Cross-Linked Poly(methacrylic acid-*co*-poly(ethylene oxide) methyl ether methacrylate) Microspheres and Microgels Prepared by Precipitation Polymerization: A Morphology Study

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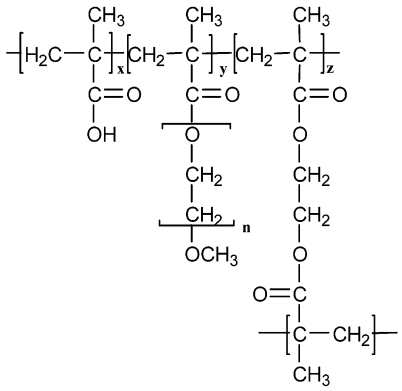
ABSTRACT: We applied the concept of precipitation polymerization in organic solvents to the polar and hydrogen-bonding monomers methacrylic acid (MAA) and poly(ethylene glycol) methyl ether methacrylate (PEGMM), with ethylene dimethacrylate (EDMA) as cross-linker. Soluble copolymers, swellable microgels, microspheres, macrogels, and coagulum were observed after copolymerization in mixtures of methyl ethyl ketone and heptane. Increasing the amount of covalent cross-linker or decreasing the solvency of the reaction medium caused a change of morphology from microgels to microspheres. The ratio of acid to ethylene oxide groups present in the comonomers also dramatically changed the polymer−polymer interactions and hence the morphology. Three types of cross-linking are proposed to exist in this system: covalent cross-linking by EDMA and hydrogen-bonding cross-linking between two acid units as well as between acid and ethylene oxide groups. The size of the particles increased with decreasing solvency, decreasing EDMA concentration and increasing PEGMM concentration.

Introduction

Cross-linked copolymers of methacrylic acid and poly(ethylene glycol) methacrylate (PEGMA) are known to swell in response to changes in pH, temperature, or solvent composition.[1,2] Under acidic conditions, the ethylene glycol ether units hydrogen-bond to the methacrylic acid units, causing desolvation and collapse of the network. This phenomenon is analogous to the cloud point observed upon heating a solution containing the two corresponding homopolymers above the lower critical solution temperature (LCST). Increasing the pH causes ionization and reswelling of the network. Klier and Peppas have described the temperature, pH, and solvent dependence of the swelling response of bulk copolymer networks comprising methacrylic acid, PEG methacrylate, and ethylene dimethacrylate as cross-linker[1−3] and explored their potential uses as drug delivery systems.[4,5] Analogous MAA and PEGMM copolymer microspheres have been prepared by suspension polymerization,[6] but these microspheres are polydisperse and may contain significant amounts of stabilizers. Other approaches describe *N*-isopropylacrylamide-based minigel particles prepared by inverse suspension polymerization[7] and functional methacrylic acid microgels prepared by precipitation polymerization.[8] Recently, Peppas and co-workers described the preparation and swelling behavior of lightly cross-linked poly(methacrylic acid-*g*-ethylene glycol) nanospheres by precipitation polymerization in water.[9] Such narrow disperse nanospheres would show both larger, and faster, swelling responses, compared to the corresponding macrogels. Their larger surface areas provide a potential advantage for drug release or uptake.

The present study describes the preparation of a related, though wider range of microgels, microspheres, and space-filling gels by precipitation copolymerization of methacrylic acid, poly(ethylene glycol) methyl ether methacrylate (PEGMM300), and ethylene dimethacrylate (EDMA) in organic solvents.



In addition, this work also aims to map the polymer network morphologies attainable through control of comonomer composition and solvent polarity. We have earlier prepared monodisperse microspheres and microgels by surfactant and stabilizer-free precipitation copolymerization of styrenic, methacrylic ester, and maleic anhydride monomers in the presence of cross-linker. Thus, an additional objective of this study was to explore whether precipitation polymerization could be extended to the polar and hydrogen-bonding methacrylic acid and PEGMA. The microspheres and microgels formed from such comonomers might be of use as affinity chromatography resins and as reactive building blocks in polyelectrolyte complexation.[10]

Experimental Section

Materials. Ethylene dimethacrylate (EDMA, 98%), methacrylic acid (MAA, 98%), and poly(ethylene glycol) methyl ether methacrylate 300 (PEGMM 300, 98%, with on average 4.5 ethylene glycol units) were used as received from Aldrich Chemical. The solvents methyl ethyl ketone (MEK, 99%), ethyl acetate (EA, 99%), *tert*-butyl alcohol (*t*-BuOH, 99%), acetonitrile (ACN, 99%), butyronitrile (99%), toluene (Tol, 99%), and *n*-heptane (Hep, 99%) were purchased from Caledon Laboratories. 1,2-Dimethoxyethane (DME, 100%) was obtained from

