Synthesis of a Well-Defined Chitosan Graft Poly(methoxy polyethyleneglycol methacrylate) by Atom Transfer Radical Polymerization

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ABSTRACT: Graft copolymerization of vinyl monomers onto chitosan and other natural polymers using atom transfer radical polymerization has only recently attracted interest. This technique could potentially provide new ways to utilize this abundant natural polymer. It would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. In this work, a chitosan macroinitiator was prepared by the reaction of chitosan with 2-bromo-isobutyryl bromide, after the chitosan amino group had been protected as the imine. The aqueous grafting of methoxy capped (PEG 350) methacrylate onto chitosan is described. The kinetic study revealed a first order polymerization reaction. Polydispersities of about 1.25 were obtained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 901–912, 2003

Key Words: polymerization (ATRP), biopolymers, graft copolymers, polysaccharides

INTRODUCTION

Radical polymerization is probably the most important method for the synthesis of linear and graft polymers. There are several advantages to this type of polymerization including faster reaction time, easier manufacturing technique, and rapid formation of high molecular weight polymers.[1] However, there are drawbacks to these types of polymerizations. These include the lack of macromolecular structure control that can be achieved with other types of polymerization,[2] poorly defined product and high polydispersities. With the advent of controlled radical polymerization, it is possible to overcome these deficiencies.[3]

A few years ago, Matyjaszewski's group[4] and Sawamoto and coworkers[5] independently developed transition metal catalyzed living radical polymerization, which has become known as atom transfer radical polymerization (ATRP).[4] ATRP seems to be the most robust system to control radical polymerization of styrenes,[6,7] acrylate,[8,9] methacrylate,[10–12] and acrylonitrile.[13] ATRP is typically initiated by an alkyl halide (R-X) and catalyzed by a transition metal complex, such as CuX / bipyridine. Although the mechanism of ATRP is not yet fully understood, it is generally believed that the pseudo-living nature of the polymerization is due to the relatively low concentration of polymer radicals, which leads to the suppression of classical termination relative to propagation.

It was reported by both Matyjaszewski et al[4] and Sawamoto et al[5] that the presence of a small amount of water during ATRP synthesis in nonaqueous media had no deleterious effect, and in some cases, moderate rate enhancements were observed. Matyjaszewski's first example of ATRP in water was of 2-hydroxyethylacrylate (HEA), polymerized directly at 90°C for 12 h with 87% monomer conversion and 1.34 polydispersity for the final product.[13] Armes[14,15] and his coworkers succeeded in polymerizing different vinyl monomers directly via ATRP in aqueous media using polyethylene oxide-based macro-initiators. The resulting copolymers were obtained in good yield and had narrow molecular weight distributions, as evidenced by aqueous gel permeation chromatography (GPC).

Graft copolymerization of vinyl monomers onto chitosan and other natural polymers[18] using ATRP has only recently attracted interest. This technique could potentially provide new ways to utilize this abundant natural polymer. It would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. Such grafted materials have been used as adhesives, membranes and to modify the surfaces of films and fibers.

Chitin is one of the most abundant polysaccharides obtained from nature. It is often considered a cellulose derivative although it does not occur in organisms producing cellulose. Cellulose consists of β-(1-4)-**D**-

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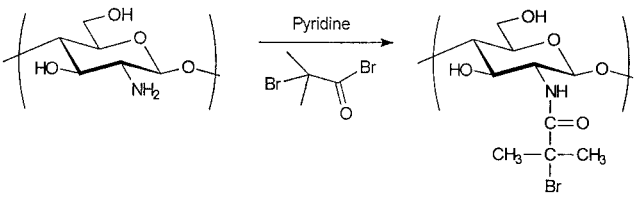
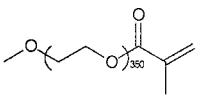


Chitosan and its derivatization with 2-bromo-isobutyryl bromide.



Methoxy capped (PEG350) methacrylate.

Figure 1 The reaction schemes for preparing a chitosan macroinitiator and the monomer it was grafted with: Methoxy capped (PEG350) methacrylate.

glucopyranose units. In contrast, chitin has the same backbone but the 2-hydroxy has been replaced by an acetamide group, resulting in mainly β-(1-4) 2-acetamindo-2-deoxy-**D**-glucopyranose structural units. Chitosan is the N-deacetylated derivative of chitin, though this N-deacetylation is almost never complete. A sharp nomenclature border has not been defined between chitin and chitosan based on the degree of N-acetylation.[16] Chitin is insoluble in water, while chitosan is easily soluble in most aqueous organic acids such as formic, acetic, citric, pyruvic and lactic.[17] Chitin and chitosan have a wide range of applications in the biomedical, pharmacological, agricultural, and textile fields.

Our current interest has focused on the synthesis of chitosan-based graft copolymer by ATRP, in which the chitosan has been modified to serve as a coinitiator. This allows the preparation of synthetic polymers with well-defined chitosan functionality at specific places within each macromolecule. The ATRP of methoxy capped (PEG 350) methacrylate onto chitosan is described (Fig 1). The ATRP procedure for this type of monomer was first reported by Wang and Armes.[19] Preparation of the chitosan macroinitiator was carried out by the reaction of 2-bromo-isobutyryl bromide with chitosan in the presence of pyridine as a base. The effect of the main parameters affecting the rate of polymerization was examined, including the concentration of chitosan macroinitiator and Cu(I)Br / bipyridine complex.

EXPERIMENTAL

Material

Methoxy-poly(ethylene glycol) methacrylate MeO-(PEG350)MA, was kindly donated by Laporte Specialties, Hythe, UK. The monomer was passed through an alumina column to remove inhibitor immediately before use. Pyridine, 2- bromo-isobutyryl bromide, triethylamine (TEA), lithium chloride, dimethylacetamide, tetrahydrofuran (THF), diethyl ether, copper(I) bromide, 2,2′-bipyridine(bipyr), sodium thiosulfate, potassium bromide, potassium bromate and potas-

