Synthesis, Characterization, and Modeling of Cationic Amphiphilic Model Hydrogels: Effects of Polymer Composition and Architecture

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ABSTRACT: Group transfer polymerization (GTP) was used for the preparation of eight amphiphilic networks based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) and methyl methacrylate (MMA). Seven of the networks had linear segments of well-defined molecular weight between cross-links; i.e., they were model networks. In the eighth network the lengths of the segments between cross-links had a wide molecular weight distribution (random network) since the cross-linker was copolymerized with the monomers. Five model networks were based on ABA triblocks with polyDMAEMA mid-blocks and polyMMA end-blocks. In these networks the degree of polymerization (DP) of the polyDMAEMA mid-block was 20, while the overall DPs were 25, 30, 40, 60, and 120. The sixth model network was based on an equimolar BAB triblock with a polyMMA mid-block and an overall DP = 40. The seventh model network was based on an equimolar statistical copolymer with a total DP = 40. The degrees of swelling (DSs) of the networks increased below pH 7. The DSs at low pH increased with the percentage of the hydrophilic monomer. The statistical copolymer-based model network exhibited higher DSs than the isomeric triblock copolymers. Calculations based on a molecular thermodynamic model provided aqueous DSs of ionized networks with the same qualitative trends as the experimental ones, although 30 times higher, reflecting catenation. The model also predicted microphase separation in most ionized ABA triblock-based networks.

Introduction

Synthetic hydrogels[1,2] are of considerable current attention.[3] However, their structure is usually poorly controlled: the length of the segments between cross-links varies widely, and the comonomer distribution (in the case of copolymer hydrogels) is not uniform. Improved structures may broaden hydrogels applications and provide a better understanding of the relationship between their structure and properties.

The first efforts to achieve better control over hydrogel structure were undertaken by using anionic polymerization, which provided uniform segments between cross-links.[4] These well-defined gels have been termed model networks. Ionic model hydrogels were prepared only recently.[5−8] A subtype of ionic model networks are amphiphilic ionic model networks comprising both ionic and nonionic−hydrophobic blocks. Kennedy and co-workers[9] described the two-step preparation of such networks: first, the synthesis of a hydrophobic polyisobutylene segment of precise length using “living” carbocationic polymerization,[10] followed by free-radical polymerization which achieves growth of the ionizable segment and simultaneous cross-linking. Although these networks displayed some new properties, including improved biocompatibility,[11] their structure is not ideal due to the free-radical polymerization step, which leads to a nonuniform length of the hydrophilic segment.

The production of well-defined amphiphilic ionic model networks is described here using a method in which the syntheses of both blocks as well as the cross-linking step were performed by group transfer polymerization (GTP).[12−15] 2-(Dimethylamino)ethyl methacrylate (DMAEMA) and methyl methacrylate (MMA) were used as monomers.[16] GTP allowed the synthesis of three equimolar isomeric networks with different segments between cross-links: ABA, BAB, and statistical copolymer-based networks. The aqueous degrees of swelling of the ionized networks were measured. The statistical copolymer-based network swells 50% more than its two triblock copolymer-based counterparts due to microphase separation in the latter type of networks. The microphase separation hypothesis in the block copolymer-based hydrogels is confirmed by a molecular thermodynamic model.[17]

The present investigation extends our previous work[16] by shifting the focus to polymer composition rather than polymer architecture. Thus, five ABA copolymer-based networks were prepared in which the DMAEMA/MMA ratio was varied systematically. The linear precursors are illustrated schematically in the central column of Figure 1. (The polyDMAEMA is white while the polyMMA is black.) The theoretical degrees of polymerization are also shown. The central row depicts the four equimolar isomers, which comprise the BAB and ABA triblocks, the statistical copolymer, and the randomly cross-linked statistical copolymer; the ethylene glycol dimethacrylate (EGDMA) units are gray.

Experimental Section

Materials and Methods. Chemicals were from Aldrich, Germany. Figure 2 shows the chemical formulas and names of the monomers, DMAEMA and MMA, the cross-linker, EGDMA, and the bifunctional initiator, 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane (MTSMC), used for the network synthesis. The MTSMC initiator was synthesized according to the literature.[18] The catalyst was tetrabutylammonium bibenzoate (TBABB), prepared as described by Dicker and co-workers.[14] It was stored under vacuum. Tetrahydrofuran (THF) was dried by refluxing over a sodium/potassium alloy for 3 days and freshly distilled. The monomers and cross-linker were passed through basic alumina columns. They were stirred overnight over calcium hydride to remove the last traces of moisture and protonic impurities. This was done in the presence of an added free radical inhibitor, 2,2-diphenyl-

