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Amphiphilic Model Conetworks Based on Combinations of Methacrylate, Acrylate, and Styrenic Units: Synthesis by RAFT Radical Polymerization and Characterization of the Swelling Behavior

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ABSTRACT: Reversible addition−fragmentation chain transfer (RAFT) polymerization was employed for the preparation of homopolymer and copolymer (co)networks based on four monomer units, belonging to three monomer types: methacrylates, acrylates, and styrenics. In particular, *n*-butyl methacrylate and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (hydrophobic and hydrophilic-ionizable methacrylate monomers, respectively), *n*-butyl acrylate (hydrophobic) and styrene (hydrophobic) were used. Amphiphilic block copolymer conetworks were prepared by RAFT via the cross-linking of linear triblock copolymer precursors possessing two active polymer ends, which were subsequently interconnected by chemical cross-linking to a three-dimensional network, by using the appropriate cross-linker: ethylene glycol dimethacrylate for methacrylates, ethylene glycol diacrylate for acrylates, and 1,4-divinylbenzene for styrenics. The homopolymer and copolymer precursors to the (co)networks were characterized by gel permeation chromatography and ^{1}H NMR spectroscopy for their molecular weights and compositions, respectively. The degrees of swelling (DSs) of all (co)networks were determined in tetrahydrofuran and, where the ionizable (DMAEMA) was present, the DSs were also measured in neutral and acidic water. The conetworks swelled more in acidic than in neutral water due to the ionization of their DMAEMA units.

Introduction

Covalent polymer networks are three-dimensional structures that are interconnected via chemical cross-links. Such materials are insoluble in all solvents but can absorb solvents compatible with them. Amphiphilic polymer conetworks consist of hydrophilic and hydrophobic monomer units, capable of absorbing both water and organic solvents.[1,2] These materials have also the tendency to adsorb hydrophilic as well as hydrophobic solutes, such as drugs; hence, they can be used as drug delivery systems.[3−5]

The most general and common procedure for the synthesis of amphiphilic polymer conetworks is free radical polymerization.[6] However, this method does not provide any control over the conetwork architecture, or the elastic chain molecular weight (MW), composition, or MW distribution (MWD). Controlled methods, such as anionic[7,8] or group transfer polymerization (GTP),[9] have been used for the synthesis of amphiphilic polymer conetworks with greater degree of perfection. Controlled radical polymerization methods have also been used in the preparation of networks,[10] one of them being reversible addition−fragmentation chain transfer polymerization (RAFT).[11] The RAFT process represents a new, versatile polymerization technique, which allows for the preparation of well-defined polymers of various functionalities[12] and complex architectures such as stars,[13] graft polymers,[14] microgels,[15] or hyperbranched materials.[16] It is compatible with a wide range of monomers such as methacrylates, acrylates, styrenics, and acrylamides, as well as functional monomers containing carboxylic acid, acid salt, hydroxy, or tertiary amine groups.[17] This as well as the fact that there are no particular limitations in the reaction conditions, such as temperature or solvent,[18] makes this technique more advantageous compared to other controlled radical polymerization methods such as atom transfer radical polymerization (ATRP) or nitroxide mediated polymerization (NMP).[19]

Table 1. Polymerization Yields and Size Characteristics of the Homopolymers Synthesized

		GPC results[a]		degree of polymerization		
monomer	yield, %	M_n	M_w/M_n	theory[b]	GPC[a]	^{1}H NMR
DMAEMA[c]	95	7600	1.30	50	50	51
DMAEMA[c]	99	14 400	1.32	98	100	114
DMAEMA[c]	90	23 600	1.30	180	150	160
BuMA[c]	98	18 600	1.40	98	132	144
St[d]	28	2600	1.30	28	28	28
BuA[c]	40	17 700	1.35	80	138	120

[a] GPC calibrated with PMMA standards. [b] (mol monomer)/(mol RAFT agent) × (polymerization yield). [c] Polymerization in benzene. [d] Polymerization in xylene; molar ratio of AIBN/CTA = 0.625; monomer concentration = 3 M; DMAEMA = 2-(dimethylamino)ethyl methacrylate; BuMA = *n*-butyl methacrylate; BuA = *n*-butyl acrylate; St = styrene. Polymerization time: 20 h.

Last year, we reported the synthesis of amphiphilic polymer conetworks via RAFT based on methacrylate units.[20] Herein, we report the preparation of amphiphilic polymer conetworks based on three different monomer units: methacrylates, acrylates and styrenics. The degrees of swelling (DSs) of all conetworks are determined in tetrahydrofuran (THF) and, where the ionizable 2-(dimethylamino)ethyl methacrylate (DMAEMA) is present, the DSs are also measured in neutral and acidic water.

