Synthesis and Characterization of Electrolytic Amphiphilic Model Networks Based on Cross-linked Star Polymers: Effect of Star Architecture

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Amphiphilic model networks of a new structure, that of cross-linked "in-out" star copolymers, were synthesized by a one-pot preparation using group-transfer polymerization. The networks comprised hydrophobic methyl methacrylate and hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA) moieties. Ethylene glycol dimethacrylate served as the cross-linker. Two heteroarm star-, two star-block-, and one statistical star copolymer-based networks were prepared. The synthesis of the heteroarm star-based networks involved a four-step addition of monomer/cross-linker/monomer/cross-linker. The simultaneous or sequential addition of two monomers between cross-linking gave statistical- or block-copolymer-based star networks, respectively. The linear, "arm-first" and "in-out" star network precursors were characterized in terms of their molecular weight distribution by gel permeation chromatography. Static light scattering was used to assess the absolute weight-average molecular weight of the star network precursors. The compositions of the "in-out" star precursors were determined by ^{1}H NMR. The effects of network architecture (heteroarm, block, and statistical), solvency (THF and water), and pH on the swelling behavior of the networks were investigated. The degrees of swelling increased at low pH because of the ionization of the DMAEMA residues. The higher degree of swelling of the statistical-copolymer-based network as compared to the swelling of the star-block and heteroarm star analogues is attributed to the proposed microphase-separated structure of the latter in the aqueous medium compared to the disordered structure of the former.

Introduction

The technological importance of aqueous solutions of amphiphilic (=hydrophilic/hydrophobic) block copolymers as surfactants with improved properties compared to those of the lower molecular weight surfactants has attracted the attention of the scientific community and resulted in extensive experimental[1,2] and theoretical studies[3] on these materials. Although first synthesized in 1970,[4] charged amphiphilic block copolymers (with the charged block being the hydrophilic block) started to receive comparable interest only during the past 15 years.[5] There is now extensive experimental[6−9] and theoretical[10−12] work on the aqueous self-assembly of charged block copolymers.

Two other interesting polymer systems are star polymers[13−21] and polymer networks.[22] Applications of star polymers include such uses as toughening of plastics and coatings[23,24] with good processibility due to low solution and melt viscosity imparted by the inherent molecular compactness of these polymers.[25] Applications of traditional hydrophobic polymer networks include uses as coatings and structural materi-

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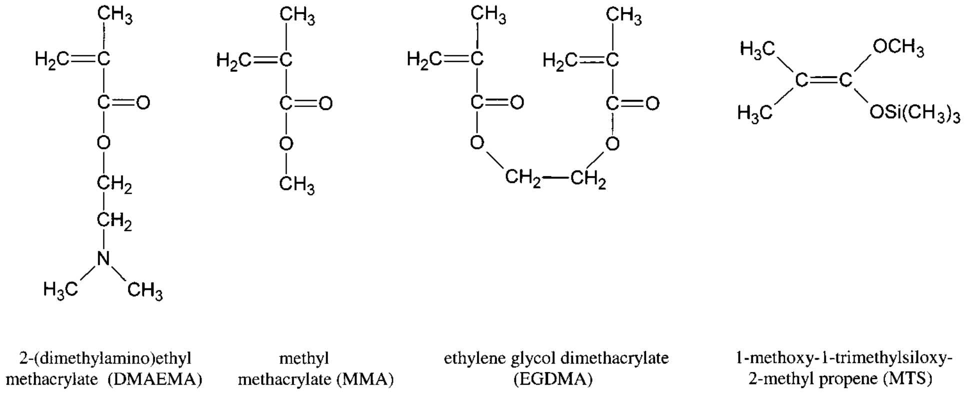

Figure 1. Chemical formulas and names of the main reagents used for the network synthesis.

als,[22] while modern hydrogels (water-compatible networks)[26,27] are used as superabsorbents,[28,29] drug release systems, and tissue engineering scaffolds[30] and can be potentially used for the construction of actuators, valves, sensors, and artificial muscles for robotics.[31]

The objective of the present study was the combination of all three polymeric structures mentioned above in a single material which would have new properties and new potential applications. Thus, we synthesized by group-transfer polymerization (GTP)[32−35] and characterized model[36] networks (accurate size and composition of their components) based on cross-linked ionizable amphiphilic star polymers. Although ionizable amphiphilic model networks based on interconnected linear chains have been reported,[37−39] there is no published example of cross-linked ionizable amphiphilic star polymers. A first effort to this direction was our recent work on cross-linked hydrophilic star homopolymers,[40] which we extend in this manuscript to cover various structures of cross-linked amphiphilic star copolymers.

Experimental Section

Network Synthesis. *Materials.* All chemicals used were commercially available and were purchased from Aldrich, Germany. Figure 1 shows the chemical formulas and names of the main reagents used for the network synthesis: the monomers, 2-(dimethylamino)ethyl methacrylate (DMAEMA, ionizable hydrophilic) and methyl methacrylate (MMA, neutral hydrophobic), the cross-linker, ethylene glycol dimethacrylate (EGDMA), and the monofunctional initiator, 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS). The polymerization catalyst, tetrabutylammonium bibenzoate (TBABB), was in-house synthesized by the method of Dicker et al.[34]

Methods. The methods used in this investigation were the same as those employed for typical GTP syntheses. The polymerization solvent, tetrahydrofuran (THF), was dried by refluxing it over a potassium/sodium alloy for 3 days prior to use. The monomers and the cross-linker were passed through basic alumina columns to remove inhibitors and protic impurities. They were subsequently strirred over calcium hydride in the presence of a free-radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), and stored at 5 °C. All monomers and the cross-linker were freshly distilled under vacuum and kept under a dry nitrogen atmosphere until use. The initiator was distilled once prior to the polymerization. The dried catalyst powder was stored in a round-bottom flask under vacuum until use. All glassware was dried overnight at 120 °C and assembled hot under dynamic vacuum prior to use. The polymerizations were carried out in 100-mL round-bottom flasks fitted with a rubber septum. Catalytic amounts (5−10 mg) of TBABB catalyst were transferred to the reactor, which was immediately purged with dry nitrogen. Freshly distilled THF was subsequently transferred directly from the still into the reactor via a syringe, followed by the addition of the initiator, monomers, and cross-linker.