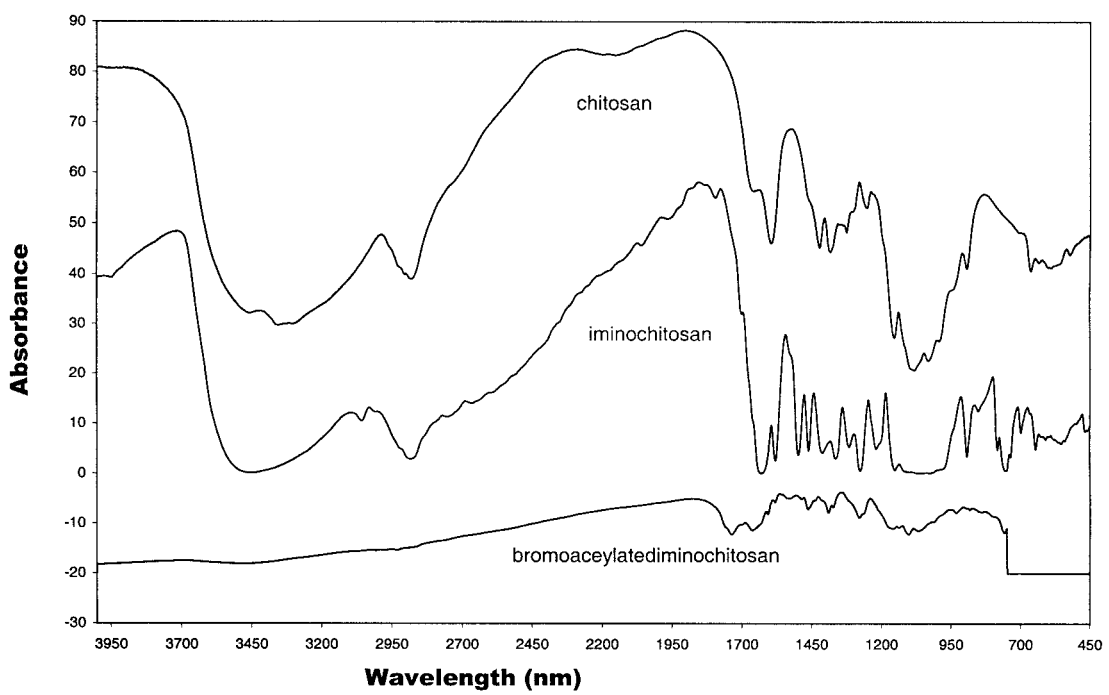


Figure 2 The FTIR-spectra for chitosan, iminochitosan and the chitosan macroinitiator.

TABLE I
Elemental Analysis Results for Chitosan and the Chitosan Macroinitiators

Product	C	H	N	Br
Chitosan	39.75	7.18	7.55	0
Iminochitosan	55.4	5.86	4.86	0
Chitosan macroinitiator	45.16	4.4	2.62	27
Theoretical data for the chitosan macroinitiator	44.88	2.49	4.2	28.5

sium iodide were all purchased from Aldrich (Milwaukee, WI) and were used without any further purification. Chitosan was kindly supplied by FMC/Pronova Biopolymer, Inc (Philadelphia, PA).

Preparation and characterization of macroinitiators

Preparation of PEG-Macroinitiator

The preparation of PEG-macroinitiator was as reported by Wang and Armes[19] with little change in the molar ratio of 2-bromo-isobutyryl bromide to TEA. It's better to use an equivalent amount of both of them to facilitate the purification of the final macroinitiator. A dry three neck flask was evacuated and back filled with argon, then 2-bromo-isobutyryl bromide (5.7 mL, 46 mmol) and polyethylene glycol 350 (7.4 mL, 23 mmol) were mixed in THF (20 mL) at 0 °C for 30 min. under continuous stirring and Argon bubbling. A 26.5 mL aliquot of 24.5% (w/v) THF solution of TEA (6.5 ml, 46 mmol) was added dropwise. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 24 h. The solution was filtered to remove the precipitated TEA. Hydrogen bromide and THF were removed by using a rotary evaporator. The resulting product was dissolved in deionized water and extracted several times with diethyl ether. The collected diethyl ether was dried over $MgSO_4$ and then removed under vacuum to obtain the yellow PEG-macroinitiator.

$$CH_3(OCH_2CH_2)_7OH + Br{-}COC(CH_3)_2Br \rightarrow CH_3(OCH_2CH_2)_7O{-}CO{-}C(CH_3)_2Br \quad (1)$$

The structure of the PEG-macroinitiator was characterized by ^1H NMR with THF as a solvent [δ = 4.06 (t, 2H); 3.49 (t, 2H); 3.4 (s, 32 H); 3.1 (t, 2H); 1.7 (s, 6H)]. The IR-spectrum of the PEG-macroinitiator recorded the presence of a carbonyl peak at 1740 cm,$^{-1}$ which indicates the formation of α-bromocarbonyl ester. The elemental analysis of the PEG- macroinitiator was: C; 40.2%; H, 6.3%; Br, 31.3%.

