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Amphiphilic Polymethacrylate Model Co-Networks: Synthesis by RAFT Radical Polymerization and Characterization of the Swelling Behavior

Theodora C. Krasia[†] **and Costas S. Patrickios***

Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus

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ABSTRACT: Reversible addition−fragmentation chain transfer (RAFT) controlled radical polymerization was employed, for the first time, to prepare well-defined (model) amphiphilic polymer co-networks based on *n*-butyl methacrylate (BuMA, hydrophobic monomer) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, hydrophilic ionizable monomer) cross-linked with ethylene glycol dimethacrylate (EGDMA) and bearing elastic chains having the following comonomer distributions: BuMA-*b*-DMAEMA-*b*-BuMA and DMAEMA-*b*-BuMA-*b*-DMAEMA triblock and BuMA-*co*-DMAEMA statistical copolymers. Two randomly cross-linked (not model) amphiphilic co-networks were also synthesized, the one by RAFT and the other by conventional free radical polymerization. The amphiphilic triblock copolymer-based model co-networks were obtained by stepwise synthesis in three stages: (1) the synthesis of linear homopolymers bearing two active ends by using a bifunctional chain transfer agent (CTA), (2) the sequential addition of the second monomer on the macro-CTAs (homopolymers) to yield linear ABA or BAB triblock copolymers, and (3) the inter-linking of the linear copolymer chains at both ends using EGDMA cross-linker to form the final model co-networks. The homopolymer and copolymer precursors to the networks were characterized using gel permeation chromatography and ^{1}H NMR spectroscopy. The swelling behavior of the networks was investigated in tetrahydrofuran and water. The co-networks swelled more in acidic than in neutral water due to the ionization of their DMAEMA units. The low pH aqueous swelling of the statistical co-network was higher than those of its triblock counterparts due to the lack of microphase separation with the statistical copolymer chains.

Introduction

Amphiphilic polymer co-networks are copolymer networks composed of both hydrophilic and hydrophobic monomer repeat units, capable of *absorbing* both water and nonpolar organic solvents, and *adsorbing* hydrophilic as well as hydrophobic solutes.[1] The arrangement of the hydrophilic and the hydrophobic units in separate blocks or segments yields segmented amphiphilic co-networks, possessing a large tendency for microphase separation in aqueous media.[2,3] Various synthetic methodologies have been developed for the synthesis of segmented amphiphilic co-networks, employing free radical polymerization,[4,5] “quasi-living” carbocationic polymerization,[6,7] anionic polymerization,[8,9] and group transfer polymerization.[10−12] Compared to free radical polymerization, the other above-mentioned methods provided co-networks of better-controlled structure, but they were synthetically more demanding.

The recently developed method of atom transfer radical polymerization (ATRP) for controlled radical polymerization combines polymer products of well-defined structure with synthetic simplicity.[13,14] Another particularly attractive controlled radical polymerization method is the newly developed reversible addition−fragmentation chain transfer (RAFT) polymerization, which is compatible with a wide range of monomers and reaction conditions.[15] Moreover, RAFT has already been successfully used for the preparation of various polymer architectures, such as block[16−18] and multiblock copolymers,[19] dendronized polymers,[20] and star and graft polymers.[21−24] Although there is a limited number of experimental[25,26] and theoretical[27] reports dealing with homopolymer networks prepared by ATRP, there is no report on the synthesis of amphiphilic polymer model[28] co-networks by ATRP or RAFT. Thus, the aim of this investigation was the evaluation of RAFT for the preparation of block copolymer-based covalent networks.

Experimental Section

Materials. *n*-Butyl methacrylate (BuMA, purity > 99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), basic alumina, calcium hydride (CaH_2, 90−95%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%), sulfur (powder ∼ 100 mesh), sodium methoxide (30% solution in methanol), benzyl chloride (99%), 1,3-diisopropenylbenzene (97%), silica gel (60 Å, 70−230 mesh), and potassium metal (98%) were all purchased from Aldrich. 2,2′-Azobis(isobutyronitrile) (AIBN, 95%), ethanol (99.6%), *n*-hexane (≥ 99%), and deuterated chloroform ($CDCl_3$) were purchased from Merck. Sodium metal was purchased from Fluka, whereas carbon tetrachloride (≥ 99.8%) was purchased from Riedel de Haën. Tetrahydrofuran (THF, 99.8%, both HPLC and reagent grade), methanol (99.9%), and diethyl ether (99.5%) were purchased from Labscan. Benzene (99%) was received from BDH.

Methods. The monomers used, BuMA and DMAEMA, and the cross-linker used, EGDMA, were passed through basic alumina columns to remove inhibitors and protic impurities, were stirred over CaH_2 in the presence of the free radical inhibitor DPPH, and were freshly distilled prior to use. The AIBN radical initiator was recrystallized from ethanol. Benzene was dried over CaH_2 and distilled prior to use, whereas THF was dried by refluxing it over a potassium/sodium alloy for 3 days. The bifunctional chain transfer agent (CTA) 1,3-bis(2-(thiobenzoylthio)prop-2-yl)benzene (TBTPB) was synthesized following the procedure published by Rizzardo et al.[21] Figure 1 shows the chemical structures and names of the monomers, the cross-linker, the initiator, and the bifunctional CTA used for polymer synthesis.

