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Synthesis and characterization of polymeric emulsifiers containing reversible hydrophobes: poly(methacrylic acid-*g*-ethylene glycol)

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Abstract

A series of poly(methacrylic acid-*g*-ethylene glycol) copolymers of varying molecular architectures were synthesized in a custom-built semi-batch reactor by a free radical copolymerization of methacrylic acid with the macromonomer methoxy poly(ethylene glycol) methacrylate (MPEGMA). By virtue of intramolecular hydrogen bonding between the oligo(ethylene glycol) grafts and the poly(methacrylic acid) backbone, these polymers contain reversible hydrophobic segments, and may be used as reversible emulsifiers that allow emulsions to be broken and reformed. The copolymers were characterized using ^{1}H NMR to determine the polymer composition and gel permeation chromatography (GPC) to characterize the polymer molecular weight distribution. The GPC and NMR results were combined to estimate the number of grafts per chain for each of the polymer samples. The average number of grafts per chain was found to range from 0.3 to 18. As expected, for a constant initiator concentration, the average number of grafts per chain was found to increase as the amount of the MPEGMA in the reaction mixture was increased. In addition, for a constant MPEGMA content, the average number of grafts per chain decreased as the initiator concentration was increased. These studies provide important information about the relationship between the reaction conditions and the molecular architecture of the resulting reversible copolymeric emulsifiers.

Keywords: Methacrylic acid; Methoxy poly(ethylene glycol) monomethacrylate; Polymer complexation

1. Introduction

Block copolymers containing alternating hydrophilic and hydrophobic segments are widely used as dispersing agents and stabilizers for particles and emulsions in water [1–4]. In these polymers one block of the dispersing agent is designed to adsorb onto the surface of the stabilized particle or penetrate into the oil phase, while the other block extends into the continuous phase and provides steric stabilization. For example, diblock and triblock copolymers of ethylene oxide and propylene oxide have received considerable attention due to their relatively simple architecture and the ease with which the block lengths can be controlled by living anionic polymerization.

Recently, we reported a new approach for designing emulsifiers in which the hydrophobic blocks are formed spontaneously and reversibly by the complexation of two hydrophilic segments of a comb-type graft copolymer [5]. These copolymers consist of a polymeric Lewis acid backbone and grafts of an oligomeric Lewis base and are synthesized by a simple, one-step free-radical polymerization. In our previous paper, we illustrated this approach with copolymers containing a backbone of poly(methacrylic acid) and grafts of poly(ethylene glycol) such that hydrogen-bonded complexes are formed under acidic conditions, but not under basic conditions. Because the complexes are considerably more hydrophobic than the constituent polymers, the polymers form alternating blocks of hydrophilic (uncomplexed) and hydrophobic (complexed) segments when the complexes are formed, but are rendered completely hydrophilic (a comb-type graft copolymer) when the complexes are broken. The polymer complexes can be reversibly disrupted and reformed by a change in pH, solvent type or possibly temperature. These block/graft copolymers thereby allow emulsions and dispersion to be broken reversibly and reformed by controlling the formation of the hydrophobes.

In our previous contribution, we demonstrated the feasibility of emulsifiers containing reversible hydrophobes. Using three representative molecular architectures, we

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demonstrated that the emulsions could be formed and broken at will, and characterized the emulsification properties as a function of pH. In this paper, we focus on the synthesis and characterization of the novel emulsifiers containing reversible hydrophobes. Using a semi-batch polymerization reactor, we synthesized and characterized a series of poly(methacrylic acid-*g*-ethylene glycol), P(MAA-*g*-EG), copolymers of varying molecular architectures. The length of the oligomeric ethylene glycol grafts was the same for all of the polymers, however, the number of grafts incorporated into the poly(methacrylic acid) backbone was varied by controlling the monomer composition during synthesis, while the degree of polymerization was varied by varying the initiator concentration. The molecular architecture was characterized using ^{1}H NMR to determine the polymer composition, and gel permeation chromatography (GPC) to characterize the polymer molecular weight distribution.

2. Materials and methods

2.1. Materials

The P(MAA-*g*-EG) copolymers were synthesized by free radical copolymerization of methacrylic acid (MAA, Aldrich) with the macromonomer methoxy poly(ethylene glycol) monomethacrylate 1000 (MPEGMA 1000, Polysciences, Warrington, PA). In this nomenclature, the "1000" denotes the average molecular weight of each oligomeric ethylene glycol chain in the macromonomer. This corresponds to an average of 22.7 ethylene glycol repeat units per macromonomer. Polymerization was initiated using sodium persulfate (Aldrich). All reactants were of high purity and were used as received.

2.2. Copolymer synthesis

The copolymers were synthesized using a semi-batch reactor in which the monomer was fed continuously into the well-mixed system using programmed syringe pumps (KD Scientific, Boston, MA) with gas-tight syringes (SGE, Austin, TX). The reactor contents were mixed using a Trubore® stirring system driven by a heavy-duty air motor (Cole Palmer Instrument Co., Chicago, IL). The speed (rpm) of the stirrer was measured with an optical tachometer TACH-4-AR (Monarch Inst., Amherst, NH). The sealed reactor was equipped with a reflux condenser and was kept under a nitrogen blanket to eliminate the presence of oxygen, which can inhibit free radical polymerization. All glassware components used in the reactor were purchased from ACE Glass Inc. (Vineland, NJ). The temperature of the reaction vessel was maintained at a constant value of 75°C using a PID temperature controlled heating unit, purchased from Ace Glass.