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Table 1. Summary of Copolymerization of MAA, PEGMM, and EDMA in Various Solvents[a]

solvent	Hildebrand solubility parameter[a] δ (MPa$^{1/2}$)	polar Hansen parameter[c] δ_p (MPa$^{1/2}$)	hydrogen-bonding Hansen parameter[c] δ_h (MPa$^{1/2}$)	observation	size (μm)	distribution (%)
t-butanol	21.7	5.7[d]	14.5[d]	soluble polymer		
methyl ethyl ketone	19.0	9.0	5.1	spherical microgels[b]	0.77	0.44
MEK/Hep 70/30	17.83	6.3	3.57	spherical microgel[b]	0.93	
MEK/Hep 50/50	17.05	4.5	2.55	coagulum		
MEK/Hep 30/70	16.27	2.7	1.53	coagulum		
methyl isobutyl ketone	17.2	6.1	4.1	irregular microparticles[b]	2.79	20.3
ethyl acetate	18.6	5.3	7.2	irregular microparticles[b]	2.14	10.5
propyl acetate	18.0	4.5[e]	6.8[e]	irregular microparticles[b]	2.16	11.5
butyl acetate	17.4	3.7	6.3	irregular microparticles[b]	2.26	22.4
dimethoxyethane	17.6	6.1[f]	9.2[f]	soluble polymer		
heptane	15.1	0	0	coagulum		
toluene	18.0	1.4	2.0	gel		
acetonitrile	24.3	18.0	6.1	aggregate		
butylonitrile	20.1	12.5	5.1	aggregate		

[a] The ratio of acid to ether was 10:4, and EDMA concentration was 12.5 vol % of the total monomer. Initiator concentration was 3 wt % relative to total monomer, and total monomer loading was 2 vol %. [b] The yields of microgels and microspheres are over 90%. [c] From *Polymer Handbook*.[20] [d] The values were from 2-butanol. [e] The values were estimated from ethyl acetate and butyl acetate. [f] The values were from bis(2methoxyethyl) ether.

Fisher Scientific. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) from Spectrum Quality Products Inc. was used without further purification.

Typical Polymerization Procedure. 0.800 mL of total monomer and 0.015 g of AIBN (0.090 mmol, 2 wt % relative to total monomer) were dissolved in 20 mL of total solvent in 25 mL Teflon-sealed screw cap glass vials, resulting in 4% w/v total monomer concentrations. The MAA:ether functional group ratio was varied from 10:4, to 1:1, to 1:4, and the EDMA fraction of total monomer was set to 12.5, 25, 50, and 75 vol % of the total monomer. For example, a 10:4 acid:ether ratio at 50 vol % EDMA corresponds to 0.30 mL of MAA (0.31 g, 3.54 mmol), 0.10 mL of PEGMM (0.11 g, 0.35 mmol), and 0.4 mL of EDMA (0.42 g, 2.12 mmol). The reaction solvent was either a neat solvent such as MEK or a binary mixture of MEK and *n*-heptane.

Several reaction vials were placed on the horizontal steel rollers of a modified and thermostated hot-dog roller and rolled at a constant rate of 5 vial revolutions per minute and a temperature of 70 °C for 24 h. The initially clear reaction mixtures turned opalescent or milky during microgel and microsphere formation, respectively, or gelled macroscopically in the case of space-filling gel. Microgels and microspheres were collected by filtration and purified by repeated centrifugation, decanting, and resuspension in acetone. Space-filling gels were not studied further in this work.

Characterization. The morphologies of the polymers obtained were studied using a Philips ElectroScan 2020 environmental scanning electron microscope (ESEM). ESEM specimens were prepared by diluting the particle dispersions with acetone and placing one drop each on a cover glass. The drops were dried at room temperature and then coated under vacuum with approximately 4 nm of gold**.** Particles sizes were obtained from the electron micrographs, by taking the average of about 100 individual particle diameters. Particle yield was measured gravimetrically.

Results and Discussion

Background. We have in the past reported the formation of monodisperse microspheres by precipitation polymerization of divinylbenzene-55[11−14] and divinylbenzene-80[15] and by precipitation copolymerization of divinylbenzene with chloromethylstyrene[15] and with a series of methacrylates and methacrylic cross-linkers such as EDMA.[16] Subsequently, we described the formation of P(DVB-*alt*-MAn)[17,18] copolymer particles, which are more polar and contain anhydride groups suitable for subsequent functionalization. In all these cases, low monomer loading, covalent cross-linker, and a near-θ reaction medium are required to form microspheres. We have mapped the formation of microgels, microspheres, space-filling gels, and coagulum as a function of cross-linker loading and solvency of the medium.[13] More polar acrylic ester[16] or maleic anhydride[18] containing microspheres were only formed in correspondingly more polar solvent mixtures.

Accordingly, copolymerization of MAA, PEGMM, and EDMA was expected to require even more polar solvent mixtures, though access to aqueous polymerization media was precluded due to the hydrophobicity of the EDMA cross-linker. In addition, the use of organic solvents as polymerization media was expected to promote the formation of interchain hydrogen bonding between both acid and ether as well as between two acid groups. This hydrogen bonding was expected to reduce the polymer−solvent interactions and hence affect the network morphology.