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* To whom correspondence should be addressed. E-mail: costasp@ucy.ac.cy.

[†] E-mail: krasia@ucy.ac.cy.

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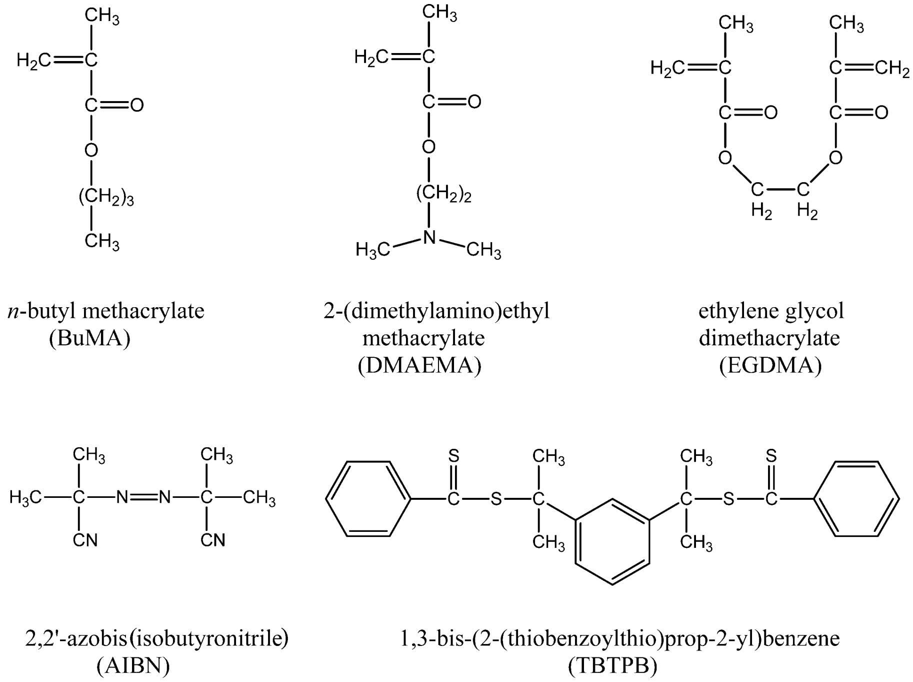


Figure 1. Chemical structures and names of the main reagents used for the co-network synthesis.

Kinetic Study of a RAFT Homopolymerization. The homopolymerization by RAFT of DMAEMA in benzene and in the presence of the bifunctional CTA TBTPB was followed kinetically for 23 h. Samples were withdrawn at different reaction times, isolated by precipitation in *n*-hexane, and dried in a vacuum oven. The monomer-to-polymer conversion was determined gravimetrically from the dried mass of the recovered polymer, whereas the polymer molecular weights (MWs) and polydispersity indices (PDIs) were characterized by gel permeation chromatography (GPC).

Synthesis of the Linear Precursors to the Networks. Synthesis of Homopolymers. DMAEMA and BuMA homopolymers were synthesized first.[16] A typical polymerization procedure is described as follows: TBTPB and AIBN were dried under high vacuum for 1 day. The polymerization flask was placed under dynamic vacuum and heated at high temperatures to remove all traces of moisture. After the polymerization flask was cooled to room temperature, AIBN (23.5 mg, 0.143 mmol), TBTPB (200 mg, 0.429 mmol) and BuMA (8.94 g, 63.0 mmol) in benzene (3.5 mL) were transferred into the flask via a syringe. During the transfer, the flask was continuously purged with dry nitrogen. Subsequently, the solution was degassed by three freeze−evacuate−thaw cycles and placed under a dry nitrogen atmosphere. Finally, the polymerization flask was placed in an oil bath at 65 °C for ca. 24 h. The obtained polymer was separated from the unreacted monomer by precipitation in methanol and was left to dry for 2 days under vacuum. Yield: 5.0 g (56%). Number-average MW: $M_n = 14\,144$ g mol^{-1}; $M_w/M_n = 1.35$. (M_w is the weight-average MW.)

Synthesis of Triblock Copolymers. The homopolymers obtained were further grown by the addition of the second monomer. A typical synthetic procedure followed for the synthesis of the BuMA-*b*-DMAEMA-*b*-BuMA triblock copolymers is described as follows: The bifunctional macroTBTPB (polyDMAEMA) was dried under high vacuum for 1 day prior to use. AIBN (6.80 mg, 0.041 mmol), polyDMAEMA (1.00 g, 0.097 mmol), and BuMA (0.894 g, 6.30 mmol) in benzene (1.3 mL) were transferred into the polymerization flask via a syringe, under an inert nitrogen atmosphere, followed by three freeze−evacuate−thaw cycles for degassing. Finally, the reactor was again placed under inert atmosphere and heated in an oil bath at 65 °C for ca. 24 h. The resulting polymer was recovered by precipitation in *n*-hexane and was left to dry for 2 days under vacuum. Yield: 1.68 g (76%). $M_n = 24\,080$ g mol^{-1}; $M_w/M_n = 1.64$. Copolymer composition by ^{1}H NMR: 58.4 mol % DMAEMA.