Stock solutions of the monomer MPEGMA 1000 were prepared by dissolving known amounts of the monomers into a 50/50 (v/v) mixture of 200 proof ethanol and HPLC grade water under stirring. Similarly, initiator solutions were produced by dissolving solid sodium persulfate in HPLC grade water, and the solution was stored in a refrigerator at 40°F until further use (solutions were used within three days of their preparation). Before each run, 200 ml of a 50/50 (v/v) ethanol/water mixture were poured into the 500 ml reactor, and the system was sealed except for one opening through which reactants were fed. The dissolved oxygen was removed by bubbling nitrogen through the solvent for about 5 min, and then the nitrogen inlet valve was opened to cover the reactor contents with a nitrogen blanket before the system was completely sealed. A 100 ml syringe and two 50 ml syringes were filled with pure methacrylic acid, 50 ml of MPEGMA solution and 30 ml of initiator solution, respectively. Each feed pump was programmed to deliver a predetermined constant volumetric flow rate selected for the specific reaction. For example, for the P(MAA-*g*-EG) 5/10 copolymer, the flow rate of the methacrylic acid feed, the MPEGMA solution feed and the initiator solution feed were selected as 1.000, 1.111 and 0.500 ml/min, respectively. In the remainder of this paper, the copolymers will be specified with the ethylene glycol content followed by the initiator concentration. For example, a copolymer labeled as P(MAA-*g*-EG) 5/10 is polymerized with an EG content of 5 wt.% of the total monomer, and an initiator concentration of 10 wt.% of the total monomer. The feedlines were degassed before the monomer feed was begun, and the automatic shut off time was 45 min for all syringe pumps. When the pumping was complete, the system was removed from the heating source, and the reactor was allowed to cool to room temperature in a post-polymerization step.

Using this reactor, an array of polymers was produced with theoretical ethylene glycol contents of 0, 2.5, 5, 10, 20, 30 wt.% and varied chain lengths due to initiator concentrations of 10, 5,1, 0.5, 0.1 wt.% of total monomer mass.

2.3. Gel permeation chromatography

The GPC studies were performed using an HP 1090A instrument (Hewlett-Packard, Palo Alto CA) equipped with a factory-installed autosampler. For these experiments a set of two PL aquagel-OH MIXED 8 μm (Polymer Laboratories) columns were used in series following a guard column containing the same packing. A HP 1047A refractive index detector equipped with a thermostated optical system was used in these studies. The data was collected and analyzed online using the Instrument software Chemstation for LC (Hewlett-Packard) and the Software package PL Caliber for HP Chemstation version 4.01 (Polymer Laboratories). This software allowed the calculation of the various moments of the molecular weight distribution, including the number average and weight average molecular weights.

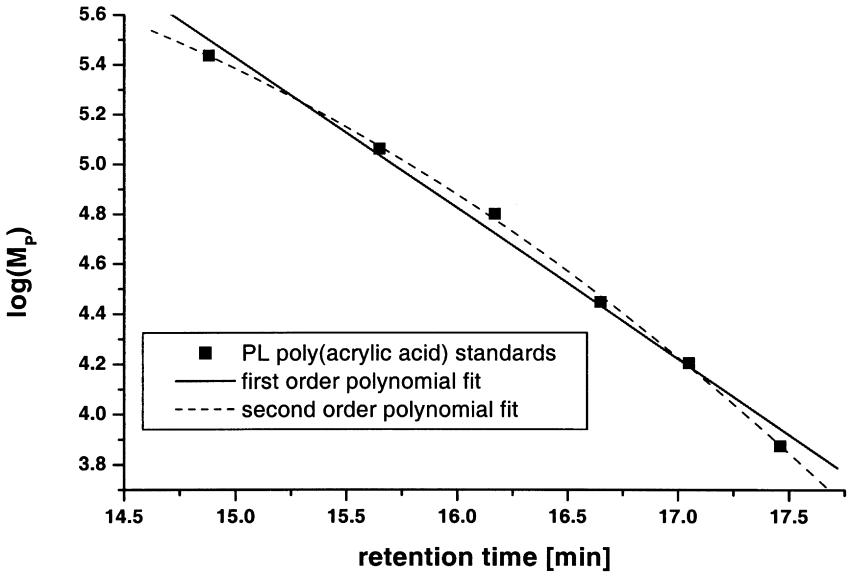

Fig. 1. Calibration curves prepared using commercially available monodisperse poly(acrylic acid)-sodium salt standards with molecular weights of 7500, 16,000, 28,000, 620,900, 115,000, and 272,900.