Experimental Section

Materials. THF (HPLC grade, LabScan) was dried over a Na/K (Fluka, Aldrich) alloy under reflux conditions for 3 days before distilling it under an inert nitrogen atmosphere immediately prior

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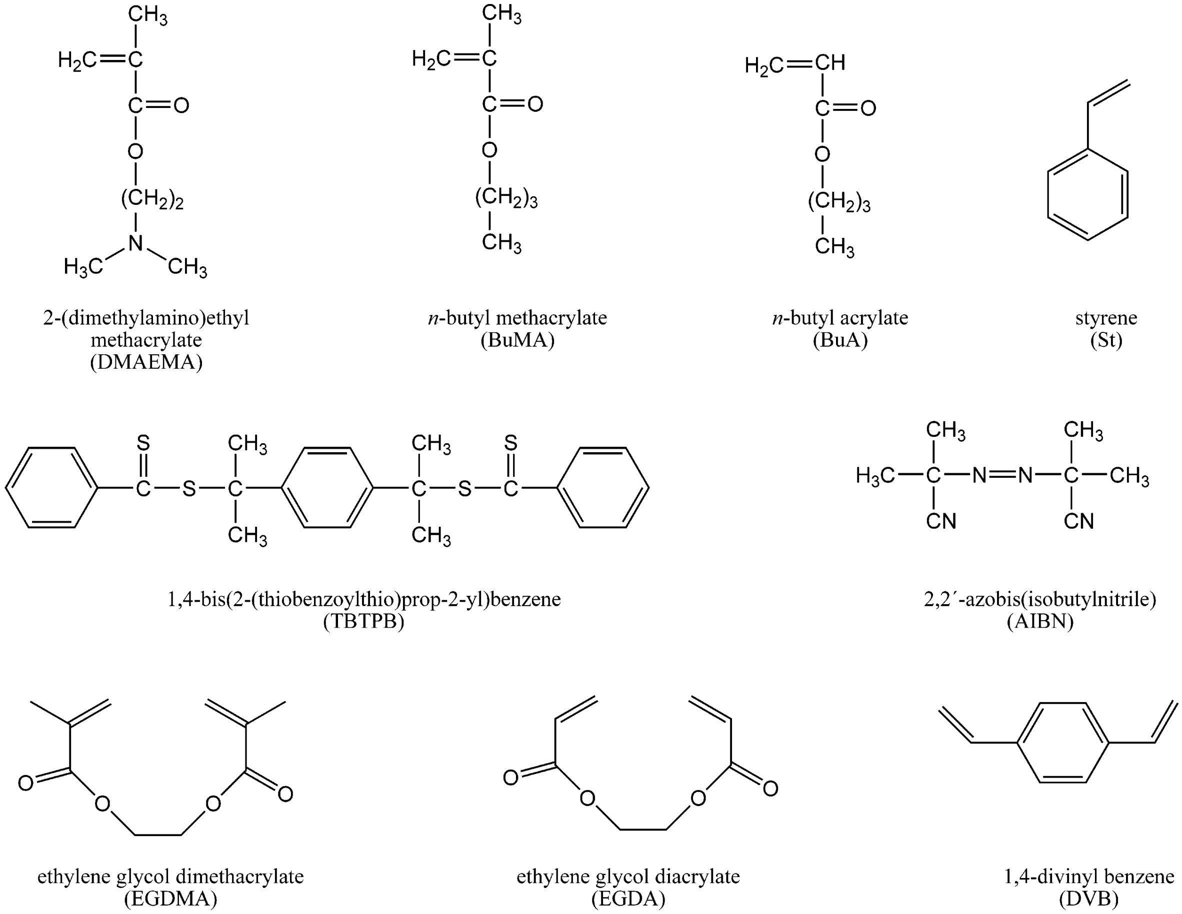

Figure 1. Chemical structures and names of the main reagents used for the (co)network synthesis.