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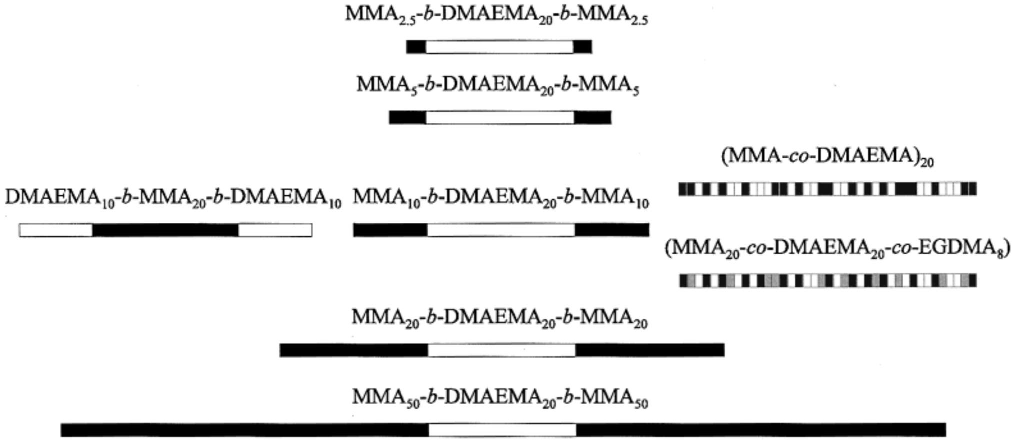

Figure 1. Schematic representation of the structures of the linear segments between the cross-links of the networks in this study. The white color represents the DMAEMA units, the black color the MMA units, and the gray color the EGDMA (cross-linker) units.

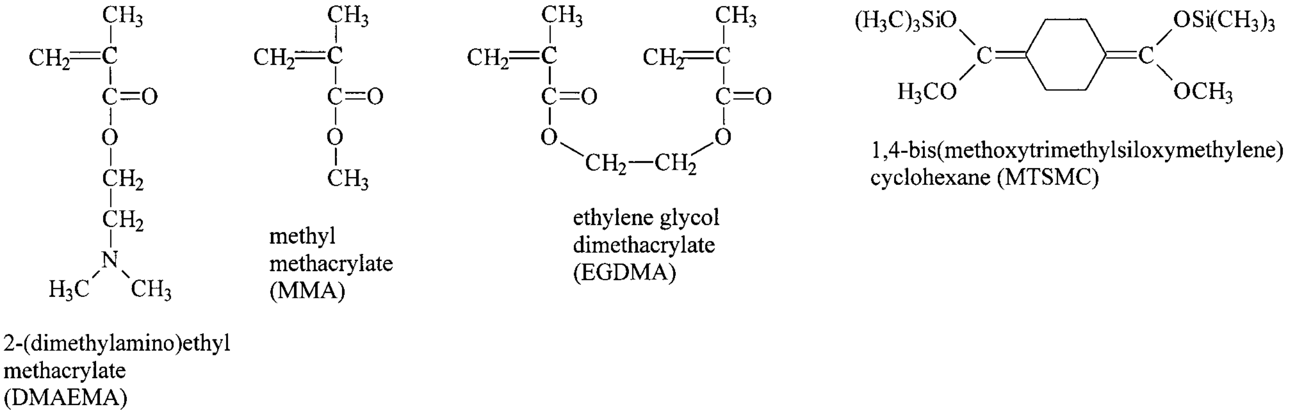

Figure 2. Chemical structures and names of the monomers, the cross-linker, and the initiator used for the preparation of the networks.

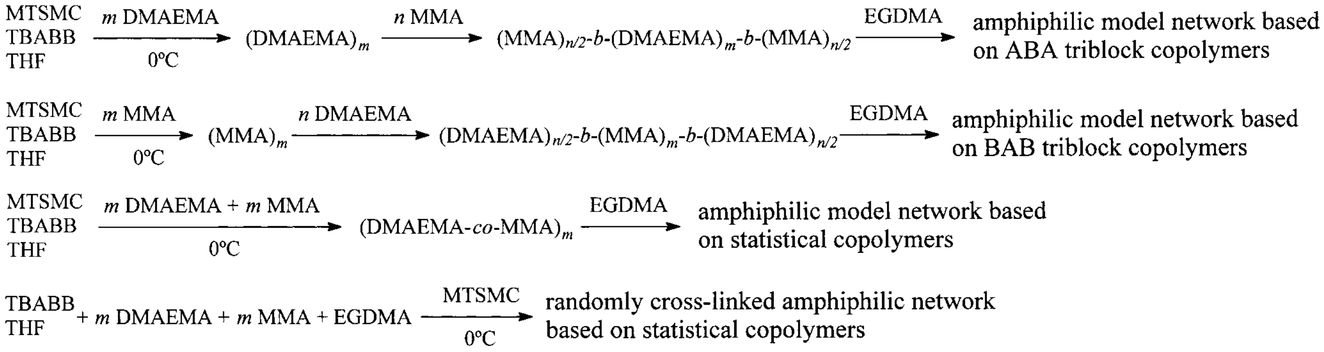

Figure 3. Synthetic routes followed for the preparation of the four different network architectures.