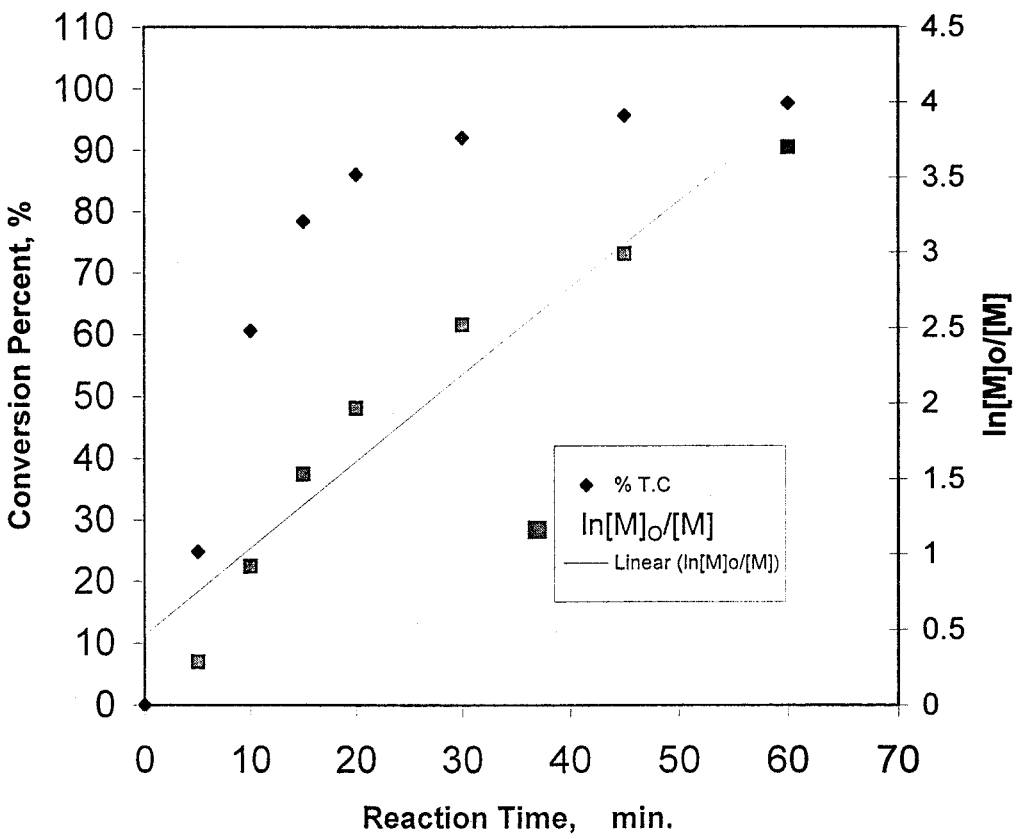


Figure 3 Plot of reaction time vs conversion percent and ln[M]o/[M]. Polymerization conditions: Cu(I)Br, 0.1 mmol; Bipy., 0.2 mmol; MeO(PEG)MA, 1 mmol; PEG-macroinitiator, 0.1 mmol; Temp. 25°C; H_20, 5 mL.

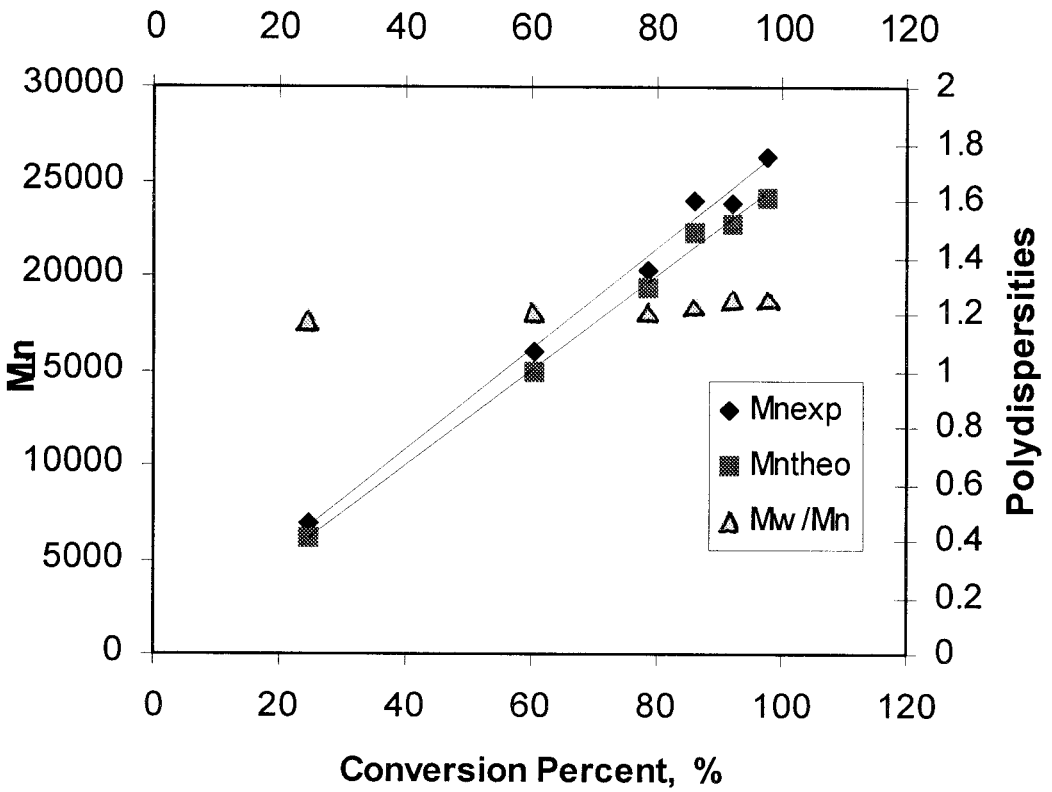


Figure 4 Plot of conversion percent vs Mn and Mw/Mn. Polymerization conditions: Cu(I)Br, 0.1 mmol; Bipy., 0.2 mmol; MeO(PEG)MA, 1 mmol; PEG-macroinitiator, 0.1 mmol; Temp. 25°C; H_20, 5 mL.

Preparation of chitosan macroinitiator

Deacetylation of chitosan. The deacetylation of chitosan was carried out by the gradual addition of 100 g of chitosan to a three necked flask containing 2 L of sodium hydroxide (50%) under continuous stirring and bubbling with Ar. The mixture was heated to 120°C for 3 h. Afterwards, the chitosan was filtered, washed with deionized water until neutral, and then dried under vacuum. The degree of deacetylation was determined to be 90%, based on the conductometric titration of the free amino groups.[20] The viscosity average molecular weight of chitosan was determined to be 16,000 Daltons, according to the intrinsic viscosity method reported by Wang et al.[21]

Synthesis of chitosan-macroinitiator One of our main goals is the preparation of chitosan macroinitiator with high Br-content distributed homogeneously along the chitosan backbone in order to prepare a grafted chitosan of well-defined macromolecular architecture. Two methods for the preparation of chitosan macroinitiator (a bromoacylated chitosan) are reported. The first method depends upon Austin's[22] report that the solubility of chitosan is enhanced greatly in the N,N- Dimethylacetamide / LiCl solvent system by increasing the degree of N-acetylation, since it's well known that chitosan is almost insoluble in most organic solvents. The bromoacylation of chitosan was carried out with a molar ratio of NH_2 : 2-bromo-isobutyryl bromide : pyridine of 1 : 30 : 30, respectively, and initially as a heterogeneous reaction. Elemental analysis (C, 43.5%; H, 7%; N, 7.6%; Br, 2%) indicated a low degree of substitution of the 2-bromo-isobutyrate (only 1.6% of the available sites reacted).

The second trial started with the preparation of iminochitosan, by protecting the free amino group of chitosan with salicylaldehyde followed by bromoacylation as follows. Iminochitosan was prepared by the reaction of deacetylated chitosan (18 g) with salicylaldehyde (61.8 mL) in aqueous suspension for 8 h at room temperature. Afterwards the iminochitosan was washed with an acetone/water mixture (50 / 50) three times, followed by washing with methanol using a soxhlet extractor for 6 h. Finally, the yellow product was allowed to dry under vacuum.