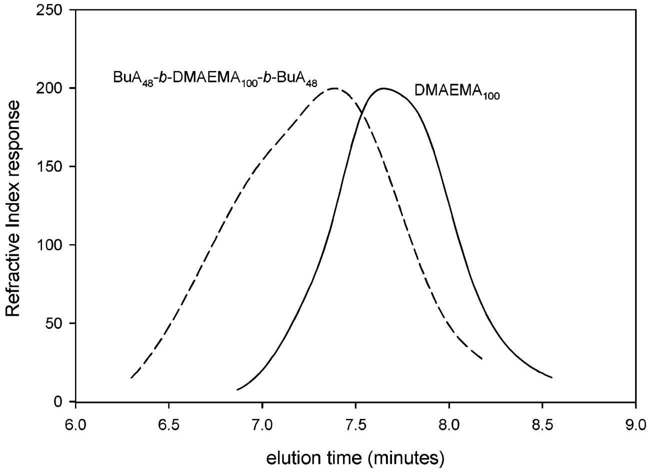

Figure 2. GPC traces of the $DMAEMA_{100}$ homopolymer and the corresponding triblock copolymer BuA_{48}-*b*-$DMAEMA_{100}$-*b*-BuA_{48} prepared by chain growth of the former with *n*-butyl acrylate being the second monomer.

to the polymerization reaction. Xylene (Merck, 99.5%) and benzene (BDH, 99%) were stored over CaH_2 (Aldrich, 90−95%), before distillation under reduced pressure immediately prior to the polymerization reactions. Ethanol (99.6%), methanol (99.9%), petroleum ether (LabScan, 99%), *n*-hexane (LabScan, 99%) and diethyl ether (LabScan, 99.5%) were used as received. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 99%), *n*-butyl methacrylate (BuMA, Aldrich, 99%), *n*-butyl acrylate (BuA, Aldrich, 99%), styrene (St, Aldrich, 99%), 1,4-divinylbenzene (DVB, Aldrich, 80%), ethylene glycol dimethacrylate (EGDMA, Aldrich, 99%) and ethylene glycol diacrylate (EGDA, Acros, 90%) were passed through basic alumina columns and stored over CaH_2 and 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, Aldrich, 95%) free radical inhibitor. This was followed by distillation under reduced pressure, and storage under nitrogen atmosphere prior to use. 2,2′-Azobis(isobutylnitrile) (AIBN, Aldrich, 95%) was recrystallized from ethanol. Sulfur (powder ∼ 100 mesh), benzyl chloride (99%), silica gel (60 Å, 70−230 mesh) were purchased from Aldrich and were used as received. Carbon tetrachloride (Riedel de Haën, ≥99.8%), 1,4-diisopropenylbenzene (TCI Europe, 98%) and deuterated chloroform (Merck) were also used as received.

Analyses. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) used as an internal standard using an Avance Bruker 300 MHz spectrometer equipped with an Ultrashield magnet. The MWs and polydispersity indices (PDIs) of the polymer precursors to the networks and the sol fraction were determined by gel permeation chromatography (GPC) using equipment supplied by Polymer Laboratories Ltd. All measurements were carried out at room temperature using a single PL-Mixed "D" column (bead size = 5 μm; pore sizes = 100, 500, 10^3, 10^4 Å). The mobile phase was THF (containing 2% triethylamine), delivered at a flow rate of 1 mL min^{-1} using a Waters 515 isocratic pump. The refractive index was measured with an ERC-7515A refractive index detector also supplied by Polymer Laboratories Ltd. The instrumentation was calibrated using poly(methyl methacrylate) (PMMA) standards with low PDIs (MWs of 630, 2680, 4250, 13000, 28900, 50000, 128000, and 260000 g mol^{-1}) supplied by Polymer Laboratories Ltd.

Syntheses. Synthesis of 1,4-Bis(2-(thiobenzoylthio)prop-2-yl)benzene (TBTPB). A bifunctional chain transfer agent (CTA), TBTPB, was synthesized following the procedure reported by Rizzardo et al.[21]

Synthesis of Linear Precursors to the Networks. Synthesis of Homopolymers. A typical RAFT polymerization procedure for the synthesis of different homopolymers is described as follows: To a round-bottom flask (50 mL) equipped with an egg-shaped

Table 2. Polymerization Yields, Size, and Composition Characteristics of the ABA Triblock Copolymers Synthesized by Chain Extension of PolyDMAEMA Macro RAFT Agents

			GPC results[b]		degree of polymerization		
macro RAFT	second monomer	yield, %	M_n	M_w/M_n	theory[a]	GPC[b]	^{1}H NMR
$DMAEMA_{150}$	BuMA	97	30 500	1.48	194	190	200
$DMAEMA_{100}$	St	28	31 750	1.70	135	128	123
$DMAEMA_{100}$	BuA	33	24 800	1.60	117	196	180

[a] (mol monomer)/(mol RAFT agent) × (polymerization yield). [b] GPC calibrated with PMMA standards; DMAEMA = 2-(dimethylamino)ethyl methacrylate; BuMA = *n*-butyl methacrylate; BuA = *n*-butyl acrylate; St = styrene. Polymerization time: 20 h.