1-picrylhydrazyl hydrate (DPPH), to avoid thermal polymerization. The monomers and cross-linker were freshly distilled prior to the polymerization.

Polymerizations. All the networks of this study were prepared by GTP in an ice bath to avoid boiling of the polymerization solution. The amount of the EGDMA cross-linker used was 8 times the number of moles of the MTSMC initiator, as determined in preliminary investigations in which the synthesis of DMAEMA star homopolymers (with the use of a monofunctional rather than a bifunctional initiator) was optimized.[7] Networks of different compositions were prepared by varying the relative amounts of the two comonomers, DMAEMA and MMA. Different network architectures were obtained by varying the order of addition of the reagents. Figure 3 presents the four addition sequences necessary for preparing the four different network architectures. Model network synthesis requires the addition of the monomers (in the appropriate order) to an initiator/catalyst solution, completed by the addition of the cross-linker. Synthesis of randomly cross-linked networks is accomplished by the addition of the initiator to a solution of monomers, cross-linker, and catalyst.

We illustrate the synthetic procedure below by detailing the preparation of the equimolar ABA triblock copolymer-based model network. This comprises a three-step sequential addition, starting with the preparation of the DMAEMA mid-block, followed by the growth of the MMA end-blocks, and completed with the incorporation of the dimethacrylate cross-linker. A 30 mL cylindrical glass vial, kept under dry nitrogen atmosphere and containing a small amount of TBABB and 13.5 mL of freshly distilled THF, was charged with 0.36 mL (0.43 g, 1.26 mmol, 0.055 M in final solution) of MTSMC initiator and subsequently with 4.3 mL (4.0 g, 25 mmol, 1.1 M) of DMAEMA, under stirring. The polymerization exotherm (0.8

to 19.0 °C) abated within 5 min, a sample was extracted for gel permeation chromatography (GPC) analysis, and 2.7 mL (2.5 g, 25 mmol, 1.1 M) of MMA was added. After the completion of the polymerization of this monomer (exotherm 6.6 to 22.7 °C) and sampling for GPC and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy analyses, 1.9 mL (2.0 g, 10 mmol, 0.44 M) of EGDMA cross-linker was added (exotherm 10.9 to 21.0 °C), which led to the gelation of the solution within seconds. The BAB triblock copolymer-based network (with an MMA mid-block) was also obtained using a similar procedure in which the order of addition of the two comonomers was reversed, whereas the statistical copolymer model network was synthesized by the simultaneous addition of the two comonomers. The randomly cross-linked network of the statistical copolymer was prepared by the addition of the MTSMC initiator to the THF solution of the monomers, cross-linker, and catalyst.

Characterization by GPC and ^{1}H NMR. Linear homopolymer and copolymer samples were obtained before cross-linking and were characterized in terms of their molecular weight and composition using GPC and ^{1}H NMR. GPC was performed on a Polymer Laboratories system equipped with a PL-LC1120 isocratic pump, an ERC-7515A refractive index detector, and a PL Mixed “E” column. The eluent was THF, and it was pumped at 1 mL min^{-1}. The molecular weight (MW) calibration was based on six narrow MW (630, 1400, 4250, 7600, 13 000, and 28 900 g mol^{-1}) polyMMA standards also supplied by Polymer Laboratories. The ^{1}H NMR spectra of polymer solutions in deuterated chloroform were recorded using a 300 MHz AVANCE Bruker spectrometer equipped with an Ultrashield magnet.

Measurement of the Degree of Swelling (DS). The degrees of swelling (DSs) of the networks were measured in THF, neutral water, and aqueous solutions of various pHs covering the range between 2 and 12. To this end, the gels were first taken out of the polymerization vials which were incised using a diamond knife and broken by the application of a hot glass rod. Subsequently, the gels were cut into pieces and equilibrated in the appropriate solvent, THF or pure water, for 4 weeks. In the latter case, the water was changed every 2−3 days to thoroughly wash away the polymerization solvent, THF. The mass of all swollen gels was determined gravimetrically. The dry mass of each sample was determined by drying in a vacuum oven at 50 °C for 48 h. The DS was calculated as the ratio of the swollen divided by the dry mass.