For the synthesis of the DMAEMA-*b*-BuMA-*b*-DMAEMA triblock copolymers, a similar synthetic procedure to the one already described was followed, with the addition of DMAEMA monomer onto polyBuMA macroinitiator. In this case, however, the addition of DMAEMA onto the two active chain ends of polyBuMA was much slower compared to the addition of BuMA onto the polyDMAEMA active chain ends and required 6 days.

Synthesis of a Statistical Copolymer. The synthesis of the statistical DMAEMA-BuMA copolymer involved the simultaneous copolymerization of the two monomers. TBTPB was dried under high vacuum for 1 day prior to use. AIBN (27.0 mg, 0.164 mmol), TBTPB (200 mg, 0.429 mmol), DMAEMA (4.66 g, 29.7 mmol) and BuMA (4.47 g, 31.4 mmol) in benzene (3.5 mL) were transferred via a syringe into the polymerization flask which was kept under an inert atmosphere, followed by three freeze−evacuate−thaw cycles. Finally, after the reactor was placed under inert atmosphere it was heated in an oil bath at 65 °C for ca. 24 h. The resulting polymer was recovered by precipitation in *n*-hexane and was left to dry for 2 days under vacuum. Yield: 6.24 g (68.3%). $M_n = 17\,360$ g mol^{-1}; $M_w/M_n = 1.50$. Copolymer composition by ^{1}H NMR: 50.0 mol % DMAEMA.

Synthesis of a Statistical Copolymer by Conventional Free Radical Polymerization. For this synthesis, the same procedure was followed as for the previous polymerization with the only difference that no TBTPB was added. Yield: 8.98 g (98.3%). $M_n = 79\,900$ g mol^{-1}; $M_w/M_n = 2.70$. Copolymer composition by ^{1}H NMR: 53.8 mol % DMAEMA.

Characterization of the Linear Precursors to the Networks. Gel Permeation Chromatography. Molecular weights (MWs) and molecular weight distributions (MWDs) of the linear polymer precursors to the networks were determined by gel permeation chromatography (GPC) at ambient temperature using a single high MW range Polymer Laboratories PL-Mixed “D” column (bead size = 5 μm; pore sizes = 100, 500, 10^3 and 10^4 Å). The mobile phase was THF, delivered at a flow rate of 1 mL min^{-1} using a Waters 515 isocratic pump. The refractive index signal was measured with an ERC-7515A refractive index detector supplied also by Polymer Laboratories. The calibration curve was based on eight linear poly(methyl methacrylate) (PMMA) MW standards of narrow MWD with MWs of 630, 2680, 4250, 13000, 28900, 50000, 128000, and 260000 g mol^{-1}.

^{1}H NMR Spectroscopy. The compositions of the linear copolymer (triblock and statistical) precursors were determined by ^{1}H

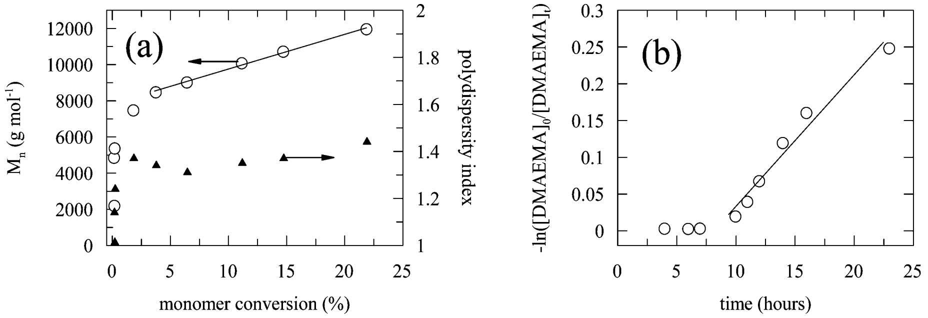


Figure 2. (a) Variation of the number-average molecular weight (M_n) vs monomer conversion and (b) kinetic plot, for the RAFT polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in benzene using 1,3-bis(2-(thiobenzoylthio)prop-2-yl)benzene (TBTPB) as the bifunctional chain transfer agent. Reaction conditions: $[\mathrm{DMAEMA}]_0:[\mathrm{TBTPB}]_0:[\mathrm{AIBN}]_0 = 89:0.33:0.11$ (mmol), benzene (5 mL), temperature = 65 °C, and reaction time = 23 h.

NMR using a 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet. The solvent was $CDCl_3$, containing traces of tetramethylsilane (TMS), which was used as an internal reference.