Table 3. Mass Percentage and Size and Composition Characteristics of the Sol Fraction (Extractables) of the (Co)Networks[a]

	extractables				precursors		
experimental network structure[b]	mass %	M_n	M_w/M_n	DMAEMA, %	M_n	M_w/M_n	DMAEMA, %
$DMAEMA_{50}$	12	6750	1.46	100	7600	1.30	100
$DMAEMA_{100}$	11	12 100	1.47	100	14 400	1.32	100
$DMAEMA_{150}$	15	19 200	1.58	100	23 600	1.30	100
$BuMA_{132}$	9	15 650	1.33	0	18 600	1.40	0
St_{28}	15	2400	1.63	0	2600	1.30	0
BuA_{138}	12	22 150	1.51	0	17 700	1.35	0
$BuMA_{20}$-*b*-$DMAEMA_{150}$-*b*-$BuMA_{20}$	12	27 400	1.69	72	30 500	1.48	79
St_{14}-*b*-$DMAEMA_{100}$-*b*-St_{14}	23	21 250	2.1	76	31 750	1.70	78
BuA_{48}-*b*-$DMAEMA_{100}$-*b*-BuA_{48}	18	ND[c]	ND	ND	24 800	1.60	56

[a] The size and composition characteristics of the corresponding linear precursors are also shown in the table. [b] DMAEMA = 2-(dimethylamino)ethyl methacrylate; BuMA = *n*-butyl methacrylate; St = styrene; BuA = *n*-butyl acrylate. [c] ND: not determined.

Table 4. Degrees of Swelling of All the (Co)Networks in Various Solvents

	degrees of swelling[a]		
experimental network structure	THF	neutral water	acid water
EGDMA-*b*-$DMAEMA_{50}$-*b*-EGDMA	3.9 ± 0.3	3.6 ± 0.1	11.9 ± 0.5
EGDMA-*b*-$DMAEMA_{100}$-*b*-EGDMA	8.1 ± 0.7	4.6 ± 0.3	38.1 ± 1.0
EGDMA-*b*-$DMAEMA_{150}$-*b*-EGDMA	8.6 ± 1.7	5.6 ± 0.4	49.9 ± 0.7
EGDMA-*b*-$BuMA_{132}$-*b*-EGDMA	11.0 ± 2.1		
DVB-*b*-St_{28}-*b*-DVB	5.8 ± 0.9		
EGDA-*b*-BuA_{138}-*b*-EGDA	11.3 ± 6.0		
EGDMA-*b*-$BuMA_{20}$-*b*-$DMAEMA_{150}$-*b*-$BuMA_{20}$-*b*-EGDMA	12.1 ± 2.0	4.8 ± 0.3	21.2 ± 0.9
DVB-*b*-St_{14}-*b*-$DMAEMA_{100}$-*b*-St_{14}-*b*-DVB	44.3 ± 4.8	8.6 ± 0.9	34.1 ± 1.7
EGDA-*b*-BuA_{48}-*b*-$DMAEMA_{100}$-*b*-BuA_{48}-*b*-EGDA	10.5 ± 1.5	5.2 ± 0.6	15.0 ± 0.8

[a] Degrees of swelling of the networks together with the 95% confidence intervals DMAEMA = 2-(dimethylamino)ethyl methacrylate; BuMA = *n*-butyl methacrylate; St = styrene; BuA = *n*-butyl acrylate; EGDMA = ethylene glycol dimethacrylate; EGDA = ethylene glycol diacrylate; DVB = 1,4-divinylbenzene; THF = tetrahydrofuran.

PTFE stirring bar and maintained under a dry nitrogen atmosphere was added freshly distilled DMAEMA (9.33 g, 59.0 mmol) using Schlenk-line techniques. CTA (275 mg, 0.59 mmol) and AIBN (61.0 mg, 0.369 mmol) were dissolved in benzene (10 mL) and were added to the monomer with the aid of a syringe. The reaction mixture was stirred at room temperature, degassed by three freeze−evacuate−thaw cycles and heated at 65 °C for 20 h. The polymerization was terminated by cooling the reaction down to room temperature. The produced polyDMAEMA (9.2 g, 98.6% polymerization yield) was retrieved by precipitation in *n*-hexane (150 mL). Similarly, polySt was also precipitated in *n*-hexane, whereas polyBuMA and polyBuA were retrieved by precipitation in methanol. After precipitation, all homopolymers were left to dry under vacuum at room temperature for 24 h.