The molecular weight calibrations were performed with commercially available narrowly dispersed poly(acrylic acid)-sodium salt standards (Polymer Laboratories). The column system was calibrated using a series of standards with molecular weights of 7500, 16,000, 28,000, 62,900, 115,000, and 272,900. The reported polydispersities of these samples were 1.34, 1.41, 1.60, 1.74, 1.67, and 1.51, respectively. Considering the fact that poly(acrylic acid) differs from poly(methacrylic acid) only by nonexistence of the α-methyl group both the constituent polymer chains have comparable radii of gyration in the formation of an expanded coil. Although a grafted copolymer is the subject of our investigation, the molar ratio of the monomer poly(-methacrylic acid) to the co-monomer MPEGMA is far greater than the one in all studied cases. Hence, poly(acrylic acid) was a reasonable choice as a standard for our polymer system. For all experiments an injection volume of 100 μl and a flow rate of 1.000 ml/min were used. The carrier solvent was a phosphate buffer solution prepared by dissolving 1.204 g of sodium dihydrogen phosphate (Aldrich, St. Louis, MO) and 21.247 g of sodium nitrate phosphate (Aldrich, St. Louis, MO) in 1.000 l of HPLC grade water. The buffer solution was pH corrected from pH 5.3 to 7.0 by the addition of about 1.6 ml 5 N sodium hydroxide solution. The columns were maintained at a temperature of 35°C throughout the experiments. As shown in Fig. 1, the calibration data for the logarithm of the molecular weight versus the elution time was fit to both first-order and second-order polynomials.

For the GPC analysis of the graft copolymers, 0.25 wt.% solutions of the P(MAA-*g*-EG) copolymers were prepared by dissolving 12.5 mg of the polymers in 5 ml of the phosphate buffer solution described above. After dissolution, the samples were filtered using Gelman Acrodisc 0.2 μm PTFE filters (Pall Corporation, East Hills, NY) and were transferred into the HP autosampler screw cap vials. For most samples, the second-order fit of the calibration data was used to find the apparent molecular weight of the graft copolymers. For very high molecular weight samples (apparent M_n greater than 560,000 g/mol), the first-order fit was used.

2.4. ^1H NMR spectroscopy

^{1}H NMR spectroscopy was performed using a 500 MHz Varian VXR-500 NMR spectrometer (Varian, Palo Alto, CA). For each spectrum, 64 scans with a spectral window size of 8000 Hz were averaged. The experiment was performed with the sample spinning at a rate of 20 Hz with the field locked to the deuterium resonance of the solvent (deuterated pyridine). Based upon T_1 inversion recovery experiments, a 11.8 μs pulse (corresponding to 90° flip angle) was chosen. A pulse repetition time of five times the maximum T_1 relaxation time of 3 sec was selected. All spectra were recorded for a sample temperature of 75°C. Fourier Transformations were carried out with zero filling, and the FID was not treated with any apodization functions before Fourier transformation. The data reduction was done using the Varian software version 5.1.

To prepare samples for the NMR studies, the reactor solutions of the P(MAA-*g*-EG) copolymers (dissolved in a 50/50 mixture of ethanol and water) were spread onto large Petri dishes and were dried in a hood for several weeks at room temperature and then dried in a vacuum oven at 40°C for two days. The dried polymer was ground into white powder; then 0.16 g of polymer was dissolved in 1.00 ml of 100 atm% deuterated pyridine-d_5 (ISOTEC, Miamisburg, OH) in a seal-capped 5 ml vial. The polymer was allowed to

Table 1
GPC results for the moments of the molecular weight distribution of P(MAA-*g*-EG) copolymers

Sample designation	MAA:EG feed ratio	M_n	M_w	PDI
0/10	na	17,000	59,000	3.4
0/5	na	33,000	117,000	3.6
0/2.6	na	40,000	142,000	3.5
0/1	na	66,000	248,000	3.7
0/0.5	na	122,000	564,000	4.6
2.5/10	19.9	17,000	58,000	3.5
2.5/5	19.9	44,000	153,000	3.5
2.5/1	19.9	116,000	323,000	2.8
2.5/0.5	19.9	126,000	304,000	2.4
5/25	9.7	9600	32,000	3.3
5/10	9.7	26,000	125,000	4.9
5/5	9.7	25,000	94,000	3.8
5/2.5	9.7	61,000	189,000	3.1
5/1	9.7	119,000	303,000	2.5
5/0.5	9.7	165,000	364,000	2.2
10/18.5	4.6	7700	23,000	3.0
10/10	4.6	15,000	54,000	3.7
10/5	4.6	25,000	96,000	3.8
10/4	4.6	31,000	120,000	3.8
10/1.7	4.6	80,000	244,000	3.0
10/1	4.6	82,000	271,000	3.3
20/10	2.0	24,000	111,000	4.7
20/10	2.0	25,000	115,000	4.6
20/5	2.0	25,000	102,000	4.1
20/3.25	2.0	41,000	169,000	4.1
20/0.5	2.0	83,000	315,000	3.8

completely dissolve for 24 h. After this period of time, each solution was filtered using 0.45 μm Gelman Acrodiscs and was transferred into a 5 mm diameter NMR tube (Kontes Scientific, Vineland, NJ).

3. Results and discussion

3.1. Gel permeation chromatography

The experimental results from the GPC studies are summarized in Table 1. In this table, the first column corresponds to the sample designation (recall that the first number in this designation corresponds to the weight percent of the ethylene glycol repeat units in the monomer mixture, while the second number corresponds to the weight fraction of the initiator relative to the total monomer). The second column in the table indicates the ratio of methacrylic acid to ethylene glycol repeat units in the monomer mixture during synthesis. Columns three through six contain the number average molecular weight, M_n, the weight average molecular weight, M_w, and the polydispersity of the sample, respectively. After the application of the statistical *Q* test for data rejection, the results for two samples with unreasonably high apparent molecular weights (considerably out of the range of the calibration) and unusually high polydispersities were discarded.