Synthesis of the Networks. The copolymers and the two homopolymers were converted to model networks via a final RAFT polymerization stage, in which EGDMA was polymerized from the active polymer ends. For the network synthesis the molar ratio of the EGDMA cross-linker to the TBTPB CTA was kept constant at 10. This number was chosen based on preliminary investigations in which the synthesis of a DMAEMA star homopolymer (using cumyl dithiobenzoate, a monofunctional rather than a bifunctional CTA) was accomplished using a molar ratio of [EGDMA]/[CTA] equal to 5. The resulting star homopolymer (66% yield in star relative to unattached linear) was characterized by GPC (M_n = 147800, PDI = 1.27) and ^{1}H NMR spectroscopy.

The detailed synthetic procedure adopted for the preparation of ABA triblock copolymer-based model networks is described as follows. The BuMA-*b*-DMAEMA-*b*-BuMA triblock copolymer was dried under high vacuum 1 day prior to use. A solution of AIBN (3.4 mg, 0.021 mmol), BuMA-*b*-DMAEMA-*b*-BuMA (600 mg, 0.031 mmol), and EGDMA (0.074 g, 0.37 mmol) in THF (2.5 mL) was transferred into the polymerization flask via a syringe under an inert nitrogen atmosphere, followed by three freeze−evacuate−thaw cycles. After the reactor was placed under a dry nitrogen atmosphere, it was heated in an oil bath at 65 °C for 24 h. Starting from a DMAEMA-*b*-BuMA-*b*-DMAEMA copolymer and following a similar experimental procedure, a BAB triblock copolymer-based network was prepared. The statistical copolymer-based model network was prepared in a similar way, using the DMAEMA-BuMA linear statistical copolymer. The two randomly cross-linked statistical copolymer networks were prepared by the simultaneous terpolymerization of DMAEMA, BuMA and EGDMA, the one in the presence (RAFT synthesis) and the other in the absence (conventional free radical polymerization synthesis) of TBTPB. With the exception of the randomly cross-linked network prepared by RAFT which required 40 h, the three model networks gelled within 24 h. Gelation was manifested by the cease of the motion of the magnetic stirring bar.

Characterization of the Networks. Determination of the Sol Fraction. The prepared networks were taken out of the polymerization flasks and were left to equilibrate in THF (100 mL) for 1 week to remove the sol fraction (extractables). Subsequently, the THF solution was recovered by filtration and was evaporated off using a rotary evaporator. The recovered extractables were further dried under vacuum for 72 h at room temperature. The sol fraction was calculated from the ratio of the dried mass of the extractables to the theoretical mass of all components in the network (i.e., polymer plus cross-linker).

Determination of the Degree of Swelling. The washed networks were cut into small pieces and their THF-swollen mass was determined gravimetrically before placing all samples in a vacuum oven for drying for 72 h at room temperature. The dry network mass was determined, followed by the transfer of the networks in neutral water and aqueous solutions where the pH was adjusted to values corresponding to degrees of ionization of the DMAEMA units ranging from 0 to 100% by the addition of the appropriate number of drops of a 0.5 M HCl standard solution. The required number of moles of HCl in each sample was calculated as the product of the desired degree of ionization times the number of moles of the DMAEMA units present in the sample. The latter was calculated as the product of the dry mass times the percentage of the DMAEMA units in the network (calculated by ^{1}H NMR analysis of the linear copolymer precursor to the network), divided by the MW of the DMAEMA unit. The samples were equilibrated for 3 weeks and the wet network masses were measured. The degrees of swelling (DSs) were calculated as the ratio of the wet network mass divided by the dry network mass.

Differential Scanning Calorimetry. A Q100 TA Instruments differential scanning calorimeter (DSC) was used to measure the glass transition temperatures (T_gs) of various networks using a heating rate of 10 °C min^{-1}. Each sample was scanned two or more times between −50 and +150 °C. The second run (heat) was used for data analysis.

Dynamic Mechanical Analysis. The mechanical behavior of the networks was investigated using a Tritec2000 Triton Technologies dynamic mechanical analyzer (DMA). The measurements were performed in the compression mode at a single frequency of 1 Hz. For the DMAEMA-containing networks, the experiments were carried out in water, whereas the BuMA homopolymer network was characterized in air.

Results and Discussion

"Living" Character of RAFT with the Bifunctional CTA. To establish the "livingness" of the RAFT process in the presence of a bifunctional CTA, the polymerization of DMAEMA was followed kinetically. Figure 2 shows that, after an induction period of approximately 8 h, the variations of (a) M_n vs monomer conversion and of (b) the term $-\ln([\mathrm{DMAEMA}]_0/[\mathrm{DMAEMA}]_t)$ vs time were both linear. This linearity is an indication of the "living" character of this polymerization for the preparation of the linear polymer precursors to the networks. An induction period has previously been observed in RAFT polymerizations with benzyl dithiobenzoate CTAs and has been attributed to the poor reinitiation efficiencies by the expelled benzyl radicals leading to inefficient transfer.[29,30] An abrupt increase of M_n with monomer conversion during the induction period has also been reported in RAFT polymerizations and has been attributed to a slower rate of addition to CTA compared to the rate of polymerization.[31]