Synthesis of ABA Triblock Copolymers. A typical RAFT polymerization procedure for the synthesis of different copolymers is described as follows: To a round-bottom flask (50 mL) equipped with an egg-shaped PTFE stirring bar was added St (1.80 g, 17.3 mmol) under a dry nitrogen atmosphere using Schlenk-line techniques. AIBN (14.2 mg, 0.086 mmol) and polyDMAEMA (M_n = 14 400 g mol^{-1}, 2.0 g, 0.14 mmol, bifunctional macroCTA) were dissolved in xylene (4 mL) and were added to the monomer with the aid of a syringe. The reaction mixture was stirred at room temperature, degassed by three freeze−evacuate−thaw cycles and heated at 65 °C for 20 h. The polymerization was terminated by cooling the reaction down to room temperature. The resulting St-*b*-DMAEMA-*b*-St triblock copolymer (2.51 g, 28.3% polymerization yield) was retrieved by precipitation in *n*-hexane (50 mL). It was then dried under vacuum at room temperature for 24 h. The copolymers of the type BuMA-*b*-DMAEMA-*b*-BuMA and BuA-*b*-DMAEMA-*b*-BuA were also retrieved by precipitation in *n*-hexane and left to dry under vacuum at room temperature for 24 h.

Synthesis of Networks. Synthesis of Homopolymer Networks. A typical procedure for the synthesis of homopolymer networks is described as follows: To a round-bottom flask equipped with an egg-shaped stirring bar was added EGDMA (0.27 g, 1.43 mmol) under an inert nitrogen atmosphere using Schlenk-line techniques. AIBN (14.6 mg, 0.089 mmol) and polyDMAEMA (M_n = 14 400 g mol^{-1}, 2.03 g, 0.142 mmol) were dissolved in THF (8 mL) and were transferred to the reaction flask with the aid of a syringe. The mixture was degassed by three freeze−evacuate−thaw cycles and it was then placed in an oil bath at 63 °C. Gelation was reached within 24 h. EGDA and DVB were also used in a similar way to cross-link BuA and St homopolymers respectively.

Synthesis of Conetworks. A typical procedure for the synthesis of copolymer networks is described as follows: To a round-bottom flask equipped with an egg-shaped stirring bar was added EGDMA (0.06 g, 0.33 mmol) under an inert nitrogen atmosphere using Schlenk-line techniques. AIBN (3.4 mg, 0.021 mmol) and BuMA-*b*-DMAEMA-*b*-BuMA (M_n = 30 500 g mol^{-1}, 1.0 g, 0.033 mmol) were dissolved in THF (4 mL) and were transferred to the reaction flask with the aid of a syringe. The mixture was degassed by three freeze−evacuate−thaw cycles, and it was then placed in an oil bath at 63 °C. Gelation was reached within 24 h. EGDA and DVB were also used in a similar way to convert to conetworks the BuA-*b*-DMAEMA-*b*-BuA and the St-*b*-DMAEMA-*b*-St triblock copolymers, respectively.