Choice of Polymerization Solvents. The first step in the present experiments was therefore to choose an appropriate solvent or solvent mixture that would allow for in-situ precipitation of the forming copolymer into narrow disperse particles. Preliminary work had suggested that hydrogen bonding between MAA units can partly replace covalent cross-linker, in particular in solvents such as esters and ketones that do not interfere with this hydrogen bonding.[19] In the present terpolymer system, the hydrogen bonding in MAA dimers, and in MAA/PEGMM complexes, is similarly considered to aid the desolvation of the copolymer and thus particle formation. We therefore explored several neat solvents in order to find a marginal solvent system able to promote hydrogen bonding and hence particle formation (Table 1).

Ketone and ester solvents generally resulted in rough but colloidally stable microspheres and microgels, while alcohols and hydrocarbons resulted in soluble polymer and in coagulum, respectively. The Hildebrand solubility parameter corresponds to the cohesive energy density of solvents and polymers[20] and is an indicator for the

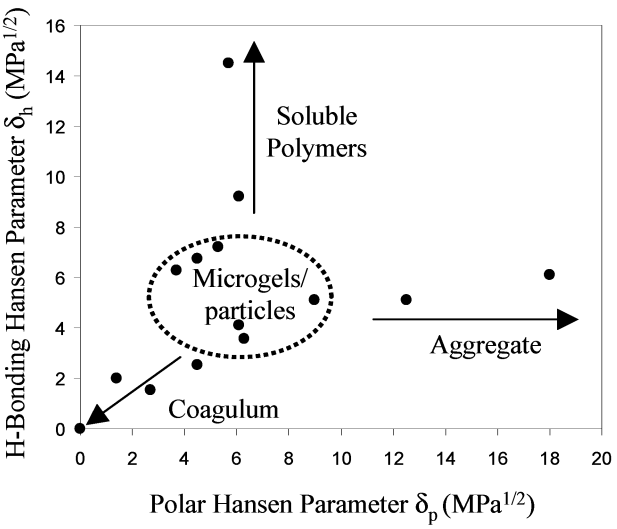

Figure 1. Plot of morphology of poly(MAA-*co*-PEGMM-*co*-EDMA) at 12.5% EDMA, and an acid:ether ratio of 10:4, as a function of δ_h and δ_p. Microspheres and microgels are only found in solvents having moderate δ_h and δ_p values.

affinity of a solute for a solvent. Most microspheres were obtained in medium polarity solvents, i.e., with a Hildebrand solubility parameter in the range of 19−17.2 MPa$^{1/2}$. In particular, good solvents for EDMA and PEGMM, but not for PMAA, facilitated microsphere formation. This seemed to suggest that the colloidal stability of these microparticles arises from steric stabilization through pendent chains and surface gels rather than from electrostatic stabilization through the acidic monomer. The solubility parameters of EDMA and PEGMM300 are estimated as 18.2 MPa$^{1/2}$, in analogy to diethylene glycol dimethacrylate which has a calculated solubility parameter of 18.2 MPa$^{1/2}$. Solvents with solubility parameters close to 18.2 MPa$^{1/2}$ would be considered good solvents for these monomers. Ketones and esters seem to satisfy this requirement. However, the one-dimensional Hildebrand solubility parameter reflects only the overall solvent properties but does not distinguish between specific effects such as dipolar interactions, hydrogen bonding, and van der Waals interactions. For example, polymerization in a mixture of 80 vol % toluene and 20 vol % DME, with a compound solubility parameter $\delta = 18$ MPa$^{1/2}$, did not give particles. Dimethoxyethane, though within the solubility parameter range at 17.6 MPa$^{1/2}$, also did not lead to particle formation, except at higher EDMA levels (results not shown). This is likely due to the excellent hydrogen bond accepting ability of DME.

The three-dimensional Hansen solubility parameters proved to be more useful than the Hildebrand parameter in understanding the role of the solvent in this system. The Hansen parameters are an attempt to break the overall interactions between a solute and a solvent into dispersive, polar, and hydrogen-bonding interactions.[20] In particular, the hydrogen-bonding parameter (δ_h) and the dipolar parameter (δ_p) (Table 1) should correlate with the key polymer−solvent interactions. Figure 1 shows the morphology of poly(MAA-*co*-PEGMM-*co*-EDMA) formed in the solvents listed in Table 1, plotted against both δ_h and δ_p. It can be seen that colloidally stable microgels and microparticles are formed in the range of moderate values for both parameters, $\delta_h = 3.6-7.2$ and $\delta_p = 3.7-9.0$, respectively. Solvents with low δ_h and δ_p lead to coagulum and solvents such as alcohols with medium δ_p but high δ_h lead to soluble copolymer, while highly polar aprotic solvents such as nitriles lead to aggregate formation.