Then, 15 g of iminochitosan was placed in a three-necked flask, the flask was sealed with rubber septa, evacuated and back filled with argon for 30 min. Using a syringe, 450 mL of dimethylformamide (DMF) was added. The suspension was stirred at room temperature for two hours. The reaction mixture was cooled to 0°C. Pyridine (33 mL) was injected, followed by the slow addition of 50.5 mL of 2-bromo-isobutyrylbromide. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. We noted that, 30 min from the addition of acyl bromide, the iminochitosan

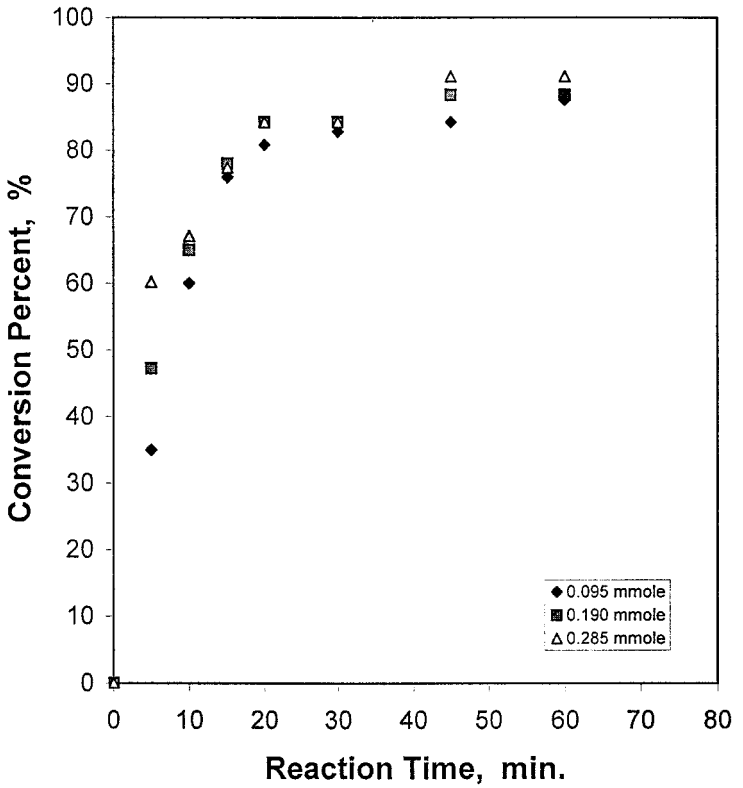


Figure 5 Plot of monomer conversion vs reaction time at different chitosan macroinitiator concentrations. Polymerization conditions: Cu(I)Br, 0.1 mmol; Bipy., 0.2 mmol; MeO(PEG)MA, 1 mmol; Temp. 25°C; H_20,5 mL.

started to dissolve in DMF as the bromoacylation proceeded. Finally the product was precipitated by pouring into cold water. Purification of the final product was carried out by redissolving the final product in DMF and reprecipitating in water. Finally, it was washed with deionized water and then vacuum dried. *Characterization of the chitosan macroinitiator.* Table I presents the elemental analysis of chitosan, iminochitosan and chitosan macroinitiator as a function of the chemical modification. The data indicate a carbon percent increase as a result of protecting the chitosan amino group. The data also indicate that the bromoacylation was carried out on both of the hydroxyl groups (primary and secondary hydroxyl).

The FTIR data for the chitosan, iminochitosan and chitosan macroinitiator agree with the elemental analysis results. In Figure 1, the absorption peak of the chitosan NH_2 (at 3339 and 3420 cm^{-1}) disappeared after formation of the iminochitosan (–N═CH–). A carbonyl peak was obtained at 1736 cm^{-1}, indicating the formation of the α-bromocarbonyl ester.

The solubility of chitosan, iminochitosan and chitosan macroinitiator was evaluated. All three were found to be insoluble in water, acetone, and methanol. The chitosan macroinitiator was found to be soluble in DMAc, DMF and DMSO, whereas the chitosan and iminochitosan were not.

Polymerization of MeO(PEG350)methacrylate using PEG-macroinitiator

To a dry Schlenk flask equipped with a stir bar were added 9.4 mg (0.095 mmol) CuBr and 29.6 mg (0.190 mmol) of bipyridine. A second Schlenk flask was charged with 5 mL of deionized water, 2 g of MeO(PEG350)MA (1 mmol) and 42 mg of PEG-macroinitiator (0.095 mmol). The flasks were sealed with rubber septa, evacuated, and back filled with Ar twice before being left under Ar for 1 h. The deoxygenated monomer solution was transferred to the other flask using a syringe, which was stirred at room temperature (25°C) to start the polymerization. It was observed that termination of the polymerization reaction occurred rapidly on exposure to air, as indicated by the color change from brown to blue as a result of the oxidation of Cu(I) to Cu(II). Finally, the reaction solution was passed through a silica column to remove the copper catalyst and a white polymer was obtained.

Polymer characterization

Kinetic studies of ATRP of MeO(PEG350)MA were carried out by monitoring the monomer conversion percent at interval times according to a method reported by Wallace.[23] Molecular weight and molecular