For the measurements of the DSs at different pHs, the appropriate number of drops of 0.5 M HCl solution were added to samples of water-swollen gels to adjust the pH within the range between 2 and 8. For each different gel about eight samples were used, each adjusted to a different pH with degree of ionization increments of about 15%. The required amount of moles of HCl in each case was calculated as the product of the desired degree of ionization times the number of moles of DMAEMA units present in the sample. The latter was calculated from the mass of the swollen (in pure water) sample, the known DS in pure water (measured earlier), and the polymerization stoichiometry. Small amounts of 0.5 M NaOH solution were added to two samples from each gel to cover the pH range from 8 to 12 (note that this does not change the degree of ionization, which is already zero in pure water). Two weeks after the addition of HCl or NaOH, the mass of the swollen hydrogel and the pH of the supernatant solution were stabilized and measured. The DS under these conditions was calculated again as the ratio of the swollen divided by the dry mass. The latter was estimated from the mass of the hydrogel swollen in pure water and the known DS in pure water of the same gel measured according to the previous paragraph.

The hydrogen ion titration curves were obtained by plotting the calculated degrees of ionization against the solution pH. The effective pK of the DMAEMA units in each gel is read off the hydrogen ion titration curves as the pH at 50% ionization.

Modeling

The aggregation state (i.e., microphase separated or not) and the aqueous DSs of the ABA triblock copolymer-based networks were predicted theoretically using a molecular thermodynamic model[17] which considers the Gibbs free energy components in the system. These are the elastic energy, the electrostatic energy, and the energy of mixing. In the microphase-separated state the interfacial energy for the contact between the hydrophobic core and water is also included. Hydrogen-bonding interactions are ignored, as in most network modeling studies.[19−21] For each state, the total Gibbs free energy is minimized with respect to the polymer volume fraction. The lowest of the two minima corresponds to the most stable state which will prevail at equilibrium. The DS is calculated as the inverse of the polymer volume fraction of the most stable state at equilibrium.

The variable inputs to the program are the number of backbone carbon atoms in each block (equal to twice the corresponding degrees of polymerization) and the degree of ionization of the ionizable block. The following constant inputs are also required. First, the polymer volume fraction at synthesis, which was equal to 0.4 in all cases. Second, the number of arms per cross-link, which was taken equal to 20, based on the number of arms in star polymers synthesized by GTP and using the same cross-linker;[22,23] various test runs indicated that the calculated equilibrium DSs (but not the equilibrium Gibbs free energies) are insensitive to the value of this parameter. And, finally, the Flory−Huggins interaction parameters between water and each of the two blocks; for the water−hydrophobe (MMA) pair a value of 2.0 (as in our original model[17]) was employed, which is typical for the value of the water−propylene oxide pair,[24] whereas a value of 0.45 (an improvement over the original model[17] where the value of this parameter was set equal to 0.0) was assigned to the interaction between water and the marginally hydrophilic monomer repeat units (DMAEMA), similar to the value assigned to the water−acrylamide pair;[25] calculations indicated an insensitivity of the predicted DSs to the value of the latter parameter.

Results and Discussion

Polymerization Methodology. The synthetic procedure for the preparation of the model networks is presented schematically in Figure 4, where the synthesis of the gel based on the MMA$_{20}$-*b*-DMAEMA$_{20}$-*b*-MMA$_{20}$ triblock copolymer is shown. The synthesis involves sequential monomer and cross-linker addition. The first step in Figure 4 results in the preparation of linear DMAEMA homopolymer with both active ends (indicated by asterisks) due to the use of the bifunctional initiator. The second step leads to the synthesis of the MMA−DMAEMA−MMA triblock copolymer with two active ends. The synthesis is completed by the addition of EGDMA cross-linker, which effects the interconnection of the polymer active ends, providing a three-dimensional network. The number of arms at the cross-links is not three, as indicated in the figure, but higher, between 20[22] and 50,[23] as determined by static light scattering on star polymers also prepared by GTP.

Molecular Weights and Composition. Table 1 shows the molecular weights and composition of the linear precursors to the networks as measured by GPC and ^{1}H NMR, respectively. The number-average molecular weights, M_n's, were found to be close to those predicted by theory, from the ratio of monomer to initiator. They were, however, systematically slightly

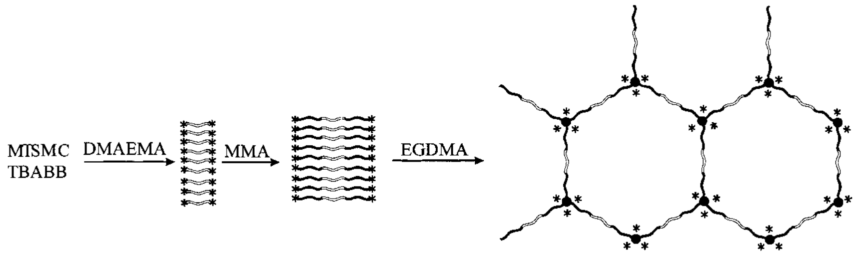

Figure 4. Schematic representation of the synthetic procedure followed for the preparation of the model network based on the triblock copolymer MMA_{20}-*b*-$DMAEMA_{20}$-*b*-MMA_{20}. The DMAEMA units are shown in white, while the MMA units are painted black. The "*" symbols indicate the "living" sites of the polymerization. The number of arms at the cross-links is not 3, as indicated in the figure, but between 20 and 50.