The data in Table 1 illustrate the effect of the initiator concentration on the molecular weight of the P(MAA-*g*-EG) copolymers. As expected, the molecular weight of the polymers increases as the initiator concentration is decreased, and is proportional to the inverse square root of the initiator concentration (as illustrated in Figs. 2 and 3 discussed below). The data also illustrate that there is no consistent

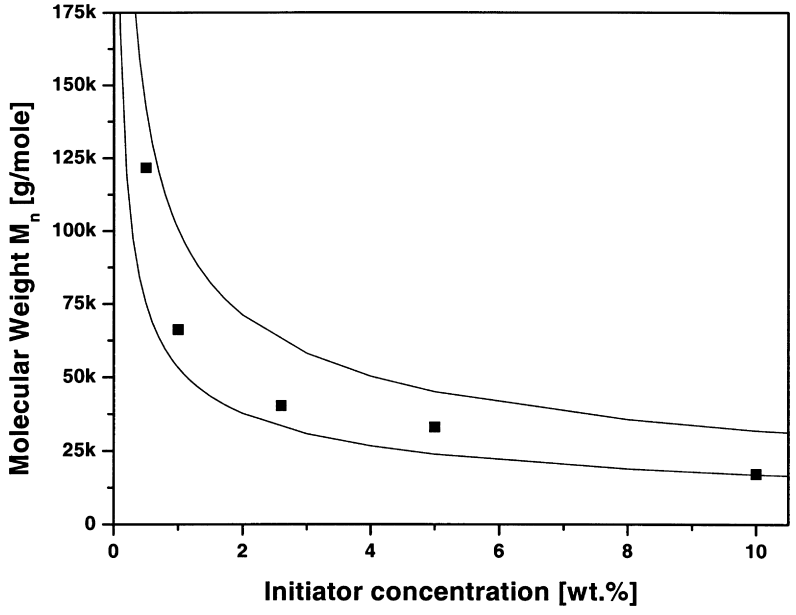

Fig. 2. Number average molecular weight M_n of poly(methacrylic acid) as a function of the weight percentage of sodium persulfate initiator fed into the reactor. The curves correspond to the upper and lower limit of the 99% confidence interval determined by nonlinear least squares fit to Eq. (1).

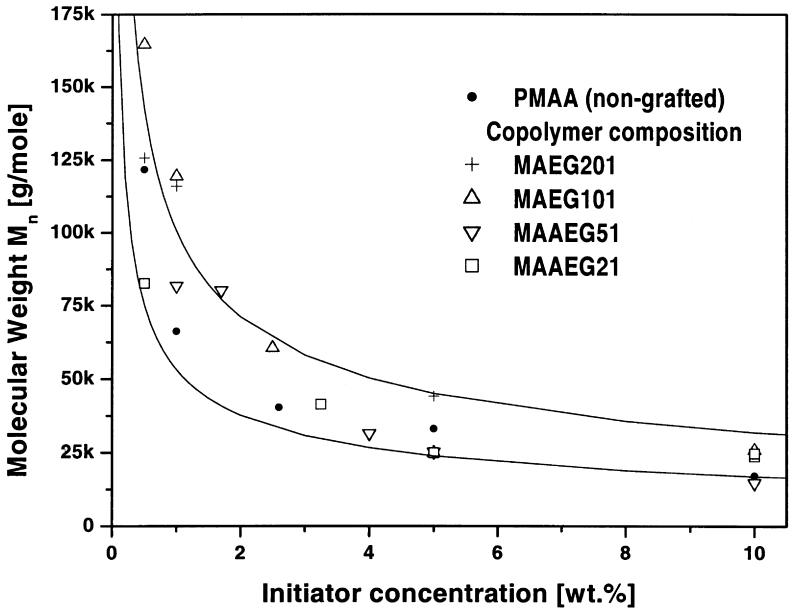

Fig. 3. Number average molecular weight M_n of poly(methacrylic acid-*g*-ethylene glycol) copolymers as a function of the wt.% of sodium persulfate initiator fed into the reactor. The curves correspond to the upper and lower limit of the 99% confidence interval determined by nonlinear least squares fit of Eq. (1) to the data for pure PMAA (as in Fig. 2).

trend for the polydispersity as a function of the MAA:EG repeat unit ratio. For repeat unit ratios ranging from infinity (pure PMAA) to 4.6 (a graft copolymer with a graft occurring about every 100 backbone repeat unit), the polydispersity remains essentially constant, with an average value of 3.4. These values of the polydispersity are typical for free radical chain polymerizations, and do not suggest that chain transfer to polymer occurs to a significant degree.

The relationship between the polymer molecular weight and the initiator concentration is illustrated in Fig. 2 in which the number average molecular weight is plotted as a function of the initiator concentration for the pure poly(-methacrylic acid) samples. In this figure, the points correspond to the pure PMAA data from Table 1 while the lines correspond to the 99% confidence interval for best fit of the data to the expected inverse square root relationship between molecular weight and initiator concentration. Fig. 2 illustrates that, as expected, the number average molecular weight is proportional to the inverse square root of the initiator, and that all the data fall into the 99% confidence interval. The best-fit mathematical relationship between the molecular weight and the initiator concentration if given below:

$$M_{\mathrm{n,PMAA}} = \frac{77,000}{\sqrt{w_{\mathrm{ini}}}} \tag{1}$$

where $M_{\mathrm{n,PMAA}}$ and w_{ini} denote the number average molecular weight of poly(methacrylic acid) (g/mol) and the weight percentage of the initiator (dimensionless) fed to the reaction system.