These results suggest that the effect of solvents is strongly correlated to the hydrogen bonding in MAA dimers and MAA−PEGMM complexes and their interruption by hydrogen-bonding solvents. It appears plausible that ketones and esters are solvents that can maintain the polymer−polymer hydrogen bonding and thus promote polymer desolvation and the formation of microgels and in particular microspheres. Both of these particles would be colloidally stabilized through their swollen surface gel layers.

Subsequent polymerizations were hence carried out in MEK mixtures with varying amounts of heptane added to further reduce solvent polarity and to explore the microparticle morphologies accessible within this so-called "marginal solvency" regime. As well, this solvent mixture allowed us to make direct comparisons between the present polar and hydrogen-bonding polymers and, earlier, less polar poly(divinylbenzene)-based systems.

Polymer Morphology Map. Copolymerizations of MAA, PEGMM300, and EDMA at different comonomer compositions were conducted as a function of solvency (MEK/heptane ratio) and cross-linker concentration. At each comonomer ratio, 2D morphology maps covering a range of EDMA levels and solvent compositions were established. Each two-dimensional morphology map shows the results of six sets of five experiments, corresponding to 30 compositional data points. These maps show the factors that affect the morphology of cross-linked polymers prepared by precipitation polymerization. Their vertical and horizontal axes illustrate the morphology transitions as a function of changes in solvent composition and cross-linker concentration, respectively. Separate 2D morphology maps were acquired, representing different acid-to-ether ratios, and combined into a 3D cubic map (Figure 2). From this perspective, the dashed line in Figure 2 indicates the effect of comonomer ratio on the polymer morphology. Figure 2 summarizes the morphology information described in Figures 3−8.

Six distinct morphologies were observed: space-filling macrogels, colloidally stable microspheres, colloidally stable microgels, phase-separated polymer gels, soluble polymers, and coagulum. The soluble polymers include both branched and linear polymers. These morphologies all correspond to samples obtained after 24 h of polymerization.

1. Solvent-Induced Morphology Transition. Our first aim was to study the effects on the poly(MAA-*co*-PEGMM-*co*-EDMA) morphology resulting from changing the solvent composition from neat MEK, a good solvent for the copolymer, to 90 vol % heptane, a poor solvent. These experiments were carried out at constant functional comonomer ratio (10:4 acid:ether units) and high cross-linker concentrations (75 and 50 vol % EDMA, respectively).

Space-filling macrogels are obtained at high (100%) MEK and high EDMA levels. Apparently, good solvency conditions at high cross-linker levels lead to a copolymer network forming in a swollen and extended state, such that it eventually fills the entire reaction volume.

Discrete spherical particles with smooth surfaces were obtained in 70 and 50 vol % MEK (Figure 3), having number-average diameters of 0.9 and 1.5 μm, respectively. The lower solvency apparently causes the oligo-

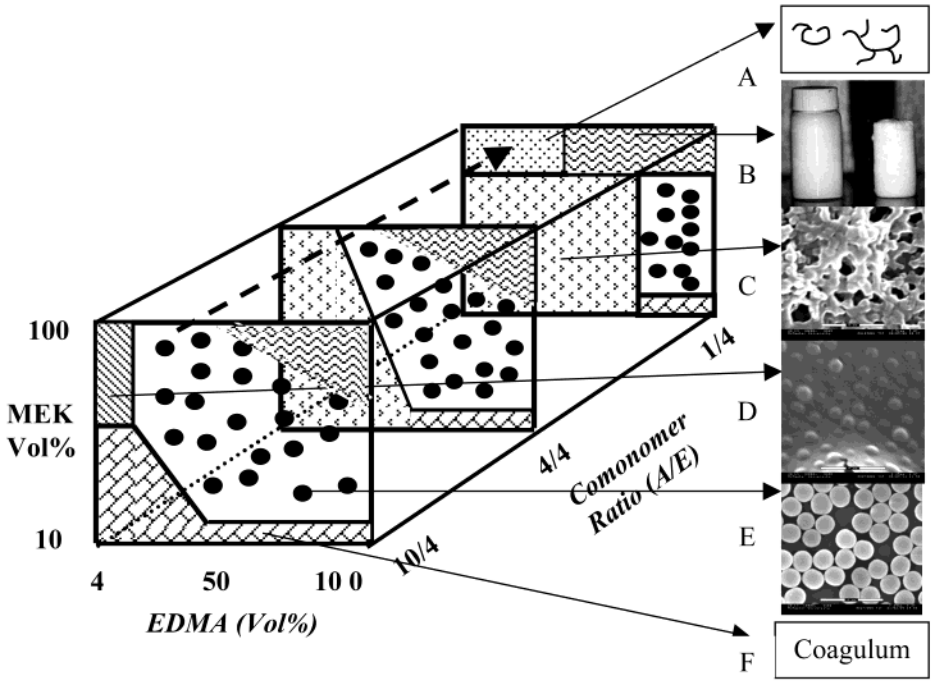

Figure 2. 3-D morphology map for poly(MAA-*co*-PEGMA-*co*-EDMA) prepared in different MEK/heptane mixtures. The 4 vol % monomer feed contained 4−100 vol % EDMA. The solvent composition for the polymerization were varied from neat MEK to 90% heptane. Distinct morphologies are illustrated in this map: soluble copolymer (A), space-filling macrogel (B), gels (C), microgels (D), microspheres (E), and coagulum (F).