Polymerizations. The synthetic procedure followed was similar to that reported previously for the preparation of cross-linked hydrophilic star homopolymers.[40] The reactions were carried out at ambient temperature (20 °C) without thermostating the polymerization reactor. The polymerization exotherm was monitored by a digital thermometer which was used to follow the progress of the reaction. The procedures for the synthesis of all cross-linked star structures are illustrated in Figure 2. Heteroarm cross-linked stars were prepared when only one monomer was added between cross-links and the monomer added second was different from that used first. If the monomer added second were the same as that added first, a homopolymer cross-linked star would be produced. The simultaneous addition of the two different monomers before each addition of the EGDMA cross-linker resulted in the preparation of arms of statistical architecture and it ultimately led to the formation of statistical copolymer cross-linked stars. The preparation of block copolymer cross-linked stars required the sequential addition of two different monomers before the EGDMA additions. The polymerization procedure for the synthesis of such a block copolymer cross-linked star with arms comprising linear diblock copolymers with 25 MMA units and 25 DMAEMA units is detailed below and is illustrated in Figure 3. To a 100-mL round-bottom flask containing a small amount (≈10 mg) of TBABB were syringed 45 mL of freshly distilled THF and 0.2 mL of MTS initiator (0.98 mmol), in

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Figure 2. Synthetic sequences employed for the preparation of the various cross-linked star architectures of this study.

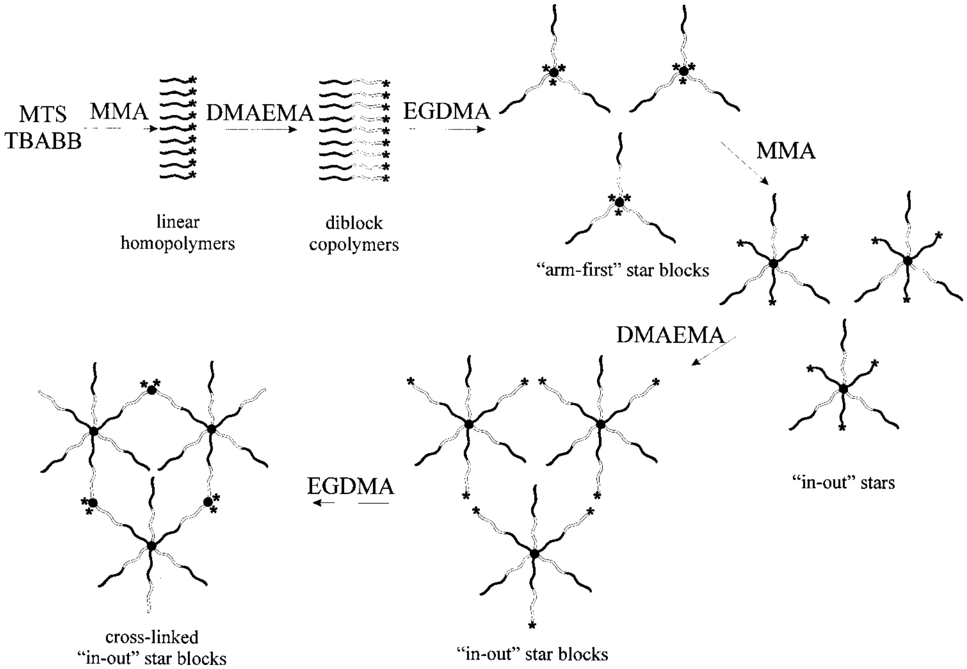

Figure 3. Schematic representation of the synthetic procedure followed for the preparation of the block-copolymer-based network [(MMA$_{25}$-*b*-DMAEMA$_{25}$)-*star*-(MMA$_{25}$-*b*-DMAEMA$_{25}$)]-*network*. The number of arms is not 3/6, as indicated in the figure, but much higher, 30/60. The black and white colors indicate hydrophobic and hydrophilic segments, respectively, while the asterisks denote active polymerization sites.

this order; 2.6 mL of MMA (24.6 mmol) was slowly added under stirring. The polymerization exotherm (27.4−36.9 °C) abated within 5 min, samples were extracted, and 4.1 mL of DMAEMA (24.6 mmol) was added slowly, giving an exotherm (36.0−41.3 °C). After sampling, 0.75 mL of EGDMA (3.94 mmol) was added, which produced an exotherm (38.7−41.5 °C). Samples were withdrawn again before 2.6 mL of MMA (24.6 mmol) was added, giving an exotherm from 39.3 to 43.6 °C. Samples were withdrawn once more, followed by the addition of 4.1 mL of DMAEMA (24.6 mmol) with an exotherm from 41.5 to 42.1 °C. In the final stage 0.75 mL of EGDMA (3.94 mmol) was added, which promoted gelation within seconds.