Table 1. Molecular Weights, Polydispersity Indices, and Composition of the Homopolymer and Copolymer Precursors to the Networks As Measured by GPC and ^{1}H NMR

					% mol MMA content	
name	chemical structure	theor MW[a]	M_n by GPC	M_w/M_n by GPC	theory	^{1}H NMR
gel 1	$DMAEMA_{20}$	3336	4190	1.16		
	$MMA_{2.5}$-*b*-$DMAEMA_{20}$-*b*-$MMA_{2.5}$	3836	4660	1.18	20.0	25.0
gel 2	$DMAEMA_{20}$	3336	3990	1.18		
	MMA_5-*b*-$DMAEMA_{20}$-*b*-MMA_5	4336	5650	1.20	33.3	40.6
gel 3	$DMAEMA_{20}$	3336	3910	1.18		
	MMA_{10}-*b*-$DMAEMA_{20}$-*b*-MMA_{10}	5336	6670	1.15	50.0	52.6
gel 4	MMA_{20}	2196	3230	1.16		
	$DMAEMA_{10}$-*b*-MMA_{20}-*b*-$DMAEMA_{10}$	5336	6710	1.14	50.0	52.1
gel 5	(DMAEMA-*co*-MMA)$_{20}$	5336	7040	1.15	50.0	55.6
gel 6	$DMAEMA_{20}$	3336	4310	1.16		
	MMA_{20}-*b*-$DMAEMA_{20}$-*b*-MMA_{20}	7336	10200	1.13	66.7	69.1
gel 7	$DMAEMA_{20}$	3336	4590	1.15		
	MMA_{50}-*b*-$DMAEMA_{20}$-*b*-MMA_{50}	13336	17900	1.12	83.3	84.5

[a] Weight from the initiator fragment (196 g mol^{-1}) included.

higher than the theoretically predicted molecular weights, probably due to partial deactivation of the initiator. Molecular weight distributions were found to be narrow, and the polydispersity indices (M_w/M_n) were calculated to be 1.2. This confirms the homogeneity of the lengths of the segments between the cross-links in the networks. The polydispersity indices decrease with the molecular weight, a feature confirming the "living" character of the polymerizations. The copolymer composition was determined from the ^{1}H NMR spectra (not shown) of the copolymers, by ratioing the signal from the three methoxy protons (3.6 ppm) in MMA to the six protons in the two azamethyl groups (2.3 ppm) in DMAEMA. The percentages of MMA determined by ^{1}H NMR were found to be close to the theoretically calculated percentages of MMA, albeit systematically slightly higher.

Degrees of Swelling and Ionization. The well-defined structure of the networks is also supported by the measured sol fraction which was found to be below 10% in all cases. The experimentally measured DSs and degrees of ionization of all the networks are plotted against pH in Figure 5. The number and structure of each network (gel) are indicated above each plot. The networks start to swell within the pH range between 5 and 7 because they contain DMAEMA, a tertiary amine that acts as a weak base by taking up protons and being ionized at pH < 8.[26−28] The chloride counterions to the charged DMAEMA units create an osmotic pressure in the network, which promotes its swelling.[21,29,30] Moreover, the charge on the DMAEMA units causes electrostatic repulsive forces between the polymer chains, leading to further swelling of the network.[29−31] The DSs present a maximum at pH 3−4, followed by a slight decrease at lower pH values (∼2), which is probably due to the increase in the ionic strength effected by the relatively high concentration of HCl under these conditions. In the same figures the hydrogen ion titration curves are plotted. A general feature of these plots is that each DS vs pH curve follows closely the corresponding degree of ionization vs pH curve, confirming the importance of charge on network swelling. The plots in Figure 5 were used to extract the p*K*'s and aqueous DS's at low and neutral pH of the networks, which are presented and discussed in the following sections.

Effective p*K*'s of the DMAEMA Units. The pH's at 50% ionization for each network were read out from Figure 5 and were taken as the effective p*K*'s of the networks. These p*K*'s are plotted against the network MMA content in Figure 6, which suggests that the p*K* values decrease as the MMA content increases. This is because the increase in the MMA content leads to an increase in hydrophobicity, a reduction of the dielectric constant, and a strengthening of the Coulombic interactions, which makes more difficult the ionization of the networks.[29,31] Another observation is that networks with the same composition but with different architectures have almost the same p*K* values, indicating that the architecture of the networks does not affect significantly their dielectric constant.