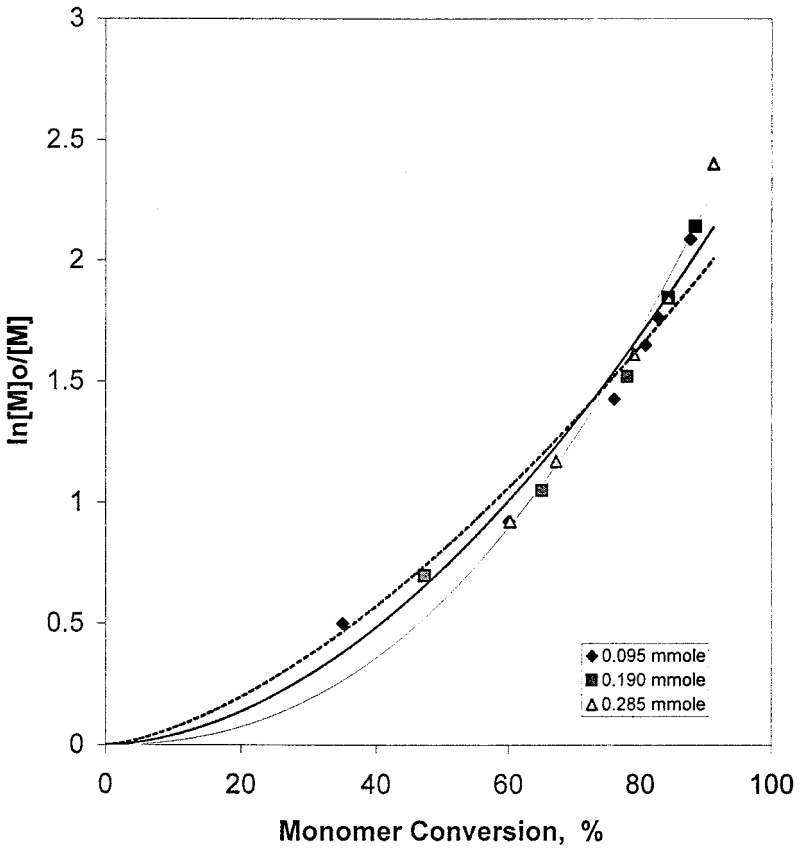


Figure 6 Plot of conversion percent vs ln[M]o/[M] for different chitosan macroinitiator concentrations. Polymerization conditions: Cu(I)Br, 0.1 mmol; Bipy., 0.2 mmol; MeO(PEG)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

weight distributions were measured by using gel-permeation chromatography (GPC) using a high pressure liquid chromatography pump. The eluting solvent was THF for homopolymerization and DMF for grafted chitosan. Calibration was achieved with polymethylmethacrylate standard (PMMA) for the homopolymerization and polystyrene for the grafted one.

RESULTS AND DISCUSSION

Mechanisms of polymerization

To clarify the advantage of using ATRP as a new technique for the control of the radical polymerization of MeO(PEG)MA onto chitosan, it's valuable to illustrate the tentative mechanism of both conventional free radical polymerization and atom transfer radical polymerization. Radical polymerization[24] includes four elementary reactions: (1) Slow initiation by the homolytic cleavage of a molecule with low thermal stability (peroxide, diazo compound with $K_d < 10^{-5}$ S^{-1}); (2) relatively fast reaction of primary radicals with monomer to generate the first growing species (because $K_d <$ Ki[M], the decomposition is the rate-determining step); (3) Fast propagation with moderate regioselectivity and low sterioselectivity, ($k_p \cong 10^3$ mol.$^{-1}$ L. S^{-1}); (4) Very fast termination between growing radicals ($k_t \cong 10^7$ mol.$^{-1}$ L. S^{-1}). Transfer reactions are usually less important, unless transfer agents are added. Thus, well-defined polymers by radical polymerization may be formed only if chains are relatively short and the concentration of free radicals is low enough.

Controlled / living polymerization enables preparation of well-defined complex macromolecular architectures for a larger number of monomers and under less stringent conditions than those used for ionic processes. This process was named atom transfer radical polymerization (ATRP) because atom transfer is the key feature controlling this reaction and radical intermediates are responsible for the chain growth. The control of the polymerization is dependent upon the establishment of an equilibrium between active and dormant species. By maintaining a low stationary concentration of radicals, the contribution of bimolecular termination between growing radicals can be suppressed and the result is a living polymerization. Therefore ATRP leads to excellent control of molecular weight, $DP_n = \Delta [M]/[I]_o$ and low polydispersities, $M_w/M_n < 1.3$.

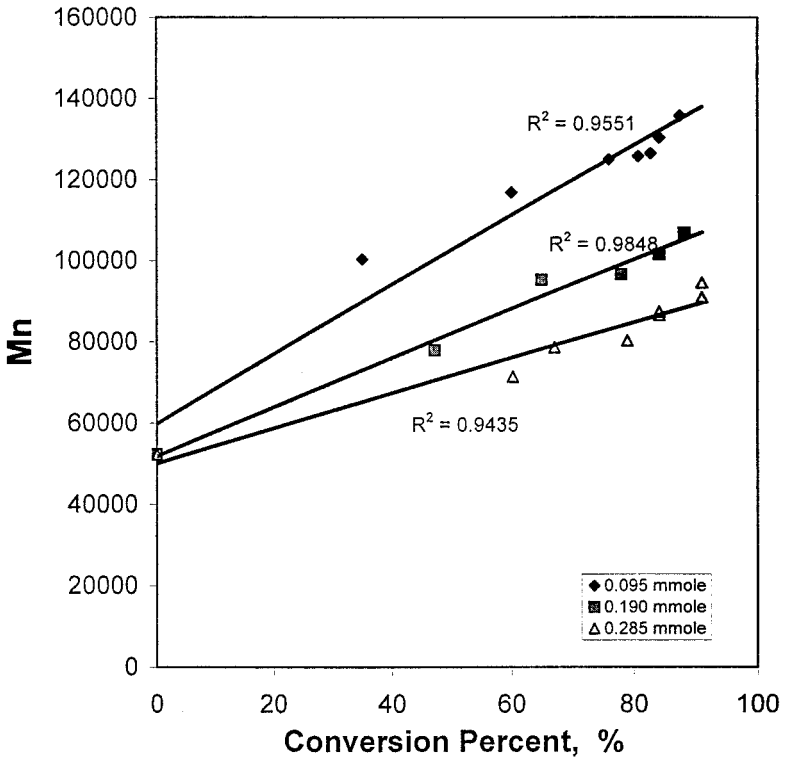


Figure 7 Plot of conversion percent vs Mn for different chitosan macroinitiator concentrations. Polymerization conditions: Cu(I)Br, 0.1 mmol; Bipy., 0.2 mmol; MeO(PEG)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

Polymerization of MeO(PEG350)methacrylate using PEG-macroinitiator

For kinetic studies, a 300 μL aliquot of the solution was removed from the flask at interval times for measuring the monomer conversion percent according to the method reported above. The samples were added to a frozen KBr / $KBrO_3$ solution, and, by the addition of 5 mL 2*N* H_2SO_4, liberated Br_2 was allowed to add to the double bond of the residual monomers. Back titration of the excess Br_2 was carried out using Iodometric titration. Another 200 μL was diluted in THF and dried over magnesium sulfate to remove H_2O prior to GPC analysis to measure molecular weight and molecular weight distribution.

It was reported by Wang and Armes[19] that the final poly[MeO(PEG)MA] is insoluble in THF, but in our case we found the final product is soluble in THF. The solubility of our polymer may be due to the low molecular weight of the original PEG of the macroinitiator (350) relative to Arme's PEG(2000).