Characterization of the Network Precursors. *Gel Permeation Chromatography.* Molecular weights (MWs) and molecular weight distributions (MWDs) of the linear, "arm-first" star and "in-out" star (see Figure 3) precursors to the cross-linked star polymers were determined by gel permeation chromatography (GPC) using a single high molecular weight range Polymer Laboratories PL-Mixed 'D' column. The mobile phase was THF, delivered at a flow rate of 1 mL min^{-1} using a Polymer Laboratories PL-LC1120 isocratic pump. The refractive index signal was measured using an ERC-7515A refractive index detector supplied by Polymer Laboratories. The calibration curve was based on seven narrow MW (630, 4250, 13 000, 28 900, 50 000, 128 000, and 260 000 g mol^{-1}) linear poly(methyl methacrylate) standards that provided rough qualitative estimates for the MWs of the star polymers.

Static Light Scattering. The absolute weight-average MWs of the "arm-first" and "in-out" star precursors to one heteroarm star- and one star-block-based networks were measured by static light scattering (SLS) using a Wyatt Technology DAWN spectrometer equipped with a laser operating at 633 nm. The polymer samples for the SLS were dissolved in HPLC-grade THF and filtered through 0.45-μm pore size filters. The refractive index increments (dn/dc) were determined using a Wyatt Technology Optilab DSP differential refractometer at a wavelength of 633 nm.

^{1}H NMR Spectroscopy. The compositions of the "in-out" star network precursors were determined by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a 300-MHz AVANCE Bruker NMR spectrometer equipped with an Ultrashield magnet. The solvent was $CDCl_3$ with TMS used as an internal reference.

Characterization of the Networks. *Determination of the Sol Fraction.* The prepared gels were taken out of the polymerization flasks and washed in 200 mL of THF for 1 week to remove the sol fraction. Next, the THF solution was recovered by filtration, the solvent was evaporated, and the extracted polymer was dried under vacuum for 24 h at 40 °C. The sol fraction was calculated as the ratio of the mass of the extracted polymer to the theoretical mass of the gel.

Characterization of the Degree of Swelling. The washed gels were cut into small cubes of size 5−10 mm. The mass of the THF swollen cubes was measured gravimetrically before placing all samples in a vacuum oven for drying for 48 h at 40 °C. The dry gel mass was determined, followed by the transfer of the gels in water. The pH of the gel samples in water was varied by the addition of the appropriate volume (typically several drops) of solutions of 0.5 M HCl or 0.5 M NaOH. The samples were allowed to equilibrate for 3 weeks and the solution pH and wet gel mass were measured. All degrees of swelling were determined in triplicate and the averages of the measurements are presented. The degrees of swelling in THF and in the aqueous phase were calculated as the ratio of the wet network mass in THF or water, respectively, divided by the dry gel mass.

Results and Discussion

Synthesis and Structure of Cross-linked Star Polymers. The GTP synthesis of the networks comprised a successful multi- (4- or 6-) step sequential addition in a one-pot preparation summarized in Figure 2. In the absence of established nomenclature for these novel network structures, we propose the nomenclature appearing in Figure 2 for the polymer networks and star polymers of this study. The synthesis of the cross-linked stars is based on the ability of GTP to produce linear "living" (co)polymers upon the addition of methacrylate monomer(s) to a solution containing monofunctional initiator and catalyst,[32−34] the conversion of these linear (co)polymers to star polymers with "living" cores upon the addition of dimethacrylate cross-linker,[23,24] the ability of these star polymers to further grow (from the core outward) upon the addition of more monomer(s), and the ability of the dimethacrylate cross-linker to interlink those stars to a network.

A schematic representation of the synthetic procedure for the preparation of a network based on a cross-linked star-block copolymer is illustrated in Figure 3, where black and white indicate the hydrophobic and hydrophilic segments, respectively, while asterisks denote the active polymerization sites. Block copolymer linear segments that are to form the primary arms of the stars and the dangling chains of the final network are prepared upon the sequential addition of the two monomers, MMA and DMAEMA. Next, EGDMA cross-linker, in a 4-fold molar excess with respect to the initiator (which satisfactorily reduces the amount of unattached chains with the introduction of a relatively small amount of cross-linker[41]), is added to yield the "arm-first" star polymers, succeeded by the sequential addition of the two monomers for a second time to lead to the formation of the secondary arms of the "in-out" star polymers and concluded by the addition of EGDMA to induce the interconnection of the "in-out" star polymers. The final network structure consists of two types of cross-linked sites: first, the primary cross-linked sites, initially formed after the first addition of EGDMA, which bear an equal number of dangling chains and elastic chains; second, the secondary cross-linked sites, formed at the final synthetic step (second addition of EGDMA), which share the elastic chains of the primary cross-linked sites but bear no dangling chains. Because of the precise control over the chain length, the intercore spacing is also controlled. The distance between a primary cross-linked site and an adjacent secondary cross-linked site is approximately between 10 nm (dry state, the SLS data of C2 in Table 2 were used in the calculation) and 28 nm (fully stretched chains, actual degree of polymerization was taken 110, as that of DMAEMA chains in C1, Table 1), depending on the degree of swelling. However, this distance is always within the nanoscopic regime.

It is noteworthy that GTP remains "living" even after six sequential additions (four additions of monomer and two of cross-linking agent), thus allowing control over the final network structure. The number of arms at the cross-links is not 3 or 6 as indicated in Figure 3, but much higher, between 30 and 60 as measured by SLS (see below). This is due to the ability of the EGDMA to be added repeatedly at the core, bringing together a large number of chains.

The present synthetic approach provides one of the first examples of a network architecture possessing a large, but controlled, number of dangling chains. Peppas and co-workers[42] and Lutz[43] have prepared similar networks based on poly(ethylene oxide) star polymers in which the final cross-linking step was performed by free radical polymerization. The cross-linking of "core-first"[44,45] and "arm-first"[46] star polymers as well as of dendrimers[47] has also been reported, but the resulting network architectures do not contain any intentional dangling chains.

Figure 4 shows all amphiphilic network structures based on cross-linked stars synthesized in this study.