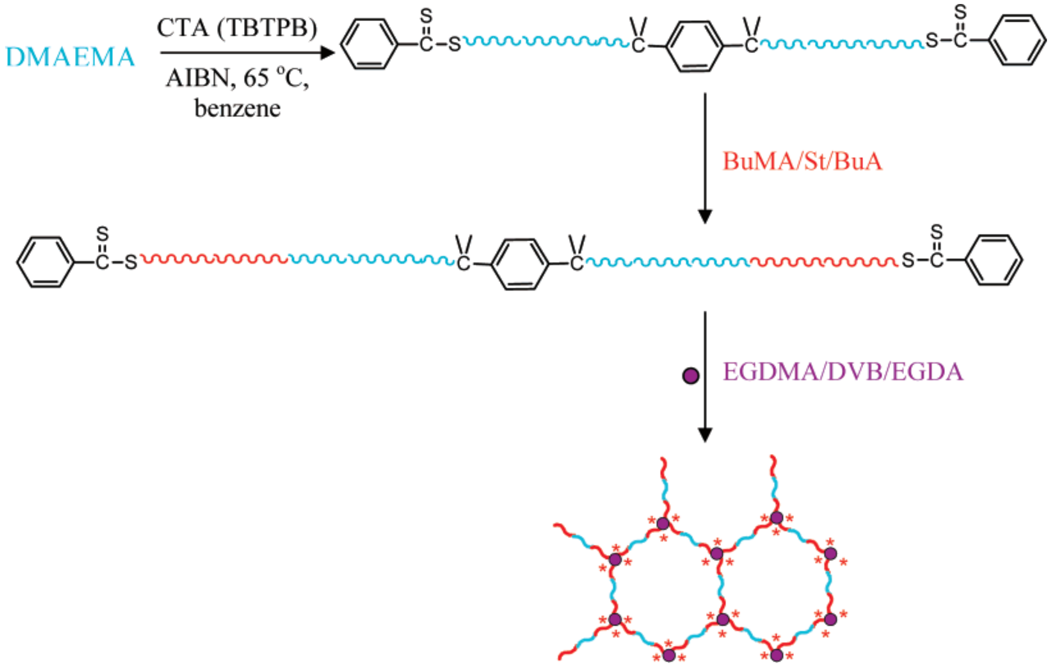

Figure 3. Schematic representation of the synthesis of the amphiphilic polymer conetworks via the RAFT process by the stepwise preparation of homopolymers and ABA triblock copolymers, and the subsequent cross-linking of the latter.

Characterization of the (Co)Networks. Determination of the Sol Fraction. The prepared (co)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 solvent was recovered by filtration and evaporated off under reduced pressure. The recovered extractables were dried under vacuum at room temperature for 72 h. The sol fraction was calculated as the ratio of the dried mass of the extractables divided by the theoretical mass of all components in the network (i.e., polymer plus cross-linker).

Determination of the Degree of Swelling. The washed (co)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 (co)network mass was then determined, followed by the transfer of the DMAEMA-containing (co)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%. This was accomplished by the addition of the appropriate number of drops of 0.5 and 0.05 M HCl standard solutions. The required number of moles of HCl in each sample was calculated as 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 (co)network mass times the percentage of the DMAEMA units in the (co)network (calculated by ^{1}H NMR analysis of the linear copolymer precursor to the (co)network), divided by the molecular weight (molar mass) of the DMAEMA unit. The samples were left to equilibrate for 3 weeks and the water-swollen co-network masses were measured. The DSs were calculated as the ratio of the swollen (co)network mass divided by the dry network mass.

Results and Discussion

Figure 1 illustrates the chemical structures and names of monomers, cross-linkers, initiator and the bifunctional CTA used for polymer synthesis.

Synthesis of Homopolymers by RAFT Using the Bifunctional CTA. Table 1 lists the synthesized homopolymers along with their polymerization yields and molecular characteristics.

All polymers were characterized by relatively narrow molecular weight distributions and low polydispersity indices ($<$1.4), demonstrating the controlled character of the RAFT process. In all cases, the degrees of polymerization determined by GPC and ^{1}H NMR were found to be in good agreement with each other. Furthermore, higher yields as well as higher degrees of polymerization were observed in the case of the methacrylate monomers (DMAEMA and BuMA) compared to BuA and St. This could be explained by the fact that in RAFT mediated polymerization where the thiocarbonyl–thio radical intermediate is stabilized by a strongly electron donating group such as phenyl, a slower fragmentation of the acrylate or styrenic radicals compared to methacrylate radicals is promoted. Therefore, even though the propagation rate of the acrylate or styrenic radicals remains unchanged, the overall polymerization rate is retarded,[17,22] leading to lower polymerization yields.

Synthesis of ABA Triblock Copolymers via RAFT. Amphiphilic ABA triblock copolymers were synthesized using polyDMAEMA as a macro RAFT agent. With the exception of the polymerization of St, which proceeded in a more controlled manner in xylene rather than in benzene or in the bulk, in all other cases benzene was used as a solvent. The degree of polymerization of the pre-synthesized polyDMAEMA was either 100 or 150. Table 2 lists the second monomer used, the polymerization yields, and the size and composition characteristics of these ABA triblock copolymers.

Higher yields and greater control over the degree of polymerization were observed in the case of the $\mathrm{BuMA_{20}}$-*b*-$\mathrm{DMAEMA_{150}}$-*b*-$\mathrm{BuMA_{20}}$ triblock copolymer compared to the cases where an acrylate or a styrenic monomer was added onto the ends of a polyDMAEMA macro CTA chain, for the same reason discussed earlier for the homopolymerizations. The PDIs of the resulting copolymers ranged between 1.5 and 1.7. In a recent publication,[20] similar PDI values corresponding to triblock, methacrylate-based copolymers of the ABA and BAB type prepared by RAFT were reported. In the same study, it was also demonstrated—on the basis of kinetic studies—that, despite the relatively high PDIs, RAFT polymerization proceeded in a controlled and "living" manner. The controlled nature of the polymerizations in this study is demonstrated in Figure 2 which displays the GPC traces of a DMAEMA homopolymer and the corresponding BuA-*b*-DMAEMA-*b*-BuA