mers to desolvate and ultimately form microspheres rather than connect in the swollen state to form a space-filling network. These microspheres are thought to be sterically stabilized by the transient solvated copolymer gel on their surface—an autosteric stabilization process.[14]

Further decreasing the MEK level to 30 vol % and below led to the formation of coagulum. Evidently, the solvency became so poor that the forming copolymer completely desolvates and hence loses all colloidal stability. The resulting aggregates neither dissolve nor swell significantly in good solvents such as methanol, suggesting that the copolymer network is highly cross-linked in its collapsed state.

These observations are in agreement with our earlier reports on the polymerization of DVB-55 in MEK/heptane mixtures. In the present work, discrete poly(MAA-*co*-PEGMM-*co*-EDMA) microspheres are obtained in a higher solvency window, ranging from 70 to 50 vol % MEK, compared to the solvency window found for the less polar DVB system, of 33−20 vol %. The same effect is seen in the analogous copolymerizations carried out with 50 vol % EDMA, where microspheres were obtained in 100, 70, and 50 vol % MEK. With this decreasing solvency, the size of the microspheres increased from 0.6 to 1.6 μm, and the surface of the microspheres changed from smooth to bumpy (Figure 4). These results confirm that higher levels of MEK contribute to the colloidal stability of the primary particles formed, while at lower MEK levels, i.e., MEK/heptane 50/50, the homo-coagulation period of primary particles was prolonged, resulting in final microspheres with irregular shapes and surfaces.

2. Cross-Linker-Induced Morphology Transition. The effect of EDMA cross-linker concentration was studied in detail at a 10:4 acid:ether ratio in neat MEK. In the absence of cross-linker, soluble linear poly(MAA-*co*-PEGMM) was obtained. Addition of 2% EDMA still resulted in a clear solution of branched copolymer. Soft swellable microgels were obtained at EDMA concentration between 4 and 25 vol %, while hard and narrow disperse microspheres were formed at 50 vol % EDMA. The reaction mixture formed a macrogel at 75 vol % EDMA.

Higher cross-linker concentrations reduce swelling and aggregation in the good solvent MEK and hence lead to smaller, narrow disperse microspheres. The interparticle spacing, seen in Figure 5, reflects the deswelling of these microspheres upon drying on the glass cover slide used for ESEM. Residual interconnects between particles are visible and confirm the presence of a swellable surface layer, in accordance with the autosteric colloidal stabilization of these particles.

The particles formed at 70% MEK (not shown) and 12.5−75% EDMA were generally similar to those formed in neat MEK. At 50% MEK, particles only formed at EDMA levels of 50% and preferably 75%. The particles formed at 50% EDMA already show evidence for an extended homo-coagulation period, resulting in the final cluster shape familiar from other, methacrylate precipitation polymer systems at the edge of the solvency composition.[16] At both 70% and 50% MEK, the solvency is lower due to the presence of heptane, and the microspheres show less of a size dependence on cross-linker level (Table 3).

3. Acid:Ether Ratio Induced Morphology Transition. The effect of acid:ether ratios on polymer network morphology was studied at three MEK volume fractions of 100%, 70%, and 50%, with four EDMA levels each, for a total of 12 experimental sets (Table 2). At constant MEK and EDMA levels, changing the acid:ether ratio affects the polarity and hydrogen-bonding properties of the polymer and hence its morphology.

Terpolymerizations in neat MEK at 75 vol % EDMA gave space-filling gels at all comonomer ratios, due to efficient overlap and cross-linking of the originally

Table 2. Summary of Morphologies Obtained from Cross-Linking Polymerization of MAA and PEGMM at Three Different MEK/Heptane Ratios

MEK (vol %)	EDMA (vol %)	MAA only	MAA/PEGMM 10:4	MAA/PEGMM 4:4	MAA/PEGMM 1:4
100	75	microspheres	SFG[a]	SFG	SFG
100	50	microspheres	microgels	SFG	SFG
100	25	microspheres	microgels	coagulum	coagulum
100	12.5	microspheres	microgels	coagulum	coagulum
70	75	microspheres	microspheres	microspheres	microspheres
70	50	microspheres	microspheres	microspheres	coagulum
70	25	microspheres	microgels	microgels	coagulum
70	12.5	microspheres	microgels	coagulum	coagulum
50	75	microspheres	microspheres	microspheres	microspheres
50	50	microspheres	microspheres	microspheres	microspheres
50	25	coagulum	coagulum	SFG	SFG
50	12.5	coagulum	coagulum	SFG	SFG

[a] SFG = space-filling macrogel.