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Table 1. GPC and ^{1}H NMR Characterization of the Cross-Linked Star Network Precursors

network	theoretical structure[a]	theoretical MW	apparent M_n by GPC	M_w/M_n by GPC	peak MWs (M_p's) by GPC	theoretical composition, D−M	composition by ^{1}H NMR, D−M
C1	D$_{50}$	7961	17400	1.07	18100		
	D$_{50}$-*star*		53500	1.68	103000		
	D$_{50}$-*star*-M$_{50}$		115000	2.80	212000	50−50	47−53
C2	M$_{50}$	5100	8500	1.08	9060		
	M$_{50}$-*star*		29400	2.10	74000		
	M$_{50}$-*star*-D$_{50}$		103000	1.39	123000	50−50	49−51
C3	D$_{25}$	4030	5900	1.08	6210		
	D$_{25}$-*b*-M$_{25}$	6530	10200	1.11	11500		
	(D$_{25}$-*b*-M$_{25}$)-*star*		28500	2.42	87000		
	(D$_{25}$-*b*-M$_{25}$)-*star*-D$_{25}$		36200	2.44	102000		
	(D$_{25}$-*b*-M$_{25}$)-*star*-(D$_{25}$-*b*-M$_{25}$)		44900	3.02	130000	50−50	51.5−48.5
C4	M$_{25}$	2600	4600	1.12	4870		
	M$_{25}$-*b*-D$_{25}$	6530	11400	1.15	12800		
	(M$_{25}$-*b*-D$_{25}$)-*star*		27400	2.48	87600		
	(M$_{25}$-*b*-D$_{25}$)-*star*-M$_{25}$		41300	2.57	109000		
	(M$_{25}$-*b*-D$_{25}$)-*star*-(M$_{25}$-*b*-D$_{25}$)		51400	2.72	134000	50−50	51−49
C5	D$_{25}$-*co*-M$_{25}$	6530	14100	1.08	14600		
	(D$_{25}$-*co*-M$_{25}$)-*star*		42400	1.81	90000		
	(D$_{25}$-*co*-M$_{25}$)-*star*-(D$_{25}$-*co*-M$_{25}$)		201000	1.67	201000	50−50	53−47

[a] D and M are (additional) abbreviations for DMAEMA and MMA, respectively.

Table 2. Absolute Weight-Average MWs (M_w's) Measured by Static Light Scattering (SLS) for the Star Precursors of the Networks (M$_{50}$-*star*-D$_{50}$)-*network* and [(D$_{25}$-*b*-M$_{25}$)-*star*-(D$_{25}$-*b*-M$_{25}$)]-*network*

name	sample[a]	M_w by SLS	MW from eq 2	total no. of arms[b]
C2	M$_{50}$-*star*	288000		29
C2	M$_{50}$-*star*-D$_{50}$	799000	723000	58
C3	(D$_{25}$-*b*-M$_{25}$)-*star*	344000		30
C3	(D$_{25}$-*b*-M$_{25}$)-*star*-D$_{25}$	609000	554000	60
C3	(D$_{25}$-*b*-M$_{25}$)-*star*-(D$_{25}$-*b*-M$_{25}$)	923000	688000	60

[a] M and D are (additional) abbreviations for MMA and DMAEMA, respectively. [b] Calculated from eq 1.

These are isomeric structures with equimolar MMA−DMAEMA compositions and overall theoretical degrees of polymerization of the primary and secondary arms constant and equal to 50. (It has been shown, however, that network formation is also possible when the degrees of polymerization of the secondary arms are either smaller or greater than those of the primary arms.[40]) The same color coding was employed as that in Figure 3. The two network structures on the top, C1 and C2, are cross-linked heteroarm star polymers whose primary and secondary arms are different types of homopolymers. The next two network structures, C3 and C4, are cross-linked star-block copolymers whose arms are diblock copolymers. The last network structure, C5, is based on cross-linked statistical copolymer stars. Inverse star-block copolymers, similar to the structures C3 and C4, but not cross-linked to a network, and with exactly four arms, have been prepared and studied by Hadjichristidis and co-workers.[48]

Molecular Weights and Compositions. Figure 5 shows the GPC chromatograms of the five precursors to the C4 block copolymer network [(MMA$_{25}$-*b*-DMAEMA$_{25}$)-*star*-(MMA$_{25}$-*b*-DMAEMA$_{25}$)]-*network*. The MWDs of the linear MMA homopolymer and MMA−DMAEMA diblock copolymer are narrow and unimodal, as expected. The MWD of the main peak corresponding to the “arm-first” star is also narrow but the distribution is multimodal, containing a small amount of unattached linear chains in addition to the stars. A fraction of these chains has originated from accidental deactivation during synthesis and thus it cannot grow upon further addition of monomer. A second part has not participated in the reaction with EGDMA but it is still “living” and grows upon addition of more monomer, as evidenced by the decrease in the amount of unattached linear chains during the next step of the synthesis. A small third peak corresponding to the “dimer”, formed by the coupling reaction between two “living” linear chains with one EGDMA molecule, is also observed in the chromatogram of the “arm-first” star. Similar observations have been reported for the synthesis, via anionic polymerization, of heteroarm star polymers using the same “arm-first” method[49] but the direct comparison of the star polymer yields obtained in the two studies is not possible as both the MW of the linear precursors and the cross-linker/living-ends mole ratio which affect the amount of unattached linear chains are different in the two cases. However, high star polymers yields (>86%, determined from the relative peak areas in GPC) were obtained in all cases in the present study. The chromatograms of the “in-out” stars are also multimodal for the same reasons as above but with a narrow MWD of the main peak corresponding to the star polymers. The MW of the main peak is increasing from the initial homopolymer to the final “in-out” star polymer, as expected, indicating the growth of the structure as a whole. Similar results were obtained for the precursors to all networks synthesized.