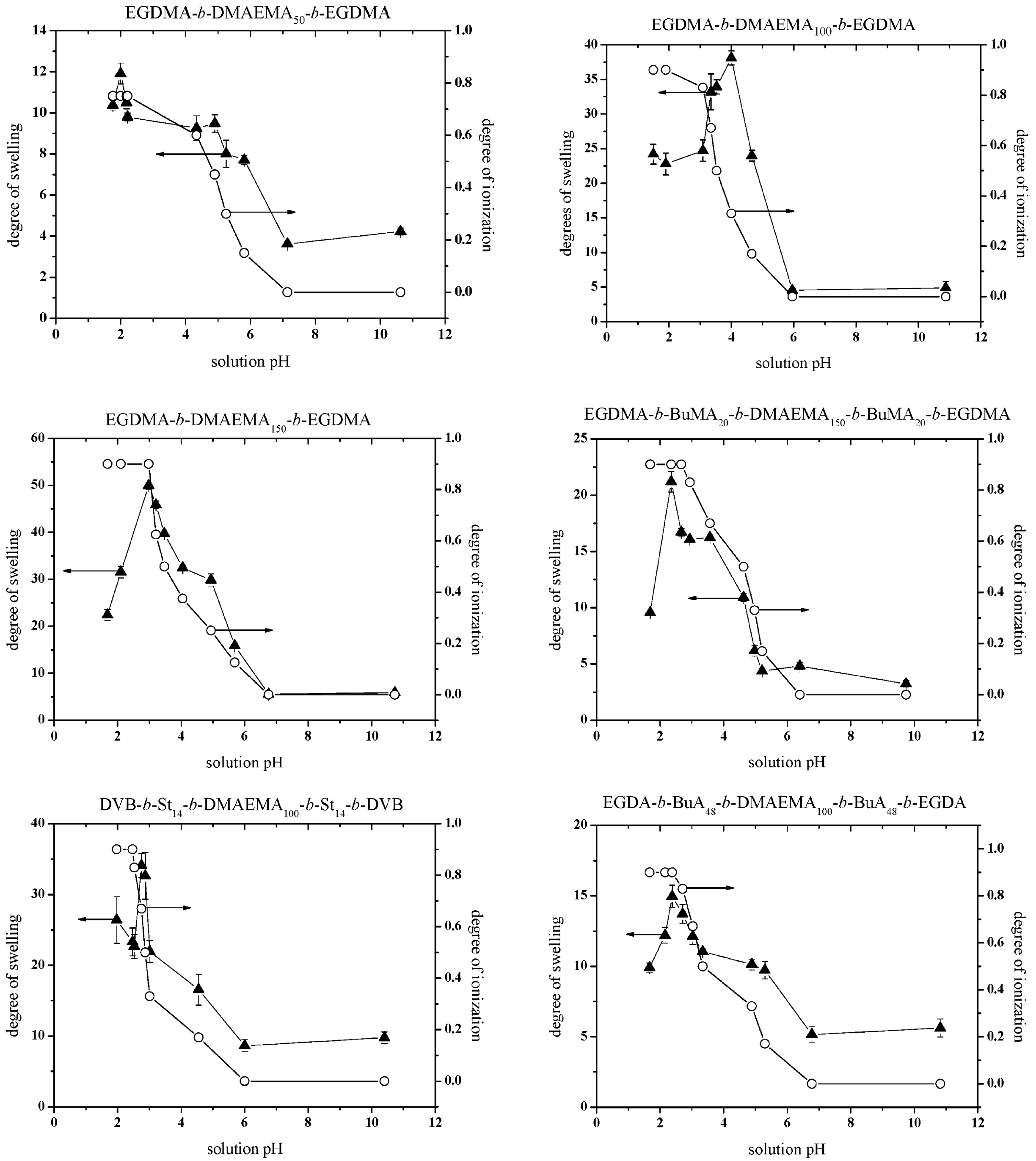

Figure 4. Degrees of swelling and degrees of ionization of all the 2-(dimethylamino)ethyl methacrylate-containing networks as a function of pH. DMAEMA = 2-(dimethylamino)ethyl methacrylate; BuMA = *n*-butyl methacrylate; BuA = *n*-butyl acrylate; St = styrene; EGDMA = ethylene glycol dimethacrylate; EGDA = ethylene glycol diacrylate; DVB = 1,4-divinylbenzene.

triblock copolymer. The MWD of the triblock copolymer is shifted toward higher MWs compared to that of the homopolymer, demonstrating the block efficiency from homopolymer to block copolymer. However, the high MW shoulder present in the chromatogram indicates partial recombination of polymer chains.