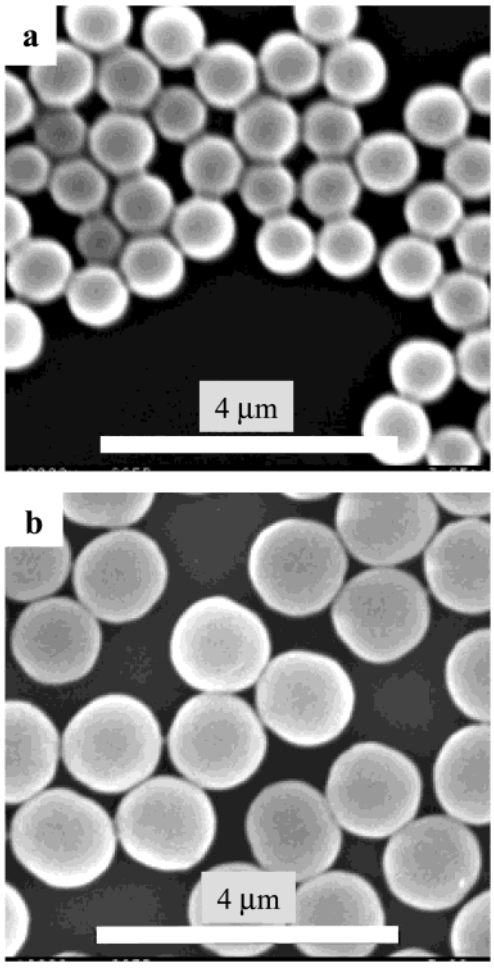

Figure 3. Scanning electron micrograph of poly(MAA-*co*-PEGMM-*co*-EDMA) microspheres prepared at 10:4 acid-to-ether ratio, 75 vol % EDMA, 4 vol % total monomer loading in a mixture of (a) 70:30 MEK:heptane and (b) 50:50 MEK:heptane, respectively. The scale bar is 4 μm in length.

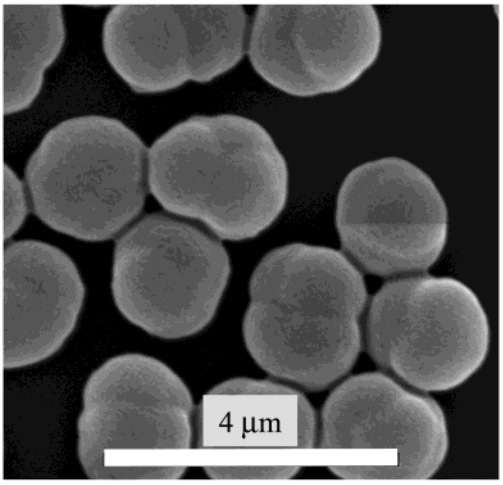

Figure 4. Evidence of a prolonged homo-coagulation period at lower solvency system. Scanning electron micrograph of poly(MAA-*co*-PEGMM-*co*-EDMA) microspheres prepared from 10:4 acid-to-ether ratio, 50 vol % EDMA, 4 vol % total monomer loading in a mixture of 50:50 MEK:heptane. The scale bar is 4 μm in length.

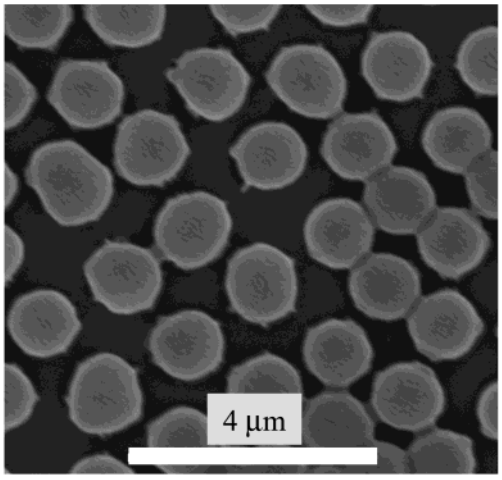

Figure 5. Scanning electron micrograph of deswollen poly(MAA-*co*-PEGMA-*co*-EDMA) microspheres. The microspheres were prepared at 25 vol % EDMA and 10:4 acid:ether ratio in neat MEK. The scale bar is 4 μm in length.

formed microgels. At lower EDMA levels, microgels formed the final morphology in the presence of excess acid, while coagulum dominated in the presence of both stoichiometric and excess amounts of ether groups. This contrasts with binary poly(MAA-*co*-EDMA) microgels (no PEGMM) that were obtained over a wide range of EDMA levels.

There is a significant trend to form larger networks with increasing PEGMM level, especially at lower cross-linker levels. Larger, swellable, and more deformable microgels were obtained by incorporating more PEGMM (Figure 6). In presence of excess PEGMM, only soluble branched polymers were obtained.