Fig. 3 illustrates the effect of the oligo(ethylene glycol) macromonomer on the GPC results for the polymer molecular weight as a function of initiator concentration. The figure contains five series of data points, with each series corresponding to a different MAA:EG repeat unit ratio during synthesis. This data are superimposed on the 99% confidence interval determined from the GPC results for pure PMAA. Note that the inverse square root dependence between the molecular weight and the initiator concentration is followed generally by all the data. However, the figure illustrates that the addition of the oligo(ethylene glycol) macromonomer leads to a systematic deviation from the results obtained for pure PMAA with the data falling consistently above the 99% confidence interval at low initiator concentration (high molecular weight). This trend suggests that the presence of the oligo(ethylene glycol) grafts leads to an increase in the hydrodynamic volume of the dilute polymer chains.

The apparent increase in the hydrodynamic volume upon the addition of the oligo(ethylene glycol) grafts could potentially arise from the structural differences caused by the presence of the macromonomer during synthesis, or from conformation effects of the grafts after synthesis. For example, this trend could possibly arise from the introduction of long-chain grafts as a result of chain transfer to the ethylene glycol grafts during synthesis. If this were the case, the effect should be the most pronounced for the polymers containing high ethylene glycol content (low MAA:EG repeat unit ratio). In addition, chain transfer to the grafts would reduce the primary chain length while increasing the branching, and therefore should have little effect on the number average molecular weight, but would result in an increase in the polydispersity index. The observed values

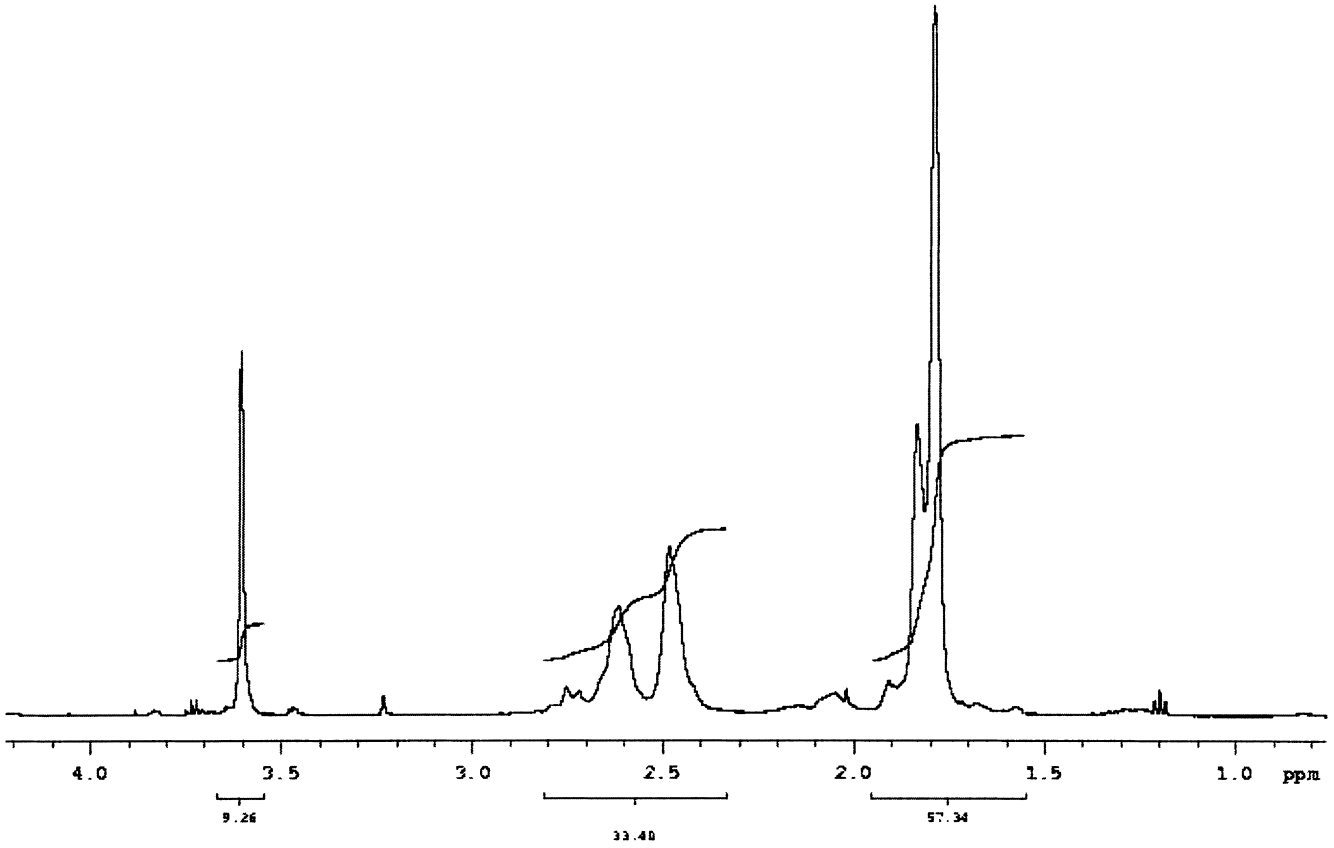

Fig. 4. ^{1}H NMR spectrum of P(MAA-*g*-EG) 5/10 from 0.8 to 4.2 ppm. The relative values for the integrated areas for the intensities of interest are also shown. Proton assignments are given in the text.

for the polydispersity index (shown in Table 1) suggest that chain transfer to polymer is not extensive. Even if there were no additional chain transfer during synthesis, the presence of the grafts could increase the hydrodynamic radius due to the excluded volume introduced by the grafts. The volume occupied by the oligo(ethylene glycol) grafts cannot be occupied by other grafts, or by the PMAA backbone. As a result, the chains will tend to expand, increasing the hydrodynamic radius.