Table 1 shows all the amphiphilic cross-linked star polymers prepared in this study and their GPC and ^{1}H NMR characterization data. The nomenclature used in the table is that introduced in Figure 2. The polydispersity indices (PDIs, M_w/M_n) of all linear polymers are low (<1.15) but their M_n's are almost twice as high as the theoretical because of partial initiator deactivation. For the “arm-first” star polymers the PDIs shown are high because both the star and the unattached chain peaks were included in the calculation because of their

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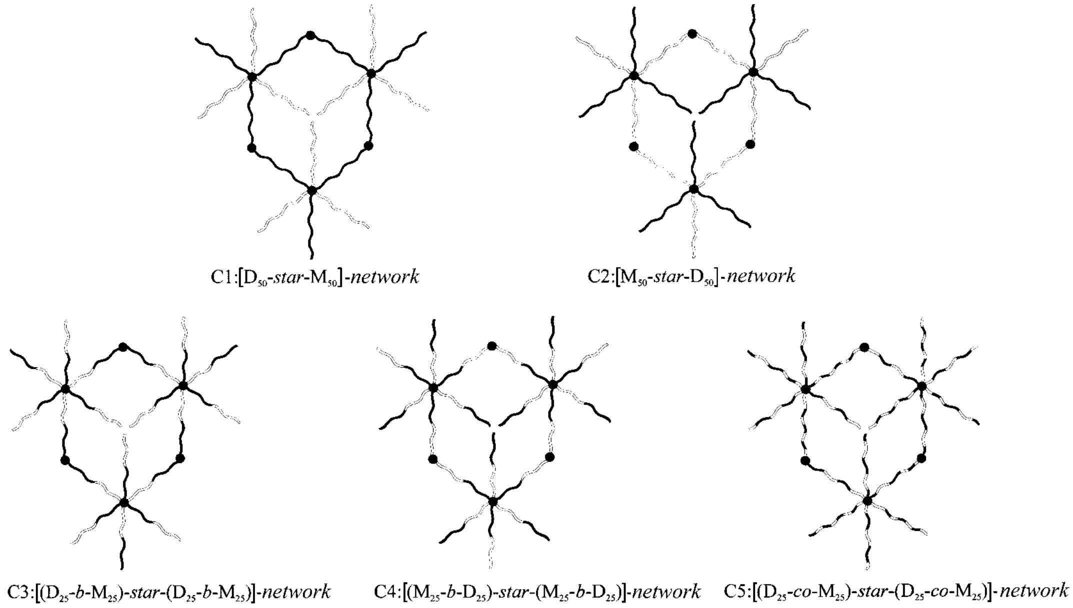
C1:[D$_{50}$-*star*-M$_{50}$]-*network*
C2:[M$_{50}$-*star*-D$_{50}$]-*network*
C3:[(D$_{25}$-*b*-M$_{25}$)-*star*-(D$_{25}$-*b*-M$_{25}$)]-*network*
C4:[(M$_{25}$-*b*-D$_{25}$)-*star*-(M$_{25}$-*b*-D$_{25}$)]-*network*
C5:[(D$_{25}$-*co*-M$_{25}$)-*star*-(D$_{25}$-*co*-M$_{25}$)]-*network*

Figure 4. Schematic representation of the architectures of the model networks of this study. The DMAEMA units are depicted white, while the MMA units are colored black.

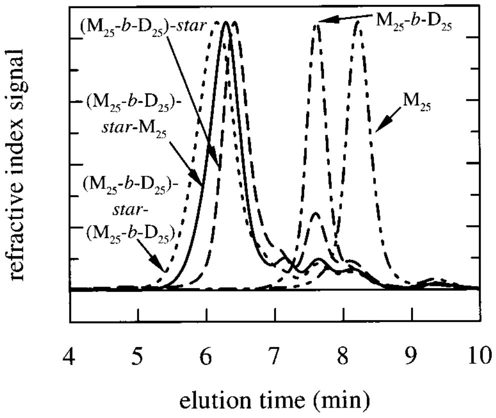

Figure 5. Gel permeation chromatograms of the five precursors to the network [(MMA$_{25}$-*b*-DMAEMA$_{25}$)-*star*-(MMA$_{25}$-*b*-DMAEMA$_{25}$)]-*network*. In the curve labeling, M and D are (further) abbreviations for MMA and DMAEMA, respectively, while the polymer nomenclature follows that introduced in Figure 2.

overlap. Similarly broad and bimodal MWDs are also obtained for the "in-out" star polymers, but their M_n's are always higher than those of the respective "arm-first" stars, as expected. The corresponding peak MWs, M_p's, are also provided and exhibit the same trend, suggesting that the whole distribution grows. It must be stressed that the M_n's determined by GPC for the star polymers are only apparent values and much lower than the actual ones because of the compactness of the star structure compared to the linear PMMA MW calibration standards.[24,50] However, these apparent values are good qualitative indicators of the increase in MW at each synthetic step, as confirmed by SLS, described in the next paragraph.