Aqueous DS's at Low and Neutral pH and DS's in THF. The DS's in low pH water (pH around 2) and neutral pH water as well as the DS's in THF for each network are presented in Figure 7a,b. Figure 7a presents the effect of polymer composition while Figure 7b focuses on the effect of polymer architecture. Figure 7a shows that the aqueous DS's in both low pH and neutral pH water decrease as the content in hydrophobic MMA increases, as expected. In particular, the DS's in low pH water decrease from about 7 down to 2 as the MMA content increases from 20 to 83%. The DS's in neutral water decrease slightly with the same compositional change, and their values remain approximately equal

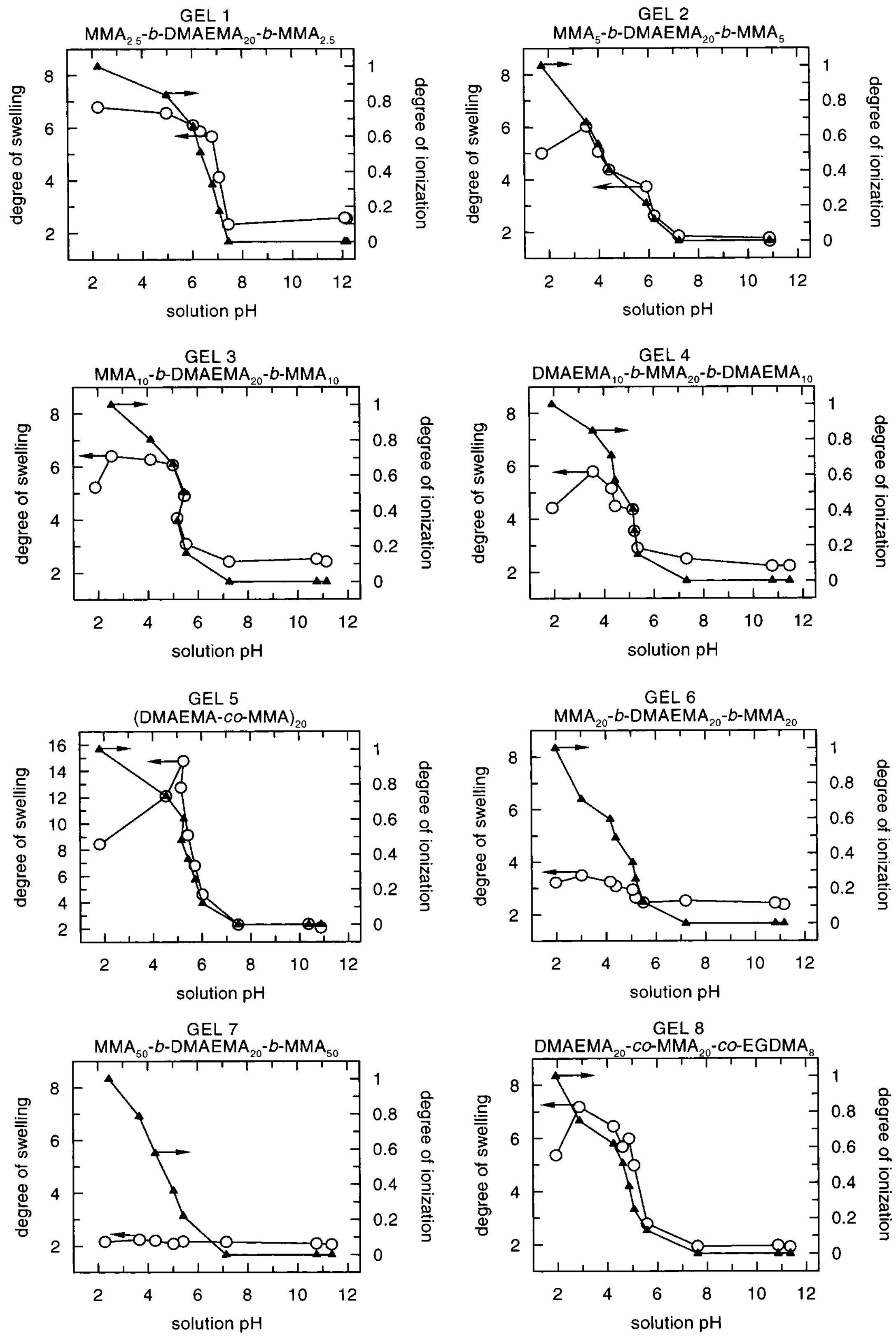

Figure 5. Degrees of swelling and degrees of ionization as a function of pH for all the networks of this study.

to 2, suggesting that the networks are practically collapsed. The behavior of the DS's of the networks in THF, a good (nonselective) solvent for both MMA and DMAEMA (the DMAEMA units were not ionized in these experiments), is opposite to that in water. Thus, the DS's in THF increase from 4 to 5 as the MMA content spans the range from 20 to 83%. This is probably due to the increase in the degree of polymerization of the chains between cross-links with their MMA content (see column of Figure 1), which would lead to a lower cross-link density and allow the networks to swell more. Focusing on the network with 20 mol % MMA, it appears that this material swells more in acidic water than in THF. This indicates that the contribution to

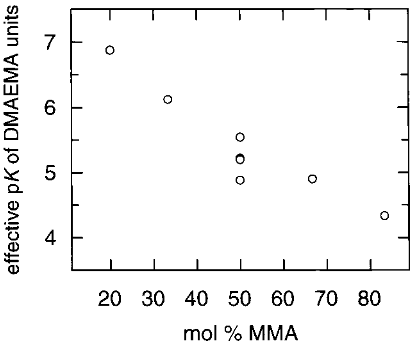

Figure 6. Dependence of the effective pK's of the DMAEMA units within the networks on their MMA content.