3.2. ^{1}H NMR spectroscopy

A representative ^{1}H NMR spectrum of a P(MAA-*g*-EG) copolymer solution is shown by the trace of Fig. 4. This spectrum corresponds to the P(MAA-*g*-EG) 5/10 (corresponding to a MAA:EG repeat unit ratio of 9.7:1 during synthesis) dissolved in pyridine-d_5. As described previously by Klier et al. [6], the spectrum contains several characteristic features that can be used to determine the composition of the graft copolymer. The set of peaks that appear between 1.7 and 2.0 ppm corresponds to the α-methyl peak of the methacrylic acid and the MPEGMA units. The resonance corresponding to the α-methyl protons are split into three spectral features. The most intense peak occurs at 1.78 ppm, and may be attributed to syndiotactic monomer triads [7–10]. The peak of the next highest intensity appears at 1.83 ppm, and arises from atactic monomer triads. Finally, a relatively weak peak that corresponds to isotactic triads [7] is observed at 1.9 ppm. In this paper we use the NMR spectrum to determine the copolymer concentration, therefore all three peaks will be integrated together to determine the total number of α-methyl protons in the copolymer.

The second region of interest in the ^{1}H NMR spectrum lies between 2.4 and 2.8 ppm where peaks arising from the methylene groups in the methacrylic acid backbone are observed. Starting at high field, four consecutive broad peaks arising from the methylene are observed; two relatively intense peaks (at 2.47 and 2.61) and two relatively weak peaks (at 2.71 and 2.74 ppm). Again, in this contribution, all four of these peaks are integrated to determine the total number of methylene protons in the copolymers. The third region of interesting in the ^{1}H NMR spectrum lies between 3.5 and 3.7 ppm where a single, relatively narrow peak attributed to the ethylene segments in the grafts is observed. This peak is not split since the resonance of the oligo(ethylene glycol) grafts is insensitive to tacticity. Three sets of very weak resonance arise from trace quantities of ethanol solvent that remain in the sample. Specifically, a triplet observed at 1.20 ppm, the quartet at 3.75 ppm and a triplet at 3.35 ppm correspond to the methyl group, the methylene group and the hydroxy group of the residual ethanol [11]. Finally, it is interesting to note that a single

Table 2
^{1}H NMR results for the MAA to EG repeat unit ratio in the P(MAA-*g*-EG) copolymers

Sample designation	MAA:EG ratio in monomer	Integral of α-methyl peaks	Integral of methylene peaks	Integral of ethylene peak	MAA:EG ratio in polymer from α-methyl	MAA:EG ratio in polymer from methylene
0/10	∞	61.4	38.6	–	∞	∞
0/5	∞	62.3	37.7	–	∞	∞
0/2.6	∞	63.6	36.5	–	∞	∞
0/1	∞	62.8	37.2	–	∞	∞
0/0.5	∞	62.0	38.0	–	∞	∞
2.5/10	19.9	61.0	35.2	3.8	21.4	18.5
2.5/5	19.9	59.9	36.4	3.7	21.3	19.4
2.5/1	19.9	59.5	37.0	3.5	23.0	21.4
2.5/0.5	19.9	59.8	36.4	3.7	21.3	19.4
5/25	9.7	58.9	35.6	5.4	14.4	13.0
5/10	9.7	57.3	33.4	9.3	8.2	7.1
5/5	9.7	57.0	35.3	7.8	9.8	9.0
5/2.5	9.7	57.4	35.2	7.5	10.2	9.3
5/1	9.7	56.5	35.8	7.7	9.7	9.2
5/0.5	9.7	57.5	35.6	7.0	11.0	10.1
10/18.5	4.6	55.3	32.8	12.0	6.1	5.4
10/10	4.6	52.6	33.1	14.4	4.8	4.5
10/5	4.6	52.8	31.8	15.4	4.5	4.0
10/4	4.6	53.6	32.1	14.3	5.0	4.4
10/1.7	4.6	53.6	32.3	14.1	5.0	4.5
10/1	4.6	54.0	33.1	12.9	5.6	5.1
20/10	2.0	45.3	26.3	28.4	2.1	1.8
20/10	2.0	45.1	26.5	28.4	2.1	1.8
20/5	2.0	45.7	27.8	26.5	2.3	2.0
20/3.25	2.0	46.2	27.6	26.2	2.3	2.0
20/0.5	2.0	43.5	26.2	30.3	1.9	1.6