Figure 7 shows the morphologies of poly(MAA-*co*-PEGMM-*co*-EDMA) microgels prepared in 70 vol % MEK as a function of cross-linker and acid:ether ratio. At 75% EDMA, spherical terpolymer microspheres were

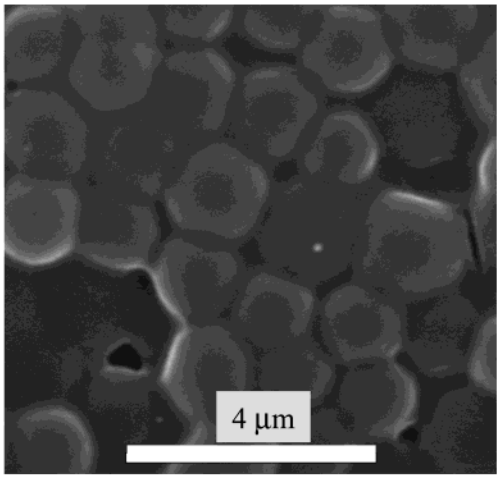

Figure 6. Scanning electron micrograph of poly(MAA-*co*-PEGMM-*co*-EDMA) swellable microgels prepared at 25 vol % EDMA in neat MEK. The acid:ether ratio was 4:4. The scale bar is 4 μm in length.

obtained at all acid:ether ratios (Figure 7-IV, a−c). The microspheres obtained at 1:4 ratio showed almost the same size as those obtained at 4:4 and 10:4 ratios, but some had aggregated into clusters. At 50 vol % EMDA, a sticky coagulum was obtained 1:4 comonomer ratio. At 25 and 12.5 vol % EDMA, microparticles were only obtained at 10:4 comonomer ratio. At higher PEGMM levels, only coagulum was observed at these low EDMA levels.

Table 3. Average Diameters (μm) of Poly(MAA-*co*-PEGMM-*co*-EDMA) Microspheres

MEK (vol %)	EDMA (vol %)	MAA only	MAA/ PEGMM 10:4	MAA/ PEGMM 4:4	MAA/ PEGMM 1:4
100	75	<100			
100	50	0.45	0.67		
100	25	0.59	1.18	1.70	
100	12.5	0.94	1.90		
70	75	0.67	0.87	1.06	1.16
70	50	0.78	0.93	1.26	
70	25	1.04	1.90		
70	12.5	1.16	0.93		
50	75	1.27	1.47	1.62	2.09
50	50	1.33	1.60	3.25	
50	25				
50	12.5				

A similar picture emerges from terpolymerizations carried out in 50 vol % MEK (Figure 8). At 75% EDMA, microspheres were obtained at all acid:ether ratios. Their size increases with increasing PEGMM levels, and their surfaces become rougher due to longer homocoagulation during growth.

At 50 vol % EDMA, the particles become less stable with increasing PEGMM levels, forming large, 3 μm diameter cauliflower-like microparticles at the stoichiometric acid:ether ratio and irregular aggregates at the 1:4 acid:ether ratio.

At 25 vol % EDMA, coagulum was observed at 10:4, and space-filling gels were observed at 4:4 and 1:4 acid:ether ratios.