Figure 3 shows the kinetic plot of the monomer conversion (%T.C.) and $\ln([M]_o/[M])$ versus time for ATRP of MeO(PEG350)MA catalyzed by CuBr/bpyr and initiated by PEG macroinitiator. The resulting slope indicates a first order reaction, which means that the polymerization proceeds with an approximately constant number of active species for the duration of the reaction. Therefore the contribution of the termination reaction could be neglected. It is also evident that the rate of polymerization of MeO(PEG350)MA (97%) in aqueous ATRP at 25°C is faster than conventional ATRP, which required a higher temperature and several hours to attain high conversion.[13] It is reported that a faster rate of ATRP is achieved in more polar solvents.[25,26]

Figure 4 shows the molecular weight evolution, M_n, and molecular weight distribution (polydispersities, M_w/M_n) of the free polymer produced in the solution as a function of conversion percent. It's clear from Figure 4 that the molecular weight of the polymer increases in a linear fashion as the monomer conversion proceeds as a first order reaction. The molecular weight measurement showed that the final molecular weights of the copolymers were close to those expected on the basis of the polymer conversion and initial ratio of monomer to initiator (DPn = P × [M]/[I], where P = conversion). The molecular weight distributions were typically narrow (1.2–1.25) during the polymerization period, hallmarks of the controlled / living polymerization process.

Polymerization of MeO(PEG)methacrylate using chitosan macroinitiator.

Controlled / living polymerization of MeO(PEG350)MA onto chitosan was carried out in a heterogeneous sys-

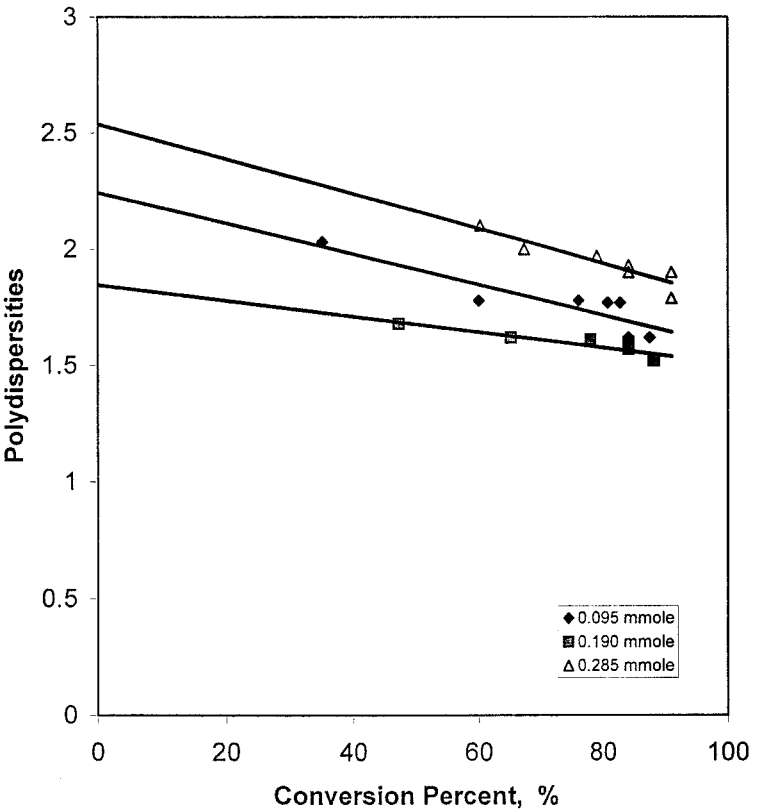


Figure 8 Plot of conversion percent vs polydispersities for different chitosan macroinitiator concentrations. Polymerization conditions: Cu(I)Br, 0.1 mmol; Bipy., 0.2 mmol; MeO(PEG)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

tem, by the same method described in the homopolymerization above. However, the iminochitosan alkyl halide was used as a macroinitiator (62–192 mg 0.095–0.285 mmol) in the presence of Cu(I)Br/bipyr as the activated complex (0.095 / 0.190 mmol) and at ambient temperature. The key to ATRP is the number of activation-deactivation cycles in which the iminochitosan alkyl halide (R-X) is reversibly transformed to the polymer radical (R*). This is expected to be better in a homogeneous polymerization rather than a heterogeneous one.

Effect of chitosan macroinitiator concentration

Figure 5 shows the plot of monomer conversion percent versus time at three different concentrations of chitosan macroinitiator (0.095, 0.190, 0.285 mM). The monomer conversion percent increases as the polymerization reaction proceeds and reaches a maximum value within 20 min, which indicates the very high transformation of Br groups between dormant and active species. At the same time, the extent and rate of polymerization increased as the concentration of chitosan macroinitiator increased and reached a maximum value (91%) at 0.190 mmol. It's clear from the data (Fig. 6) that the plot of $\ln[M]_o/[M]$ versus time can be approximated by a straight line; i.e. the polymerization process follows first order kinetics with respect to monomer conversion. In this heterogeneous system, the increase in $\ln[M]_o/[M]$ may be attributed to the accessible Br groups on the surface of the chitosan particles for formation of the chitosan propagating chains rather than the interior ones. Thus the actual molar ratio of chitosan macroinitiator to Cu(I)Br to bipy is not 1: 1: 2, since the number of Br groups is less than the theoretical value. Increasing the chitosan macroinitiator concentration will increase the number of Br groups in the polymerization medium, and thereby increase the number of propagating chains, until the maximum value, at which both the chitosan macroinitiator and Cu(I)Br are relatively equivalent, is reached.

Figures 7 and 8 show the plot of the Mn value and polydispersities (Mw/Mn) of the free polymer produced in the solution as a function of monomer conversion using three different concentrations of chitosan macroinitiator. The Mn and Mw/Mn values were estimated by a polystyrene calibrated GPC. The molecular weight of the grafted samples increased by increasing the monomer conversion for the same chitosan concentration. As the concentration of chitosan macroinitiator was increased, the molecular weight of the grafted polymer decreased. Such a decrease in the molecular weight is expected, since at a low chitosan

concentration, the number of propagating chains is lower and consequently the molecular weight of the final polymer is high. An increase in the chitosan macroinitiator concentration is accompanied by an increase in the number of propagating chains and consequently a net molecular weight decrease. The molecular weight distribution of the chitosan macroinitiator itself is relatively high. During the polymerization process, the polydispersities (Mw/Mn) decrease as the concentration of chitosan macroinitiator increases to 0.190 mM. Beyond this level of chitosan macroinitiator, the polydispersity increases, which may be related to uncontrolled polymerization as a result of chain transfer.