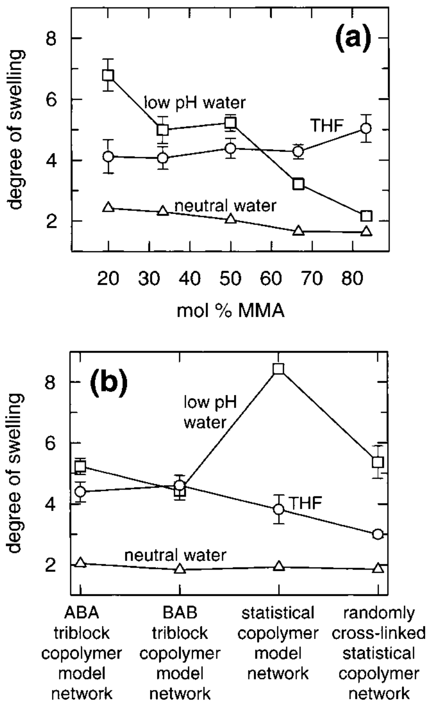

Figure 7. Degrees of swelling of the networks in THF, low pH water, and neutral water. (a) Effect of polymer composition. (b) Effect of polymer architecture.

swelling of charged DMAEMA at pH 2 (mainly electrostatic contribution) is more important than the contribution of mixing DMAEMA *and* MMA with THF for this sample. This can be understood by considering, first, that this sample is DMAEMA-rich (with very short MMA blocks) and, second, that the contribution of the electrostatic energy can dominate that of the mixing energy for highly charged systems.[17] Inspecting now all three curves in the figure, it appears that for an MMA content <55% the DS's are lowest in neutral water, higher in THF, and highest in acidic water. However, for an MMA content >55%, at which point the hydrophobic MMA blocks acquire sufficient length, the DS's are lowest (again) in neutral water, higher in acidic water, and highest in THF. We suggest that this is due to the state of each polymer block within the network. This is illustrated schematically in Figure 8, in which the conformations of the MMA_{20}-b-$DMAEMA_{20}$-b-MMA_{20} triblock copolymer-based model network (67 mol % MMA content) in THF, in acidic water, and in neutral water are presented. The figure shows that, in THF, both blocks are solvated, leading to the highest DS's. In contrast, in neutral water, both the hydrophobic MMA block and the neutral DMAEMA block are collapsed, resulting in the lowest DS's. In acidic water, the DS's acquire intermediate values as the DMAEMA block is ionized and expanded, while the hydrophobic MMA block is collapsed.

Figure 7b illustrates the effect of polymer architecture on the DS's. In neutral water, all four isomeric networks are collapsed, exhibiting minimum DS's close to 2. In acidic water, the DS's of the two triblock copolymer-based model networks are the same, within experimental error. The low pH DS of the statistical copolymer-based network is about twice as high as those of its triblock counterparts, in agreement with our previous experimental[16] and theoretical[17] studies, in which this difference was attributed to the inability of the statistical copolymer-based network to microphase separate.[32,33] In this network, the ionized DMAEMA units drag along the MMA units, which also contribute to swelling.[17] In contrast, the selective collapse of the MMA hydrophobic blocks in the triblock copolymer-based networks results in shorter effective chains between cross-links in these networks, which lowers the values of the DS's. The low pH DS of the randomly cross-linked statistical copolymer network is lower than that of the model network based on the statistical copolymer and almost as low as those of the triblock copolymer based model networks. This is surprising because the present network cannot microphase separate, and therefore, it was expected to exhibit an equally high acidic DS as the statistical copolymer-based model network. It is possible, however, that the lower than expected acidic DS of this network is due to the broad distribution of chain lengths between cross-links (contrary to the narrow size distribution of the chain lengths between cross-links in its other three model network isomeric counterparts). The presence of some (much) shorter than average chains may dominate the swelling behavior and result in the low DS observed. This explanation is consistent with the fact that the randomly cross-linked statistical copolymer-based network presents the lowest DS in THF from the four equimolar isomeric networks. The DS's in THF of the three isomeric model networks are identical, within experimental error, as expected.