Molecular Weight and Composition of the Linear Precursors to the Networks. Table 1 lists all network linear precursors along with their MW and composition characteristics. A comparison of their GPC M_ns with the theoretical values (taking into account polymer conversion calculated from the mass of

Table 1. Characteristics of the Linear Precursors to the Networks (Polymerization Yields, Molecular Weights and Compositions) and of the Networks (Degrees of Swelling)

name	experimental structure of precursor[a]	convn (%)	theor MW	GPC results[b]		DMAEMA (% mol by ^{1}H NMR)	experimental network structure	degrees of swelling		
				M_n[c]	PDI[d]			THF[f]	neutral water	acidic water
G1	B_{96}	56	11 900	14 100	1.35	0	B_{96}-*b*-E[e]	7.2 ± 1.0	-	-
G2	D_{63}	48	10 700	10 300	1.42	100	D_{63}-*b*-E	7.5 ± 1.0	17.3 ± 2.5	34.7 ± 1.0
G3	B_{58}-*co*-D_{58}	68	14 800	17 400	1.50	50.0	B_{58}-*co*-D_{58}-*b*-E	17.6 ± 2.0	4.9 ± 0.6	31 ± 8
G5	B_{32}-*b*-D_{90}-*b*-B_{32}	47	26 400	19 300	1.73	58.4	B_{32}-*b*-D_{90}-*b*-B_{32}-*b*-E	11.6 ± 0.4	3.4 ± 0.5	6.5 ± 0.5
G5a	B_{25}-*b*-D_{59}-*b*-B_{25}	73	16 000	18 700	1.60	54.1	B_{25}-*b*-D_{59}-*b*-B_{25}-*b*-E	10.4 ± 0.4	2.4 ± 0.8	8.6 ± 0.5
G6	D_{24}-*b*-B_{96}-*b*-D_{24}	58	21 200	24 500	1.59	32.0	D_{24}-*b*-B_{96}-*b*-D_{24}-*b*-E	8.0 ± 1.6	3.5 ± 0.2	8.3 ± 0.6
G7	B_{39}-*b*-D_{58}-*b*-B_{39}	73	20 300	21 000	1.70	42.6	B_{39}-*b*-D_{58}-*b*-B_{39}-*b*-E	7.2 ± 0.5	3.4 ± 0.4	4.4 ± 0.5
G8[g]							B-*co*-D-*co*-E	27 ± 3	3.3 ± 0.5	25.0 ± 0.5
G9[h]							B-*co*-D-*co*-E	13 ± 2.5	3.1 ± 0.2	8.9 ± 1.3

[a] B: BuMA = *n*-butyl methacrylate. D: DMAEMA = 2-(dimethylamino)ethyl methacrylate. [b] GPC = gel permeation chromatography. [c] M_n = number-average molecular weight. [d] PDI = polydispersity index. [e] E: EGDMA = ethylene glycol dimethacrylate. [f] THF = tetrahydrofuran. [g] Randomly cross-linked by RAFT. [h] Randomly cross-linked by conventional free radical polymerization.

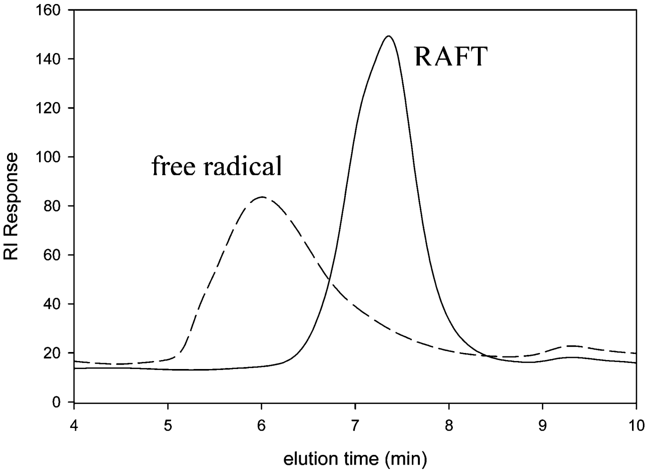


Figure 3. GPC traces of the statistical copolymers DMAEMA−BuMA prepared in the presence (RAFT synthesis) and in the absence (conventional free radical synthesis) of the bifunctional chain transfer agent.

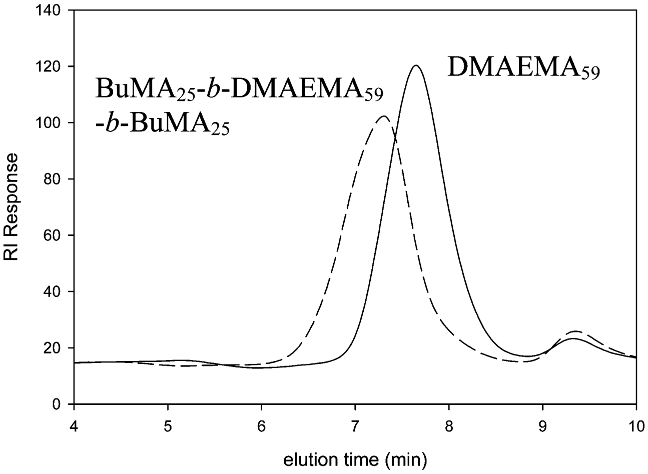


Figure 4. GPC traces of the $DMAEMA_{59}$ homopolymer and the corresponding triblock copolymer $BuMA_{25}$-*b*-$DMAEMA_{59}$-*b*-$BuMA_{25}$ prepared by the chain extension of $DMAEMA_{59}$ with *n*-butyl methacrylate.