Effect of Cu(I)Br/bipyridine complex concentration

The reactivity and selectivity in metal-catalyzed reactions is the key for controlling radical polymerization, which is accomplished by the reversible activation of the carbon-halogen bond at the dormant polymer terminal to produce a propagating radical. During the polymerization, most of the polymer chains exist as the stable dormant species, which makes the radical concentration low enough to suppress bimolecular termination reactions between the radical species. The Cu(I)Br/bipyr complex plays a dual role during ATRP: It receives a halogen from the dormant chain end and is easily oxidized but at the same time the oxidized form is easily reduced to the original state.

Our goal of studying the Cu(I)Br / bipyr complex concentration is to determine the minimum level of copper catalyst necessary to maintain sufficiently fast polymerization and control of molecular weights. This parameter was varied to influence the equilibrium between active and dormant species and thus the radical concentration. By adjustment of the equilibrium, the radical concentration could be elevated to increase the rate of polymerization or lowered to suppress termination between growing chains.

MeO(PEG350)MA was polymerized with iminochitosan alkyl halide as a macroinitiator (0.190 mmol) in aqueous medium at 25°C using three different concentrations of Cu(I)Br / bipyr complex (0.0475 / 0.0950 mM - 0.143 / 0.285 mM). Figure 9 shows the kinetic plot of the monomer conversion (% T.C) as a function of the reaction time using the three different concentrations of Cu(I)Br / Bipyridine complex. The data indicate an increase in the monomer conversion as the polymerization reaction proceeds. Also, the monomer conversion increases remarkably as the concentration of Cu(I)Br/bipyr complex increases and reaches a maximum conversion (88.3%) at 0.95 / 0.190 mM Cu(I)Br / bipyr. Increasing the concentration above this limit is accompanied by a marginal increase in the monomer conversion. Increasing the Cu(I)Br / bipyr

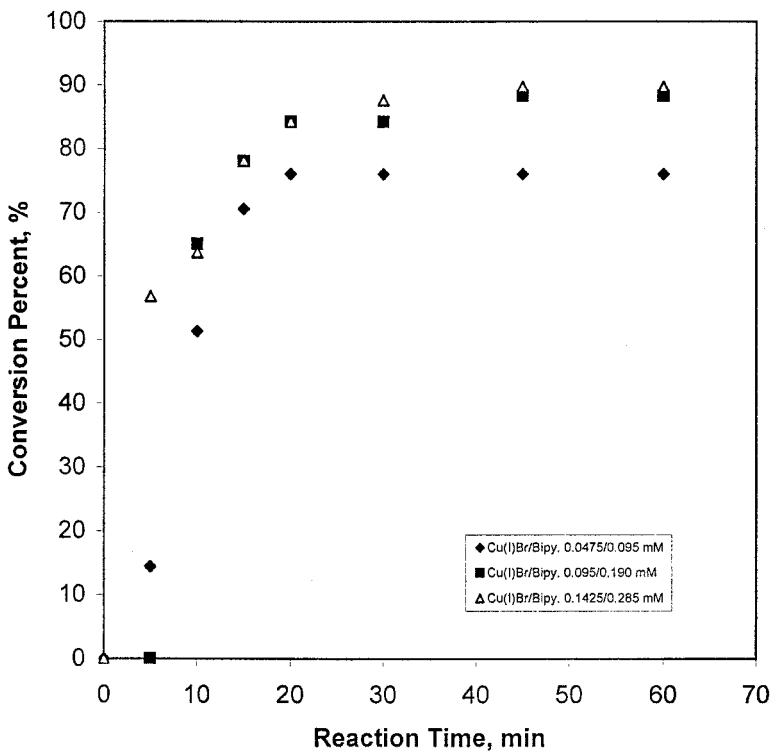


Figure 9 Plot of monomer conversion percent vs reaction time at different Cu(I) / Bipy. concentrations. Polymerization conditions: chitosan macroinitator, 0.190 mmol; MeO(PEG350)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

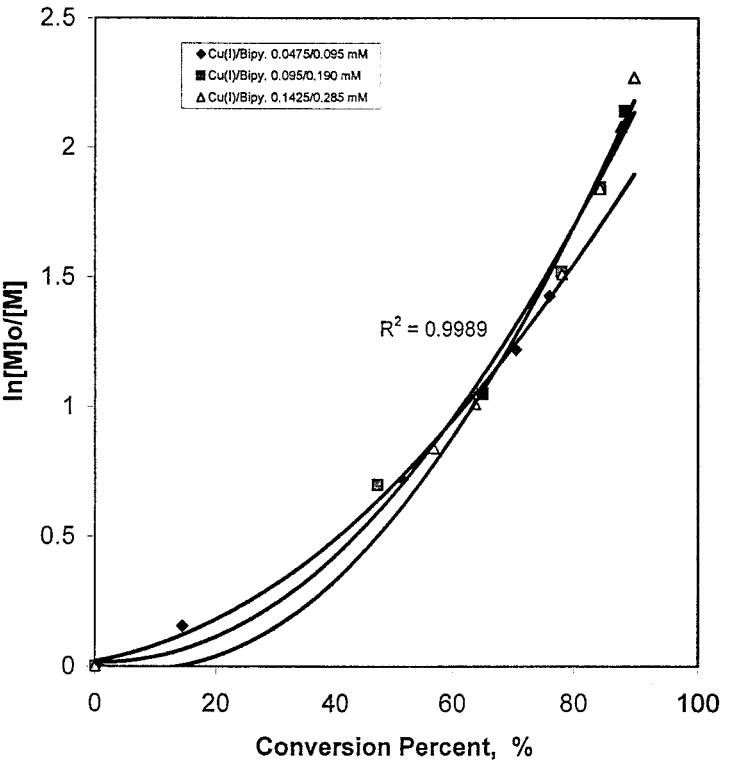


Figure 10 Plot of conversion percent vs ln[M]o/[M] at different Cu(I) / Bipy. concentrations. Polymerization conditions: chitosan macroinitator, 0.190 mmol; MeO(PEG350)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