Synthesis of Amphiphilic Co-Networks. Figure 3 represents schematically the synthetic methodology followed for the synthesis of the amphiphilic conetworks of this study. The number of arms per cross-link is not three, as indicated in the figure, but higher, typically between 10 and 20. Amphiphilic triblock copolymer co-networks were prepared by RAFT via the interconnection of the linear ABA triblock copolymer precursors at their two active ends by chemical cross-linking to a three-dimensional co-network using the appropriate cross-linker: ethylene glycol dimethacrylate for methacrylates, ethylene glycol diacrylate for acrylates, and 1,4-divinylbenzene for styrenics. The gelation point, manifested by the cease of the motion of the magnetic stirring bar, was reached within 24 h.

Determination of the Sol Fraction of the (Co)Networks. Table 3 shows the mass percentage, the number-average MWs, PDIs, and DMAEMA content of the sol fraction of the (co)networks determined by GPC and ^{1}H NMR. For comparison, the molecular characteristics (M_n, PDI, DMAEMA content) of the polymer precursors to the (co)networks are also presented. The sol fraction (extractables) of the (co)networks prepared by RAFT varied from 9 to 23%, with the highest percentage corresponding to that based on the St$_{14}$-*b*-DMAEMA$_{100}$-*b*-St$_{14}$

triblock copolymer. This is consistent with the higher DSs of this particular co-network measured in THF and neutral and acidic water presented in Table 4. Table 3 shows that the M_ns of the extractables were similar to (and in most cases lower than) the M_ns of the corresponding linear precursors. Moreover, the PDIs of the extractables were higher than those of the corresponding linear precursors, manifesting a poorer size homogeneity of the former. The DMAEMA content of the extractables was found to be similar to that of the corresponding linear precursors. The lower M_ns of the extractables than those of the precursors might be due to the presence of early deactivated chains, which, on the one hand did not grow to the average chain MW, and, on the other hand, could not add to cross-linker units. The extractables probably also contained active chains which did not add to cross-linker units due to steric hindrance. The presence of these two chain populations in the extractables led to their increased PDIs.

Determination of the Swelling Behavior of the (Co)Networks. Table 4 shows the DSs of all the (co)networks in THF and, where the ionizable DMAEMA was present, the DSs in neutral and acidic water as well. Higher DSs of DMAEMA homopolymer networks and DMAEMA copolymer conetworks were reached in acidic water rather than in neutral water or in THF. This is explained by the fact that the DMAEMA units, as tertiary amines, are capable of being positively charged below a certain pH value (in this case at pH < 8). On the other hand, the DSs of the copolymer co-networks in THF were higher than the aqueous DSs at neutral pH due to the fact that THF is a good (nonselective) solvent for both the hydrophilic (DMAEMA) and the hydrophobic (BuMA, BuA, or St) units, whereas water is a selective solvent for the DMAEMA units. All copolymer conetworks presented higher DSs in THF than the respective homopolymer networks in the same solvent, because of the higher degree of polymerization of the copolymer chains. An increase of the degree of polymerization for the DMAEMA homopolymers from 50 to 100 to 150 resulted in an increase of the DSs in all three solvents, as expected.

In Figure 4, the plots of the DSs and degrees of ionization (DI) vs the solution pH for all the DMAEMA-based homopolymer and copolymer (co)networks are presented. In all cases, a decrease in pH below 7 caused an increase in the DS that reached a maximum value at pH ~ 3. This increase is attributed to the fact that, at low pH, the DMAEMA units in the networks became ionized. The cations formed caused the generation of electrostatic repulsions between the (co)network chains. Furthermore, the accumulation of the chloride counterions established an osmotic pressure within the (co)networks. For those two reasons swelling was promoted at lower pH. At the lowest pH values the DS declined, due to the high ionic strength conferred to the system by the relatively high concentration of HCl under these conditions. This as well as the fact that the DS vs pH curves followed the DI vs pH curves, as depicted in Figure 4, confirm the dominance of the electrostatic interactions on the swelling behavior of the networks below pH 7.

Conclusions

It has been demonstrated that RAFT polymerization is a versatile method for the preparation of polymer (co)networks based on different types of monomer units, such as methacrylates, acrylates, and styrenics. A series of homopolymer and ABA triblock copolymer (co)networks of various chemical compositions were prepared, and their swelling behavior was investigated in aqueous and organic media. The large increase in the swelling observed with the DMAEMA-containing (co)networks at low pH was dominated by the electrostatic forces established by the ionization of the DMAEMA units.

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