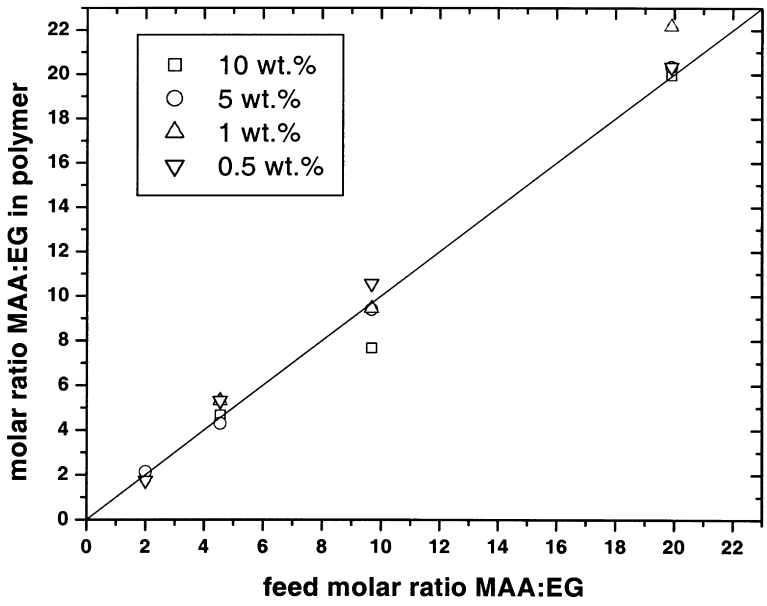

Fig. 5. MAA to EG repeat unit ratio in the graft copolymer as a function of the MAA to EG repeat unit ratio in the monomer feed. The diagonal line corresponds to equality of the polymer and monomer composition.

sharp peak is observed consistently at 3.23 ppm, and is assigned to the methoxy end group of MPEGMA [11].

The NMR data collected for the P(MAA-*g*-EG) copolymers are shown in Table 2. In this table, the first column corresponds to the sample designation (recall that the first number in this designation corresponds to the weight percent of the ethylene glycol repeat units in the monomer mixture, while the second number corresponds to the weight fraction of the initiator relative to the total monomer). The second column lists the MAA to EG repeat unit ratio in the monomer mixture fed to the reactor. Note that each MAA molecule contains one MAA repeat unit, while each MPEGMA macromonomer contains an average of 22.7 EG repeat units. Columns three, four and five list the relative peak areas for the α-methyl, methylene and ethylene peaks, respectively. These NMR peaks areas are normalized so that the sum of the integrals for the three regions of interest is 100. Finally, the last two columns list the experimental values for the MAA to EG repeat unit ratio in the graft copolymer. The data in the last two columns are calculated from the data in columns three, four and five. For example, if *P* represents the ratio of the area of the α-methyl peaks to the area of the oligo(ethylene glycol) peak, the MAA:EG repeat unit ratio in the copolymer can be calculated using the following equation:

$$\frac{n_{\mathrm{MAA}}}{n_{\mathrm{EG}}} = \frac{4}{3}\cdot P - \frac{1}{22.7} \tag{2}$$

This equation accounts for the facts that there are three α-methyl protons per MAA repeat unit, there are four ethylene protons per EG repeat unit, and that each MPEGMA molecule contains an α-methyl group. Similarly, if *Q* represents the ratio of the area of the methylene peaks to the area of the oligo(ethylene glycol) peak, the MAA:EG repeat unit ratio in the copolymer can be calculated using the following equation:

$$\frac{n_{\mathrm{MAA}}}{n_{\mathrm{EG}}} = 2\cdot Q - \frac{1}{22.7} \tag{3}$$

Again, this equation accounts for the facts that there are two methylene protons per MAA repeat unit, there are four ethylene protons per EG repeat unit, and that each MPEGMA molecule contains an α-methyl group.

Examination of the data in Table 2 reveals that the MAA to EG repeat unit ratio calculated using the area of the peaks for the methylene backbone group is consistently slightly smaller than the value obtained using the area of the α-methyl peaks. This consistent difference likely arises from the fact that the methylene peak is significantly broader than the α-methyl peak, therefore more of the signal could be lost in the baseline. However, the agreement between the two numbers is generally good, and is within the experimental accuracy of the technique. Therefore, we will average the values obtained using the α-methyl and the methylene in our further discussions.

The data in Table 2 illustrate that the experimental values for the MAA to EG repeat unit ratio in the copolymer are in good agreement with the known values for in the MAA:EG ratio in the monomer feed. The relationship between the compositions of the monomer feed and the final copolymer is illustrated in Fig. 5, which contains a plot of the MAA:EG repeat unit ratio in the copolymer as a function of the MAA:EG repeat unit ratio in the monomer feed. Note that the data in Fig. 4 generally lie close to the diagonal line that corresponds to equality of the polymer and the monomer compositions. This result is not surprising since the

Table 3
Average number of grafts per chain calculated based upon a combination of the GPC and the NMR experimental results