The absolute weight-average MWs, M_w's, and the number of arms of the star precursors ("arm-first" and "in-out" stars) to the networks (MMA$_{50}$-*star*-DMAEMA$_{50}$)-*network* and [(DMAEMA$_{25}$-*b*-MMA$_{25}$)-*star*-(DMAEMA$_{25}$-*b*-MMA$_{25}$)]-*network* as measured by SLS are given in Table 2. The homopolymer and block copolymer linear precursors to the "arm-first" stars could not be measured by this technique because of their low MWs, which were below the detection limit of the instrument. The MWs used for these samples were those measured by GPC, as this technique (based on linear PMMA standards) gave the absolute MW for linear PMMA while it provided a good estimate for linear poly(DMAEMA) and poly(DMAEMA-*b*-MMA). Taking also into account the MW of the cores (an average of four EGDMA molecules per "living" chain end[39,41]), the functionality f of the "arm-first" stars can be calculated using the formula[51]

$$f = \frac{\bar{M}_{\mathrm{w,arm-first\_star}}}{\bar{M}_{\mathrm{n,arm}} + \mathrm{MW}_{\mathrm{EGDMA}}[\mathrm{EGDMA}]/[\text{living ends}]} \qquad (1)$$

where MW$_{\mathrm{EGDMA}}$ is the MW of the dimethacrylate cross-linker of 198 g mol^{-1} and the quantities in brackets indicate concentrations. From this calculation an average functionality of 29 and 30 arms was obtained for the heteroarm and the block copolymer "arm-first" stars, respectively. The close proximity between these two values is an indication that, for arms with the same overall degree of polymerization, the number of arms in "arm-first" stars is not strongly affected by the type of monomer (MMA or DMAEMA). On the basis of the hypothesis, confirmed by Kanaoka et al.,[50] that all the active sites within the "arm-first" star core are involved in the polymerization of the next monomer feed, the number of secondary arms of the stars must be equal to the primary arms, and thus, the total number of arms should be 58 and 60 arms for the heteroarm and the block copolymer "in-out" star polymers, respectively. These values are also recorded in Table 2. Also shown in Table 2 are the MWs of the "in-out" stars, calculated

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Table 3. Sol Extractables from the Cross-Linked Star Networks

name	network[a]	w/w % extractables
C1	$(D_{50}$-*star*-$M_{50})$-*network*	5.76
C2	$(M_{50}$-*star*-$D_{50})$ -*network*	8.12
C3	$[(D_{25}$-*b*-$M_{25})$-*star*-$(D_{25}$-*b*-$M_{25})]$-*network*	7.58
C4	$[(M_{25}$-*b*-$D_{25})$-*star*-$(M_{25}$-*b*-$D_{25})]$-*network*	6.62
C5	$[(D_{25}$-*co*-$M_{25})$-*star*-$(D_{25}$-*co*-$M_{25})]$-*network*	3.98

[a] D and M are (additional) abbreviations for DMAEMA and MMA, respectively.

from the MW of the "arm-first" star and the weight fraction (W), determined by ^{1}H NMR, of the monomer added in for the "in-out" star formation, using the following relation:[51]

$$\bar{M}_{\mathrm{w,in-out\_star}} = \frac{\bar{M}_{\mathrm{w,arm-first\_star}}}{(1 - W_{\mathrm{in-out\_added\_monomer}})} \qquad (2)$$

The slightly higher MWs measured for the "in-out" stars using SLS as compared to those calculated using the above equation (799 000 vs 723 000 and 923 000 vs 688 000 g mol^{-1}) are attributed to some possible intermolecular connection between the "in-out" stars during their formation, induced by few remaining vinyl-type unsaturations existing in the cores of the stars.[24,49] However, such an intermolecular connection must occur only to a very small extent since neither gelation nor severe thickening of the reaction medium was detected during the formation of the "in-out" star polymers.

The compositions of all "in-out" star network precursors were calculated from their ^{1}H NMR spectra. The peak integral at δ 3.9−4.1 ppm, corresponding to the oxymethylene protons of the DMAEMA moieties, was compared to that at δ 3.5−3.6 ppm that arises from the contributions of the methoxy protons in the MMA residues, the methoxy protons in the initiator fragment, and the ethylene protons in the cross-linking agent. DMAEMA−MMA compositions were calculated after the subtraction of the contribution of the initiator and cross-linker to the latter peak integral. All measured compositions are shown in Table 1 and are in good agreement with the theoretical values calculated from the relative loadings of the two comonomers, also shown in the table. The absence in these spectra of peaks assigned to the two olefinic protons of the monomers at δ 5.5−5.6 ppm and δ 6.0−6.1 ppm suggests that no unreacted monomers remained after polymerization (also confirmed by the absence of a monomer peak in the GPC of the in-out star network precursors).

Sol Fraction of the Networks. Table 3 shows the sol fraction extracted from each network. In all cases the sol fraction is relatively low, with the lowest value being as low as 4% and the highest 8%. This low sol fraction supports previous findings[41] where a 4-fold molar excess of EGDMA cross-linker with respect to the initiator has been determined as the optimal ratio for sufficiently high conversion to star polymer during "arm-first" star polymer synthesis. In good agreement also are studies on both the anionic and "living" cationic "arm-first" star polymer synthesis[50,52] in which high star polymer yields (>85% for anionic) were obtained. An estimate of the extractables can be made from the GPC chromatograms of the final "in-out" star polymers by taking the ratio of the areas of the peaks of the unattached material to the main peak. Such a calculation gave similar, although consistently slightly higher, values for the extractables than those measured by extraction. This discrepancy is probably due to the incorporation into the network, during the final cross-linking step, of some of the material which is not attached to the "in-out" star polymers. Again the low amounts of extractables measured directly and calculated from GPC indicate satisfactory control over the network structure during synthesis.