Predicted Aqueous Degrees of Swelling. Figure 9 presents the model predictions for the aqueous DS's of the ABA triblock copolymer-based model networks in the ionized and in the neutral state as a function of the size of the hydrophobic end-block at a constant length of the hydrophilic ionizable mid-block. The x-axis represents the number of carbon atoms in one hydrophobic end-block. As expected, the DS's decrease with the size of the hydrophobic block. Moreover, while the DS's of all nonionized networks are in the collapsed state, those in the ionized state are about 2 orders of magnitude higher. The model predicts that the nonionized networks are in the unimer-like state; i.e., the MMA units can mix with water and the DMAEMA units. The lack of charge in these networks leads to low DS's, where the enthalpic part of the mixing energy in the unimer-like state is less unfavorable[17,34] than the interfacial energy in the micelle-like state. This, ultimately, results in a more stable unimer-like state. The situation is different in the ionized networks, which exist in the micelle-like state, with the exception of the network with the least number (5) of hydrophobic units. In this case, the high DS's, dictated by the extensive ionization, provide an advantage for the hiding from water of the hydrophobic units, which are driven into

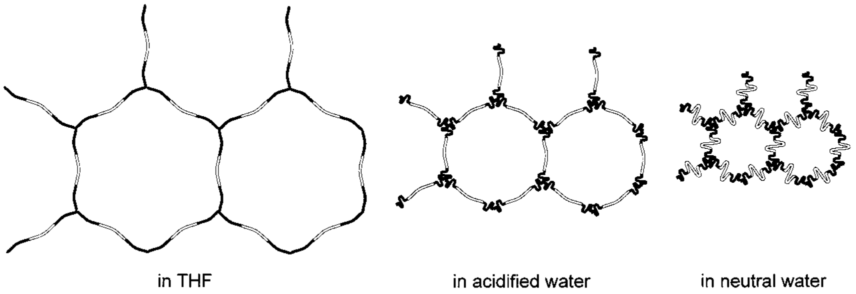

Figure 8. Schematic representation of the structures of a network based on an ABA triblock copolymer in THF, acidified water, and neutral water. The number of arms at the cross-links is not 3, as indicated in the figure, but between 20 and 50.

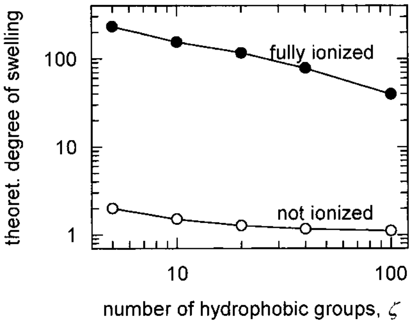

Figure 9. Composition dependence of the theoretically predicted aqueous degrees of swelling of the ABA triblock copolymer-based networks in the ionized and neutral state.

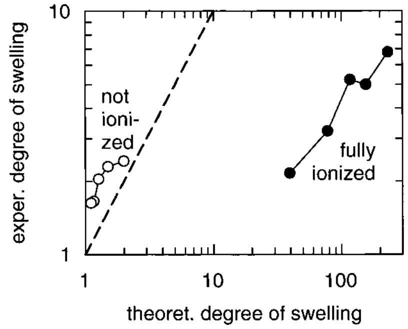

Figure 10. Comparison of the experimentally measured with the theoretically predicted degrees of swelling of the ABA triblock copolymer-based networks in the ionized and neutral states.

the micellar cores.[17] This hiding is not as efficient in the network with the shortest hydrophobic blocks, which still prefers the unimer-like state.

Figure 10 compares the experimentally measured with the theoretically predicted DS's of the ABA triblock copolymer-based model networks in the fully ionized and neutral states. The dashed line is the straight line with unit slope passing from the origin, where all points would fall if experiment and theory perfectly agreed. For neutral networks, the experimental DS's agree well with the theoretically predicted ones, although the former are slightly greater than the latter, probably due to retention of extra water within the pores of the networks. In contrast, for fully ionized networks, the experimentally measured DS's are about 30 times lower than the theoretically predicted DS's. This is probably due to extensive catenation (mechanical interlinking) between the polymer chains in the experimental system, which severely restricts chain extension.[35]

Conclusions

We employed a "living" polymerization technique, GTP, to prepare amphiphilic, ionizable hydrogels covering a range of compositions and architectures. The DS's of all networks increased by lowering the pH, which induced the ionization of the weak base monomer repeat units. The DS of the ionized hydrogels decreased as the content of the hydrophobic component increased. The high DS of hydrogels comprising amphiphilic statistical copolymer chains relative to those comprising amphiphilic triblock copolymer chains is consistent with the absence of microphase separation in the former type of networks and presence in the latter. This phase behavior is also predicted by a molecular thermodynamic model, which, however, overestimates the DS's of ionized networks by a factor of 30, suggesting extensive chain entanglement in the present experimental system.

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