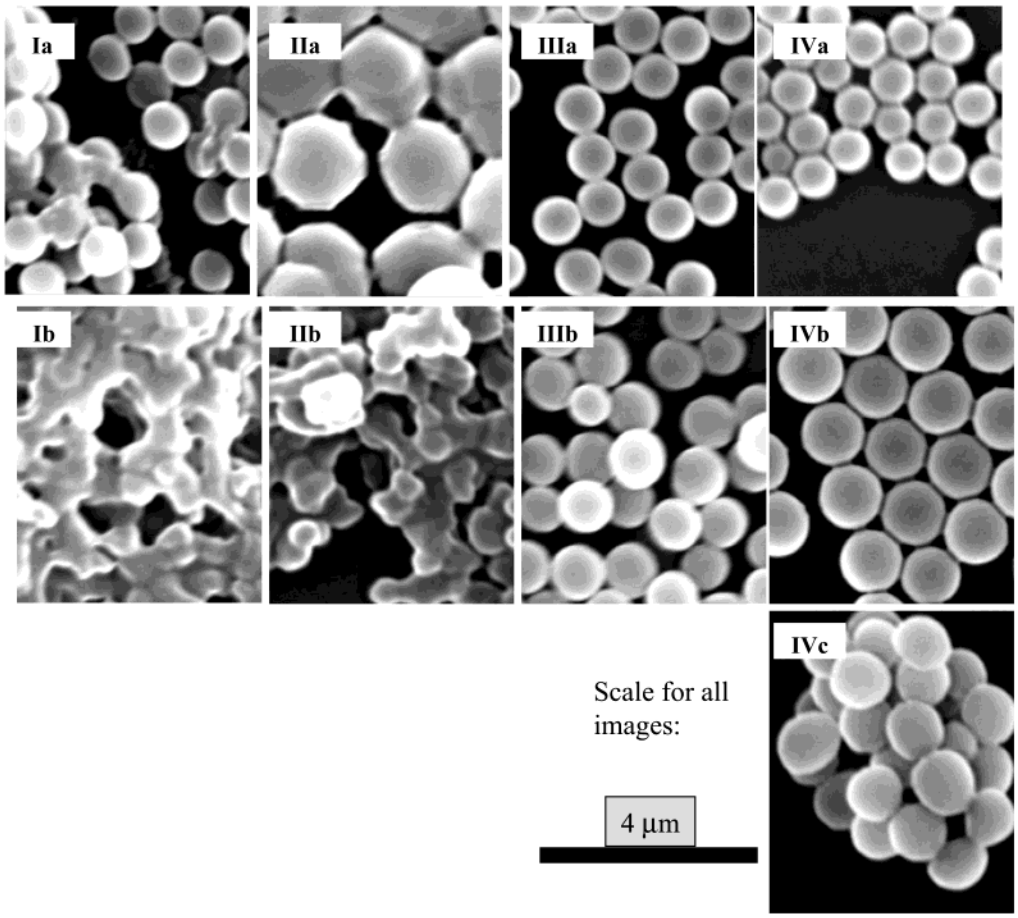

Figure 7. Morphologies transition as function of acid:ether ratio and EDMA concentrations at 70 vol % MEK. Scanning electron microscopy images of poly(MAA-*co*-PEGMM-*co*-EDMA) morphologies observed for EDMA concentrations of (I) 12.5, (II) 25, (III) 50, and (IV) 75 vol % and for acid:ether ratios of (a) 10:4, (b) 4:4, and (c) 1:4.

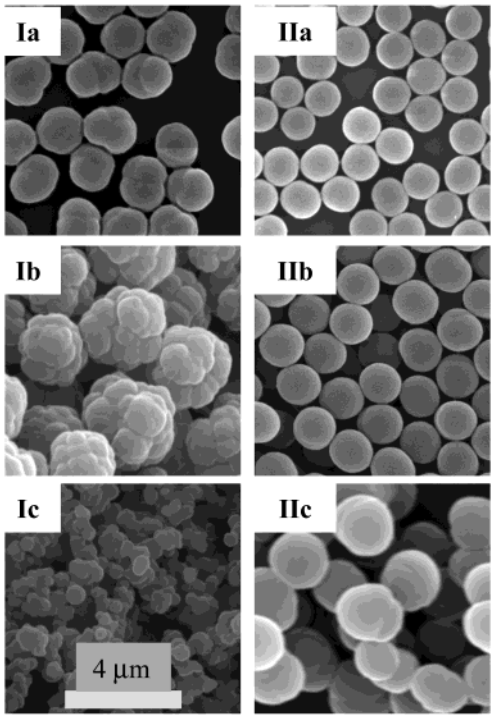

Figure 8. Morphologies transition as function of acid:ether ratio and EDMA concentrations at 50 vol % MEK. Scanning electron microscopy images of poly(MAA-*co*-PEGMM-*co*-EDMA) morphologies observed for EDMA concentrations of (I) 50 and (II) 75 vol % and for acid:ether ratios of (a) 10:4, (b) 4:4, and (c) 1:4.

Table 3 summarizes the number-average diameters of the microgels and microspheres formed in the whole range of solvents and cross-linker. They are generally narrow or monodisperse and range in diameter from 0.6 to about 3 μm. Three general trends can be seen: (1) higher MEK volume fractions lead to more favorable polymer−solvent interactions, reduces aggregation during growth, and results in smaller particles; (2) higher cross-linker levels promote entropic desolvation and hence generally also result in smaller particles; (3) finally, higher acid:ether ratios lead to smaller particles.

Conclusions

The polymer morphologies formed during precipitation copolymerization of MAA and PEGMM with EDMA cross-linker in MEK/heptane have been mapped, with particular attention paid to the microspheres and microgels formed. The morphologies formed were analogous to those observed in precipitation copolymerizations involving the less polar divinylbenzene, in that both increasing the cross-linking level and decreasing the solvency of the medium led to a transition of morphology from swellable microgels to microspheres. However, in the present polar and hydrogen-bonding comonomer system, the comonomer ratio also strongly affected the polymer−solvent interactions and hence caused a third, comonomer-induced morphology transition.

The formation of colloidally stable microgels is more favorable in the presence of excess MAA and the resulting internal MAA−MAA hydrogen bonding. At stoichiometric acid-to-ether ratio, the hydrogen bonding between PEG chain and PMAA backbone did not lead to the formation of stable particles. Accordingly, covalent cross-linking becomes more important for the formation of microspheres or microgels at stoichiometric acid:ether ratio than in the presence of excess MAA. In contrast to the initial expectation, increasing the amount of macromonomer, PEGMM, did not promote the formation of microspheres. This is probably due to the ineffective solvation of PEG by MEK, and particularly by MEK/heptane mixtures, and the decreasing cross-linking efficiency. Hence, the observed colloidal stabilization of the microspheres may be attributed to the transient, solvent-swollen copolymer gel layer at the microsphere surface rather than to any single comonomer.

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