Degrees of Swelling of the Networks. Figure 6 shows the pH dependence of the degrees of swelling (DSs) and the degrees of ionization of the five cross-linked star copolymers. At high pH values (pH > 7) where DMAEMA is not ionized, low DSs are obtained for all networks, suggesting a collapsed state for all the gels, in agreement with previous studies on DMAEMA−MMA model networks.[39] An increase in the DS at low pH values (pH < 7) is observed because of the ionization of the DMAEMA residues,[53] which results in an increase of the osmotic pressure within the gel from the counterions to the charged polymer and in electrostatic repulsions between the charged DMAEMA residues. These results are in agreement with our previous work where an increase in the DS from high to low pH values was observed upon ionization of the DMAEMA units in both homopolymer-[41,54−56] and amphiphilic-copolymer[39] based networks. The decrease in the DS of the networks below pH 2 is due to the high ionic strength of the solution at this pH conferred by the relatively high hydrochloric acid concentration, which results in charge screening in the gel.[57]

In a comparison of the DS vs pH curves of the present amphiphilic cross-linked star networks with those of the DMAEMA homopolymer analogues,[40] a less abrupt increase of the DS with decreasing pH is observed for the former. Moreover, while in Figure 6 the DS curves follow rather closely the hydrogen ion titration curves, the DS curves of the homopolymer cross-linked stars are shifted by ≈2 pH units to the right of the corresponding hydrogen ion titration curves. The swelling behavior of the homopolymer cross-linked stars is consistent with a first-order volume phase transition.[26,40,58−61] The different swelling behavior of the amphiphilic cross-linked stars is due to their microphase separation which prohibits such a transition to occur.[61]

Table 4 shows the measured effective p*K*s (taken as the pH at 50% ionization), the minimum and maximum

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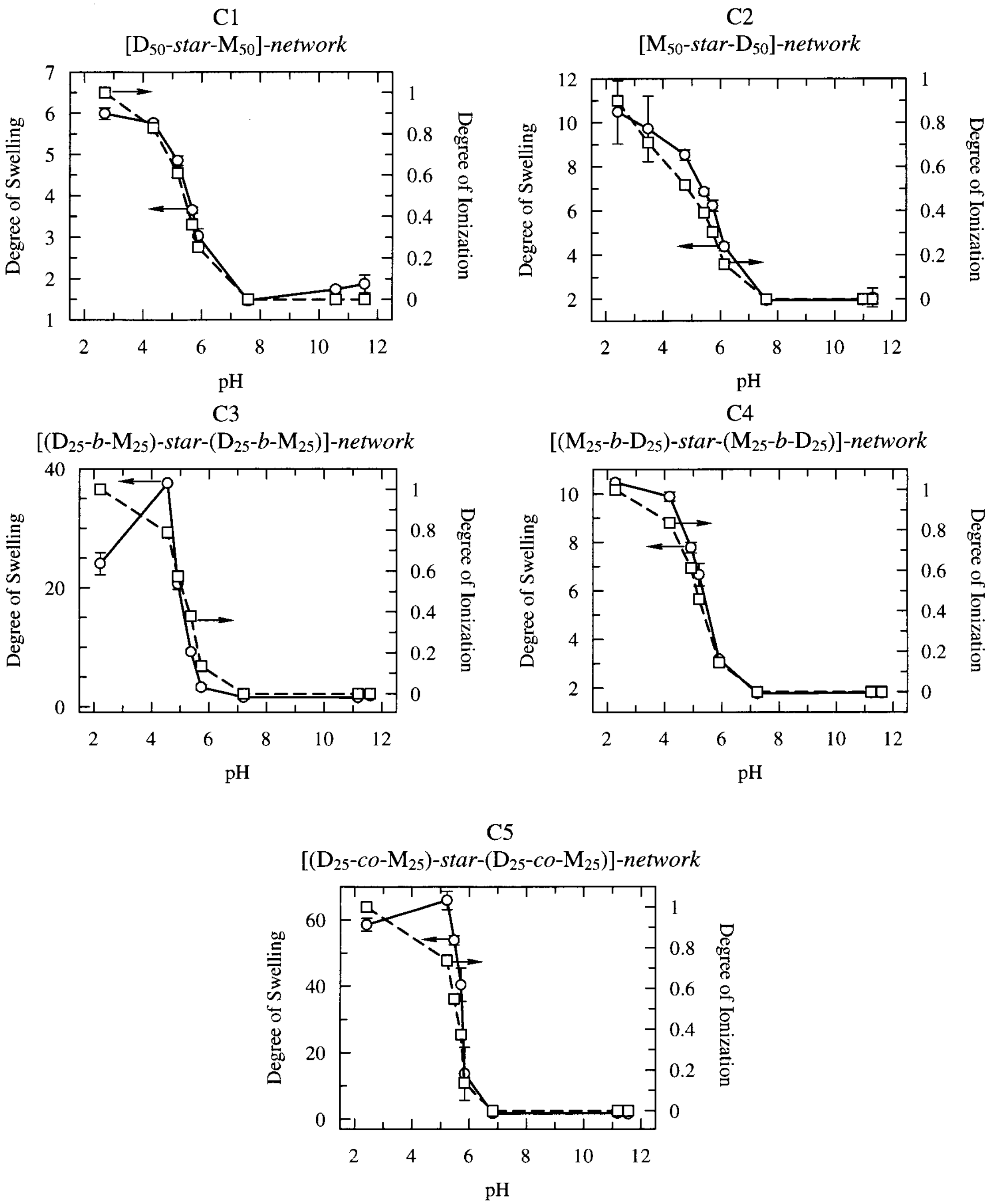

Figure 6. Aqueous degrees of swelling and degrees of ionization of the cross-linked stars as a function of the solution pH.