the recovered polymer) shows a satisfactory (given the differences in the hydrodynamic volumes between PDMAEMA and the PMMA MW calibration standards), within 30%, agreement between the two. Their PDIs (M_w/M_n) ranged between 1.3 and 1.7, and they were higher than those of similar linear polymers prepared using monofunctional CTAs, as expected. The comonomer composition of the linear precursors was determined by ^{1}H NMR spectroscopy using the two oxymethylene protons of BuMA and DMAEMA appearing at 3.94 and 4.05 ppm, respectively.

As mentioned previously, the PDIs of the linear polymer precursors to the networks ranged between 1.3 and 1.7. These values are relatively high for a controlled polymerization process. However, the investigation of the polymerization kinetics described above indicated a controlled character for the RAFT polymerization. To further demonstrate the controlled character of the RAFT process used in the preparation of these polymers, we prepared the linear statistical DMAEMA−BuMA copolymer in the presence (RAFT synthesis) and in the absence (conventional free radical synthesis) of the bifunctional CTA TBTPB in benzene at 65 °C for 24 h. The GPC traces of the two resulting statistical copolymers are shown in Figure 3. Although both MWDs are unimodal, the MW calculations indicated that the copolymer prepared by RAFT polymerization has a much more controlled structure than the one prepared by conventional free radical polymerization. In particular, the PDI of the RAFT copolymer was 1.5 compared to 2.7 of the free radically prepared one. Moreover, the M_n of the former copolymer (17400 g mol^{-1}) was much closer to the theoretically expected MW (14800 g mol^{-1}) than the corresponding values of the latter (M_n = 79900 g mol^{-1} and theoretical MW = 28700 g mol^{-1}).

The block efficiency from homopolymer to block copolymer could also be an indication of the controlled character of the RAFT process. In Figure 4, the GPC traces of a DMAEMA homopolymer together with the corresponding BuMA-*b*-DMAEMA-*b*-BuMA triblock copolymer are shown. A shift of the distribution toward higher MWs clearly demonstrated efficient block formation.

Synthesis of the Amphiphilic Co-Networks. Figure 5 represents schematically the synthetic sequences followed for the preparation of the amphiphilic co-networks of this study, having four different architectures. As previously described, the synthesis of the amphiphilic model co-networks was accomplished by stepwise additions of a hydrophilic monomer (DMAEMA), a hydrophobic monomer (BuMA) and the cross-linker (EGDMA). First, linear homopolymers bearing chains with both active ends were prepared by RAFT using the bifunctional CTA. Subsequently, the addition of the second comonomer led to the formation of triblock copolymers possessing two active polymer ends. Finally, the addition of the cross-linker resulted in a three-dimensional network via the interconnection of the active polymer chain ends, as shown in Figure 5. The number of arms per cross-link is not three, as indicated in the figure, but higher, and due to the statistical

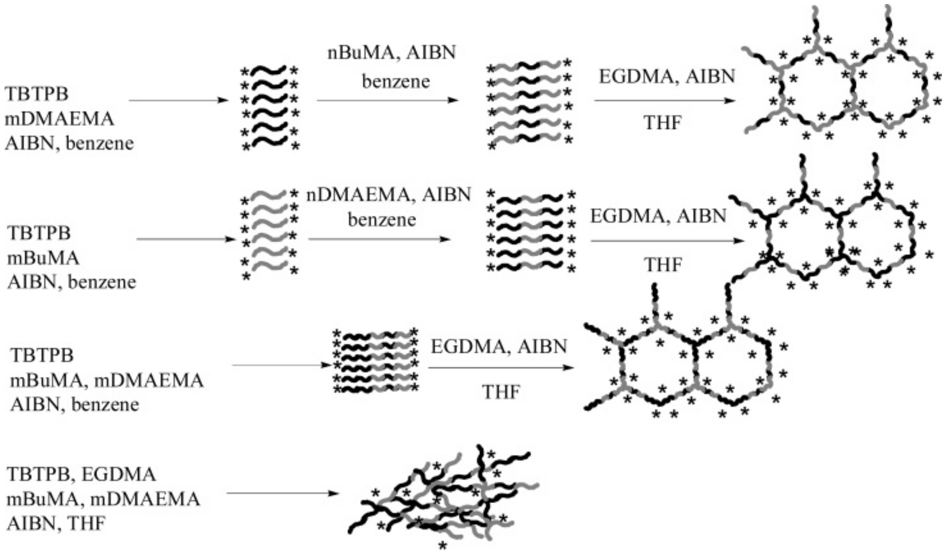


Figure 5. Synthetic sequences followed for the preparation by reversible addition fragmentation chain transfer (RAFT) polymerization of the amphiphilic polymer co-networks of four different architectures. The number of arms per cross-link is not three, as indicated in the first three architectures, but higher and it is not the same at the various cross-links. The 2-(dimethylamino)ethyl methacrylate (DMAEMA) and the *n*-butyl methacrylate (BuMA) units are indicated in black and gray, respectively, while the active polymerization sites are denoted by asterisks. EGDMA = ethylene glycol dimethacrylate; AIBN = 2,2′-azobis(isobutyronitrile); THF = tetrahydrofuran; TBTPB = 1,3-bis(2-(thiobenzoylthio)prop-2-yl)-benzene.