Sample designation	M_n from GPC	n_{MAA}/n_{EG} from NMR	Average number of grafts per chain
0/10	17,000	∞	0
0/5	33,000	∞	0
0/2.6	40,000	∞	0
0/1	66,000	∞	0
0/0.5	122,000	∞	0
2.5/10	17,000	20.0	0.4
2.5/5	44,000	20.3	1.1
2.5/1	116,000	22.2	2.6
2.5/0.5	126,000	20.3	3.1
5/25	9600	13.7	0.3
5/10	26,000	7.7	1.6
5/5	25,000	9.4	1.3
5/2.5	61,000	9.7	3.0
5/1	119,000	9.4	6.1
5/0.5	165,000	10.5	7.6
10/18.5	7700	5.7	0.6
10/10	15,000	4.7	1.5
10/5	25,000	4.3	2.6
10/4	31,000	4.7	3.0
10/1.7	80,000	4.8	7.7
10/1	82,000	5.3	7.2
20/10	24,000	1.9	4.9
20/10	25,000	1.9	5.1
20/5	25,000	2.1	4.7
20/3.25	41,000	2.2	7.7
20/0.5	83,000	1.8	18.4

polymerization is practically a homopolymerization of methacrylic acid (for example, the 19.9:1 system contains 450 MAA monomer units for every MPEGMA molecule; the 9.7:1 system contains 220 MAA monomer units for every MPEGMA molecule, etc). Therefore, the oligomeric macromonomer are dispersed as a dilute solution in the reaction mixture, and nearly every active radical center will be an MAA-terminated radical. It is extremely unlikely that a growing radical chain will incorporate two macromonomers in close succession (a MPEGMA-terminated radical will quickly become an MAA-terminated radical by propagation), therefore the grafts will be well distributed along the polymer chains.

3.3. Average number of grafts per chain

The experimental results obtained from the GPC can be combined with the ^{1}H NMR spectroscopy results to estimate the number of grafts per chain for each of the polymer samples. Using the number average molecular weight from the GPC studies and the MAA:EG repeat unit ratio from the NMR experiments, the average number of grafts per chain may be calculated using the following equation:

$$\frac{n_{\mathrm{MPEGMA}}}{\mathrm{chain}} = \frac{\bar{M}_n}{\frac{n_{\mathrm{MAA}}}{n_{\mathrm{EG}}} 22.7 \cdot M_{\mathrm{MAA}} + M_{\mathrm{MPEGMA}}} \tag{4}$$

In this equation, $\bar{M}_n$ is the number average molecular weight as given by GPC. M_{MAA} and M_{MPEGMA} represent the molecular weight of the methacrylic acid monomer and methoxy poly(ethylene glycol) monomethacrylate macromonomer, respectively.

Table 3 contains results of the calculation of the number of grafts per chain obtained using Eq. (4). As expected, for a constant initiator concentration, the average number of grafts per chain increases, as the amount of the MPEGMA in the reaction mixture is increased (recall that the first number in the sample designation is the weight fraction of MPEGMA in the monomer mixture). In addition, for a constant MPEGMA content, the average number of grafts per chain decreases as the initiator concentration is increased. This trend arises from the fact that the molecular weight decreases with increasing initiator concentration.

The average number of grafts per chain is expected to play an important role in determining the emulsification performance of the graft copolymers. Since the formation of the reversible hydrophobic blocks requires the presence of the grafts, an effective emulsifier should have an average of at least one graft per chain. It is noteworthy that three of the samples synthesized with high initiator concentrations (samples designated 2.4/10, 5/25, and 10/18.5) contain an average of less than one graft per chain. In these systems, the primary chain length is so low that many propagating radicals do not encounter a MPEGMA molecule before they terminate. These copolymers are not expected to function well as emulsifiers since many of the chains will be the homopolymer PMAA. Several of the copolymers synthesized with intermediate initiator concentrations contain an average of one to two grafts per chain. In the complexed state, these chains would resemble diblock, triblock, tetrablock or pentablock systems, depending upon the position of the graft or grafts along the backbone. Finally, many of the copolymers contain an average of three or more grafts per chain. These copolymers will resemble multiblock copolymers when the grafts are folded down and complexed with the backbone. In a future publication we will correlate the average number of grafts per chain with the effectiveness of the copolymer as a reversible emulsifier.

4. Conclusions

In this paper, we presented the synthesis and characterization of a series of P(MAA-*g*-EG) copolymers of varying molecular architectures. A semi-batch reactor was designed to synthesize the copolymers by a free radical copolymerization of methacrylic acid with the macromonomer MPEGMA. The resulting copolymers were characterized

using ^{1}H NMR to determine the polymer composition, and GPC to characterize the polymer molecular weight distribution.

The GPC results revealed that, for a given MAA:EG repeat unit ratio, the number average molecular weight is proportional to the inverse square root of the initiator concentration. In addition, for repeat unit ratios ranging from infinity (pure PMAA) to 4.6 (a graft copolymer with a graft occurring about every 100 backbone repeat unit), the polydispersity was found to remain essentially constant, with a value typical for free radical chain polymerizations. The experimental polydispersity values suggest that chain transfer to polymer does not occur to a significant extent. The GPC results also indicate that the addition of the oligo(ethylene glycol) macromonomer leads to a systematic deviation from the results obtained for pure PMAA with the data consistently falling above the 99% confidence interval at low initiator concentration (high molecular weight). This trend suggests that the presence of the oligo(ethylene glycol) grafts leads to an increase in the hydrodynamic volume of the dilute polymer chains, possibly due to the excluded volume introduced by the oligomeric grafts. The ^{1}H NMR results illustrated that the experimental values for the MAA to EG repeat unit ratio in the copolymer are in good agreement with the known values for in the MAA:EG ratio in the monomer feed. The GPC and NMR results were combined to estimate the number of grafts per chain for each of the polymer samples. The average number of grafts per chain we found to range from 0.3 to 18. As expected, for a constant initiator concentration, the average number of grafts per chain was found to increase as the amount of the MPEGMA in the reaction mixture was increased. In addition, for a constant MPEGMA content, the average number of grafts per chain decreased as the initiator concentration was increased.

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