Table 4. Degrees of Swelling and Effective p*K*s of the Cross-Linked Star Networks

			degree of swelling		
name	network[a]	p*K*	low pH	high pH	THF
H23	$(M_{50}$-*star*-$M_{50})$-*network*		1.3	1.2	
C1	$(D_{50}$-*star*-$M_{50})$-*network*	5.4	6.0	1.5	11.6
C2	$(M_{50}$-*star*-$D_{50})$-*network*	5.7	10.5	1.9	9.6
C3	$[(D_{25}$-*b*-$M_{25})$-*star*-$(D_{25}$-*b*-$M_{25})]$-*network*	5.4	24.0	1.6	9.3
C4	$[(M_{25}$-*b*-$D_{25})$-*star*-$(M_{25}$-*b*-$D_{25})]$-*network*	5.2	10.5	1.8	9.3
C5	$[(D_{25}$-*co*-$M_{25})$-*star*-$(D_{25}$-*co*-$M_{25})]$-*network*	5.6	58.5	1.6	10.3

[a] M and D are (additional) abbreviations for MMA and DMAEMA, respectively.

DSs of the amphiphilic networks at high and low pH values, respectively, and their DSs in THF. The p*K* values were all found around 5.5 (±0.2, close to estimated error of the measurement of ±0.1), presenting no dependence on gel architecture. These values were similar to those measured for the homopolymer cross-linked stars.[40] However, the effective p*K*s of the gels were substantially lower than those of their linear analogues of about 7.0 because of counterion partitioning into the gel phase.[57]

The lowest acidic aqueous DS in Table 4 is exhibited by the water-incompatible PMMA network (H23, DS =

1.3). The highest DS is presented by the statistical copolymer-based network (C5, DS = 58.5), bearing a random distribution of hydrophobic and hydrophilic units, which precludes microphase separation and thus allows its unhindered expansion.[39,61] In contrast, the low pH DSs of the four other copolymer networks are lower, between 6.0 and 24.0, as a result of some ordered structures imparted by the blockiness of the hydrophobic MMA units in these materials.[39,61−63] Microphase separation lowers the DSs because it reduces the effective chain length between cross-links.[61] The morphologies of these structures may be quite novel, other than the conventional spheres, cylinders, or lamellae[64,65] observed with linear diblock and ABA triblock copolymers because of the presence of cross-links and dangling chains in the present system. The order and lower DSs confer to these materials improved mechanical properties, preventing their breaking into small pieces (≈1 mm)[66] at low pH, as is the case with the statistical[39] and DMAEMA homopolymer networks.[40,41,56]

From the five copolymer networks, heteroarm star-based network C1 exhibits the lowest acidic DS, 6.0. This can be attributed to the fact that the elastic chains of this network are based on MMA homopolymer. Because of their high hydrophobicity, these elastic chains should be highly shrunk in water, thus severely limiting the DS. The other heteroarm star-based network, C2, bearing DMAEMA homopolymer elastic chains, swells more, presenting an acidic DS of 10.5. The same DS is also exhibited by the star-block copolymer-based network C4. This was surprising and against the expectation that C4 should present a lower acidic DS than C2 because of the higher hydrophobicity of the elastic chains of the former than those of the latter. This implies that the hydrophobicity of the dangling chains is also important in this case. In particular, the lower hydrophobicity of the dangling chains of C4 than those of C2 may counteract the higher hydrophobicity of its elastic chains. It must also be stressed at this point that the morphologies acquired by the four copolymer-based networks are not necessarily the same. Thus, hydrophobicity alone is not enough to determine the extent of expansion of the networks, but the shape of the superstructure adopted by each network is also necessary.

The two block copolymer-based networks, C4 and C3, having opposite block sequences, exhibit very different acidic DSs, 10.5 and 24.0. Given that DMAEMA−MMA equimolar model networks based on ABA and BAB triblock copolymers (no dangling chains) have the same acidic DSs,[39] this implies that the dangling chains play again a critical role in determining the DSs of the networks of this study. It is possible that the nature of the outermost block of the dangling chains of the network, whether hydrophobic or hydrophilic, dominates its swelling properties. This hypothesis would explain the higher acidic DS of C3 than C4. Indeed, such a hypothesis is supported by the results of Kanaoka and co-workers[50] who observed that amphiphilic star-block copolymers prepared by “living” cationic polymerization are insoluble in solvents which are poor for the outer block. Moreover, it is possible that, within the network structure, the freedom of the polyMMA dangling block in C4 leads to the formation of more extended hydrophobic microphases compared to those in C3, thus further restricting swelling.

The DSs of the amphiphilic networks in THF, also shown in Table 4, are all similar, around 10, and architecture-independent. This is not surprising, given that all networks are isomers and THF is a nonselective solvent for DMAEMA and MMA. The slightly different values obtained for the DSs in THF are consistent with the differences in the peak molecular weights (M_p's) of the star precursors from the networks. Thus, the two networks derived from higher MW precursors (C1 and C5) exhibit slightly higher DSs in THF. All networks are much more swollen in THF than in high pH water. This is because THF is a good solvent for both DMAEMA and MMA, while alkaline water is a nonsolvent for MMA and an almost ϑ-solvent for the DMAEMA segments.[67]

Conclusions

The successful GTP synthesis of networks based on amphiphilic cross-linked “in-out” star polymers of various structures (heteroarm, block, and statistical) was accomplished using a monofunctional initiator in a four- or six-step synthesis. It is noteworthy that GTP was “living” even after six monomer additions, allowing the synthesis of networks with such complicated structures. The length of the arms of the stars and its precise control yielded networks in which the interstar spacing is accurately controlled, falls within the nanometer range, and can be varied with network swelling. The aqueous degree of swelling of all the networks synthesized was measured and found to be affected by the solution pH and the network structure. At low pH the DMAEMA units become ionized, leading to substantial network swelling. The way the network structure influences network swelling is complex, with the compositions of both the elastic and the dangling chains being crucial structural characteristics. While the statistical copolymer star-based network must be in a disordered state, evidenced by its relatively high acidic aqueous degrees of swelling, the rest of the amphiphilic star polymer-based networks should be microphase-separated, presenting complicated, potentially novel, morphologies.

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