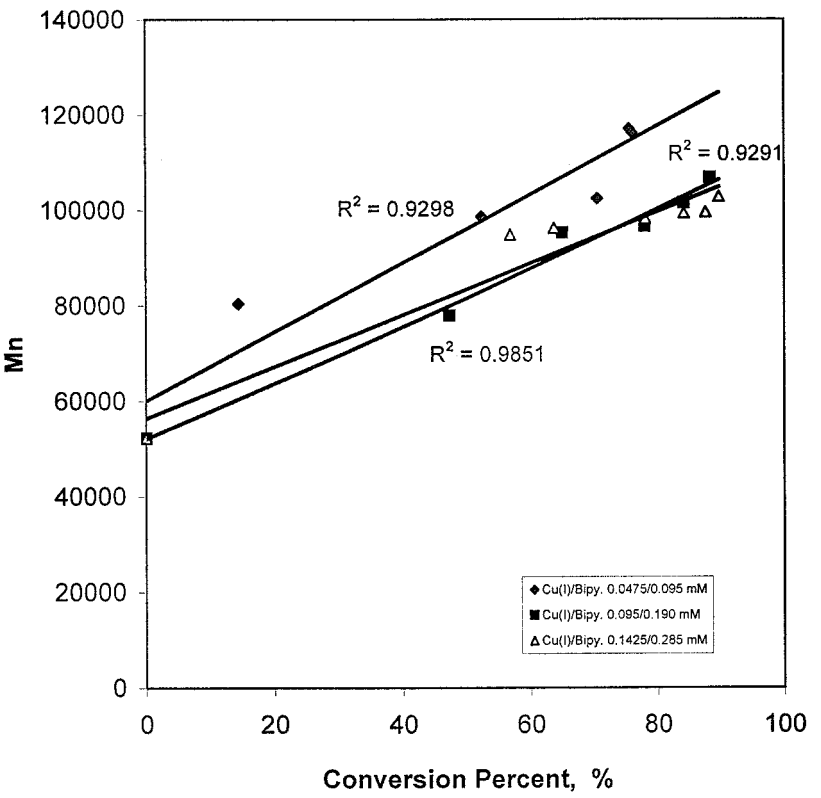


Figure 11 Plot of conversion percent vs Mn at different Cu(I) / Bipy. concentrations. Polymerization conditions: chitosan macroinitator, 0.190 mmol; MeO(PEG350)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

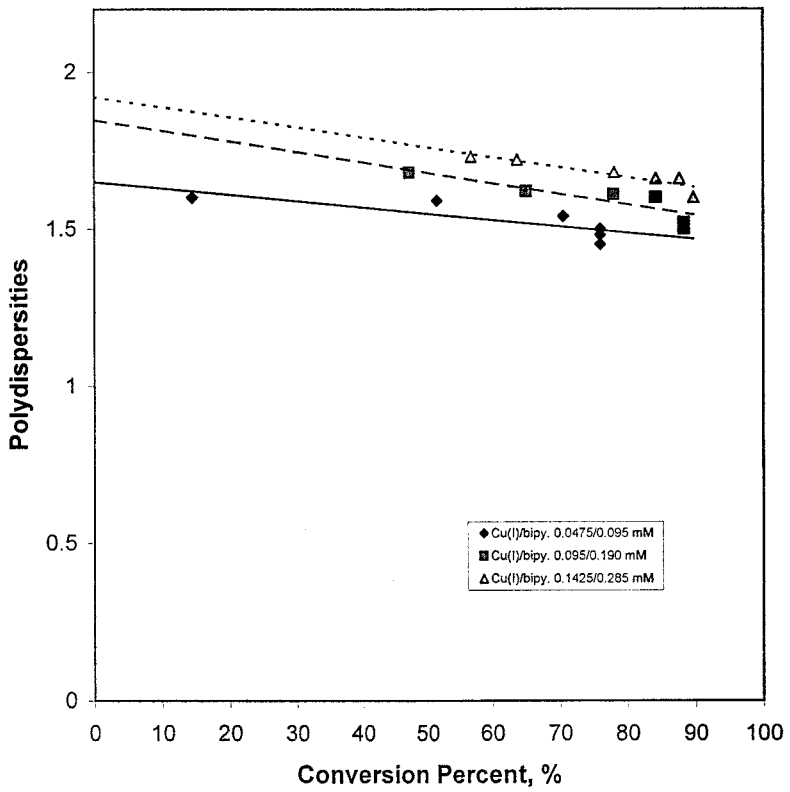


Figure 12 Plot of conversion percent vs polydispersities at different Cu(I)/Bipy. concentrations. Polymerization conditions: chitosan macroinitator, 0.190 mmol; MeO(PEG350)MA, 1 mmol; Temp. 25°C; H_20, 5 mL.

complex concentration from 0.0475 / 0.095 mM to 0.095 / 0.190 mM leads to an increase in the number of propagating chains, which is reflected by the increase in monomer conversion. Above this concentration, the copper complex has no effect on the monomer conversion.

Figure 10 illustrates the relation between the conversion percent and $\ln[M]_o/[M]$. Increasing the monomer conversion is accompanied by an increase in ln[M]o/[M] for the same Cu(I)Br / bipyr complex concentration, as expected for a first order reaction (R^2 = 0.99 for all the lines). This means that the polymerization proceeds with an approximately constant number of propagating chains during the reaction time; therefore the contribution of termination reactions can be neglected. It is clear from the data that increasing the Cu(I)Br / bipyr concentration within the range studied is accompanied by a marginal increase in ln[M]o/[M]. This indicates that the polymerization of MeO(PEG)MA using a chitosan macroinitiator is fast even at low concentrations of Cu(I)Br / bipyr complex.

Figures 11 and 12 show the number-average molecular weight (Mn) and the polydispersities (Mw/Mn) of the polymers obtained for a range of Cu(I)Br / bipyr complex levels. The Mn increased with the monomer conversion. The highest Mn of the grafted sample was obtained at a Cu(I)Br / bipyr complex level of 0.095 / 0.190 mmol. The Mw/Mn of the polymer decreased as the polymerization proceeded and became narrower as the level of Cu(I)Br/bipyr decreased.

CONCLUSION

It was demonstrated that chitosan macroinitiators would polymerize a Methoxy-poly(ethylene glycol) methacrylate(MeO(PEG350)MA) monomer via atom transfer radical polymerization. The chitosan macroinitiator was obtained by the acylation of chitosan with 2-bromo-isobutyryl bromide. Control polymerizations to demonstrate the occurrence of ATRP utilized PEG -2-bromo-isobutyryl esters macroinitiators. Heterogeneous polymerizations were conducted in water. The results indicated that controlled polymerizations occurred with first order polymerization kinetics.

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