nature of the process for the addition of the cross-linker, the number of arms is not the same at the various cross-links.

Sol Fraction of the Networks. The sol fraction (extractables) of the networks prepared by RAFT varied from 18 to 34%, with the highest percentage corresponding to the less perfect randomly cross-linked amphiphilic co-network. These values are comparable to those of networks prepared by group transfer polymerization reported earlier by our group.[32−34] The sol fraction extracted from the randomly cross-linked co-network prepared by conventional free radical polymerization was 27%, close to the value for the randomly cross-linked co-network prepared by RAFT.

Degrees of Swelling of the Networks. The degrees of swelling (DSs) in THF of the networks together with the 95% confidence intervals of the DSs are summarized in Table 1. Depending on the network architecture, the DSs varied from around 7 (for the BuMA and DMAEMA homopolymer-based model networks) to 27 (for the randomly cross-linked amphiphilic co-network prepared by RAFT). The higher DS in the latter case might be attributed again to structural imperfections in this co-network, imparting a lower cross-link density, as evidenced by the higher sol fraction. The DSs of the two triblock as well as the statistical copolymer-based model networks exhibited values intermediate between 7 and 27.

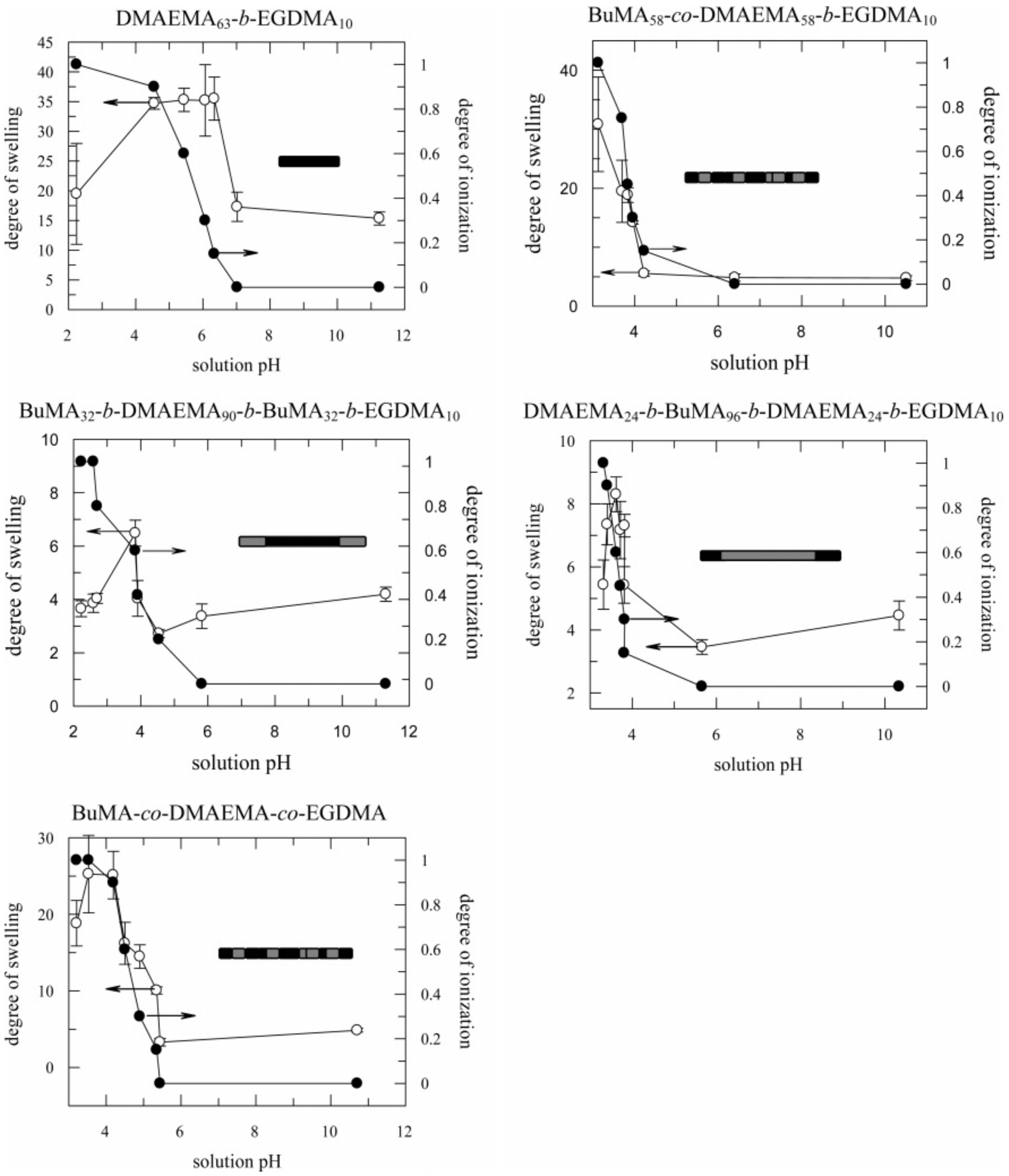
The pH dependence of the aqueous DSs of the networks is displayed in Figure 6. In all cases, the DSs increased as the pH decreased. This was because, at low pH, the DMAEMA units in the networks became ionized, creating electrostatic repulsions between the network chains and establishing an osmotic pressure within the network due to the accumulation of the chloride counterions, both of which promoted swelling.[35] The DS vs pH curves followed the degree of ionization vs pH curves, also shown in the figure, confirming the electrostatic origin of swelling. At the lowest pH values, the DSs declined due to the high ionic strength conferred to the system by the relatively high concentration of HCl under these conditions, another manifestation of the dominance of electrostatic interactions.

