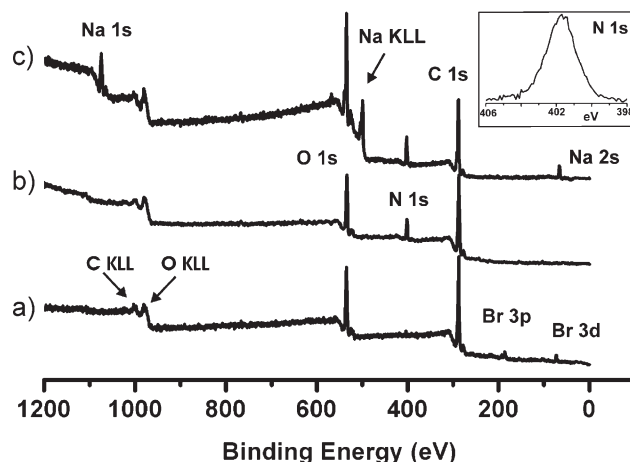


Figure 7. Full-scale XPS of poly(BEMA) microspheres (a) before and (b) after grafting with poly(MeOx) and (c) hydrolysis product of the latter. The N1s core level centered at 402 eV is given (inset).

typical N 1s core level at 402 eV in its XPS spectrum (Figure 7b). This peak appears at the same position after hydrolysis as expected (Figure 7c).

Presence of the nitrogen core level peak is also evidence for occurrence of the grafting with MeOx and successful hydrolysis yielding poly(ethyleneimine) brushes. Unexpected sodium peaks appeared at 1074, 500 and 66 eV in Figure 7c (corresponding to Na1s, Na KLL and Na2s levels respectively), are due to the contamination of NaOH solution used for neutralization of the acid-hydrolysis product. Retaining of the sodium even after successive washings with water might be due to reduced hydrophobicity of the poly(ethyleneimine) chains after neutralization with NaOH solution. Thereby, some trace of NaOH remains in the collapsed graft chains.

To inspect variation of the surface characteristics and shapes of the poly(BEMA) microspheres in the surface grafting processes, SEM pictures of the products were taken and compared with that of the starting material (Figure 8).

Figure 8a shows spherical poly(BEMA) microparticles with smooth surface. The size enlargement of the particles is observed after grafting with poly(GMA) while retaining the bead shapes, as seen in Figure 8b. The reason for the roughness of the particle surfaces is unclear, but this might be due to high grafting with GMA. In the case for the sample with poly(MeOx) surface grafts, the SEM picture (Figure 8c) shows a slight increase in diameters of the particles and the surfaces as smooth as the virgin particles.

Conclusion

A convenient procedure is described for suspension polymerization of BEMA, yielding crosslinked microspheres. The bromoethyl group of crosslinked polymer is

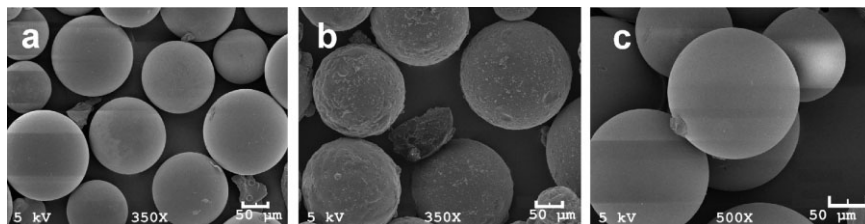


Figure 8. SEM images of (a) the bare poly(BEMA) microspheres and their surface-grafted counterparts with (b) poly(GMA) and (c) poly(MeOx).

useful for surface initiated ATRP and ROP of the GMA and MeOx monomers.

In principle, the spherical bead polymers with functional surface brushes can be considered as new generation of the functional polymers. These materials differ from conventional polymer resins having functional groups directly attached to the solid particle surfaces. Flexibility of the graft chains makes them partially mobile in liquid phase and this provides nearly homogeneous reaction conditions and faster reactions with target reagents in the solution as described before.^[24] Investigations aiming at applications of these functional hairy grafts will be subjected in the following studies.

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- [1] W. T. Ford (Ed.), *Polymeric reagents and catalysts*, Volume 38 in ACS Symposium Series, American Chemical Society, Washington 1986, Chapter 11.

- [2] A. Akelah, D. C. Sherrington, *Chem. Rev.* **1981**, *81*, 557.
- [3] D. C. Sherrington, P. Hodge, *Synthesis and separations using functional polymers*, John Wiley & Sons, Chichester 1988.
- [4] C. A. Cooper, R. L. McCullough, B. C. Gates, J. C. Seferis, *J. Catal.* **1980**, *63*, 372.
- [5] T. Balakrishnan, W. T. Ford, *J. Appl. Polym. Sci.* **1982**, *27*, 133.
- [6] S. Tanimoto, T. Miyake, M. Okano, *Synth. Commun.* **1974**, *4*, 193.
- [7] N. Bicak, M. Gazi, B. F. Senkal, *React. Funct. Polym.* **2005**, *65*, 143.
- [8] J. M. J. Frechet, E. Eichler, H. Ito, C. G. Wilson, *Polymer* **1983**, *24*, 995.
- [9] J. I. Yoshida, K. Ogura, N. Kawabata, *J. Org. Chem.* **1984**, *49*, 3419.
- [10] K. Sugiyama, H. Azuma, T. Watanabe, T. Ishizone, A. Hirao, *Polymer* **2003**, *44*, 4157.
- [11] D. Gunes, B. Karagoz, N. Bicak, *Designed Mon. Polym.* **2009**, *12*, 445.
- [12] B. H. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, A. R. Tatchell (Eds.), *Vogel's Textbook of Practical Organic Chemistry*, 4th edition, Longman Inc., New York 1978, p. 287.
- [13] M. H. Acar, N. Bicak, *J. Polym. Sci.; Part A: Polym. Chem.* **2003**, *41*, 1677.
- [14] M. Gazi, N. Bicak, G. Galli, *J. Polym. Sci.; Part A: Polym. Chem.* **2006**, *44*, 6708.
- [15] K. Matyjaszewski, D. A. Shipp, J. L. Wang, T. Grimaud, T. E. Patten, *Macromolecules* **1998**, *31*, 6836.
- [16] M. Husseman, E. E. Malmstrom, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russel, C. J. Hawker, *Macromolecules* **1999**, *32*, 1424.
- [17] G. Carrot, S. Diamanti, M. Manuszak, B. Charleux, J. P. Vairon, *J. Polym. Sci.; Part A: Polym. Chem.* **2001**, *39*, 4294.
- [18] S. Angot, N. Ayres, S. A. F. Bon, D. M. Haddleton, *Macromolecules* **2001**, *34*, 768.
- [19] G. D. Zheng, H. D. H. Stöver, *Macromolecules* **2003**, *36*, 7439.
- [20] Z. Cheng, X. Zhu, Z. L. Shi, K. G. Neoh, E. T. Kang, *Ind. Eng. Chem. Res.* **2005**, *44*, 7098.
- [21] F. J. Xu, Z. L. Yuan, E. T. Kang, K. G. Neoh, *Langmuir* **2004**, *20*, 8200.
- [22] K. Aoi, M. Okada, *Prog. Polym. Sci.* **1996**, *21*, 151.
- [23] J. H. Jeong, S. H. Song, D. W. Lim, H. Lee, T. G. Park, *J. Controlled Release* **2001**, *73*, 391.
- [24] M. Gazi, G. Galli, N. Bicak, *Sep. Purif. Technol.* **2008**, *62*, 484.