The aqueous DSs of the networks at neutral pH (∼7) and at low pH (at the swelling maximum) were taken from Figure 6 and are also displayed in Table 1 along with their 95% confidence intervals. The DSs in neutral water of the amphiphilic co-networks ranged between 3 and 5 and were much lower than those in THF. This was due to the fact that THF was a nonselective (good) solvent for both the DMAEMA and the BuMA units, while water was a selective solvent for the DMAEMA units. The insolubility of the BuMA units in water caused a reduction in the DSs of the BuMA-containing co-networks in this solvent. The DS of the DMAEMA homopolymer network in (neutral) water was higher than that in THF due to the hydrophilic nature of the DMAEMA units.

Full ionization of the DMAEMA units in low-pH water (∼3) led to increases of the network DSs relative to those in neutral water for the reasons given above. The largest increases of the DS upon ionization were observed for the DMAEMA homopolymer model network as well as the statistical model and randomly cross-linked amphiphilic co-networks, while the lowest increases were measured for the triblock copolymer amphiphilic model co-networks, reflecting microphase separation in this last type of co-networks which caused a reduction in the effective chain length and a decrease in the DS.[1−3,10−12]

Thermal Properties of the Networks. With the aim to detect self-organization, we performed thermal characterization of the co-networks in the bulk using DSC. The identification of two or more glass transition temperatures (T_gs) would be an indication for microphase separation in our materials in the bulk. The measurements provided a single T_g between 20 and 30 °C for each co-network sample. This was due to the similar T_g values of PBuMA and PDMAEMA which are both around 20 °C. Thus, DSC could not resolve the question of co-network microphase separation in the bulk due to the similar thermal properties of the two comonomers.

Mechanical Properties of the Networks. Preliminary characterization of the mechanical properties of the networks was performed using dynamic mechanical analysis (DMA). In particular, the elastic modulus in compression was determined for several of the networks. The elastic modulus of the DMAEMA-homopolymer model network (G2) in water in the neutral state was found to be 4.0×10^5 Pa, whereas the moduli



$DMAEMA_{63}$-*b*-$EGDMA_{10}$

$BuMA_{58}$-*co*-$DMAEMA_{58}$-*b*-$EGDMA_{10}$

$BuMA_{32}$-*b*-$DMAEMA_{90}$-*b*-$BuMA_{32}$-*b*-$EGDMA_{10}$

$DMAEMA_{24}$-*b*-$BuMA_{96}$-*b*-$DMAEMA_{24}$-*b*-$EGDMA_{10}$

BuMA-*co*-DMAEMA-*co*-EGDMA

Figure 6. Degrees of swelling and ionization of all the 2-(dimethylamino)ethyl methacrylate containing networks as a function of pH. The structure of the elastic chains of each network is indicated in each plot both in terms of a chemical formula and a black and gray illustration. The color-coding is the same as that in Figure 5. DMAEMA = 2-(dimethylamino)ethyl methacrylate; BuMA = *n*-butyl methacrylate; EGDMA = ethylene glycol dimethacrylate.

of two of the DMAEMA−BuMA model co-networks (G3 and G7) in water in the neutral state, presenting a much lower DS than the G2 network (Table 1), were determined to be 1.5×10^8 Pa. The elastic modulus of the BuMA-homopolymer model network (G1) in the bulk in air was also found to be rather high, 1.3×10^8 Pa.

Conclusions

The first RAFT synthesis of amphiphilic polymer co-networks has been accomplished. The aqueous swelling of these co-networks in the ionized state was highly influenced by their copolymer chain architecture, as this dictated their microphase separation behavior. Future work will involve the preparation by RAFT and characterization of co-networks of various hydrophilic/hydrophobic compositions.

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