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End-Linked Poly[2-(dimethylamino)ethyl Methacrylate]−Poly(methacrylic acid) Polyampholyte Conetworks: Synthesis by Sequential RAFT Polymerization and Swelling and SANS Characterization

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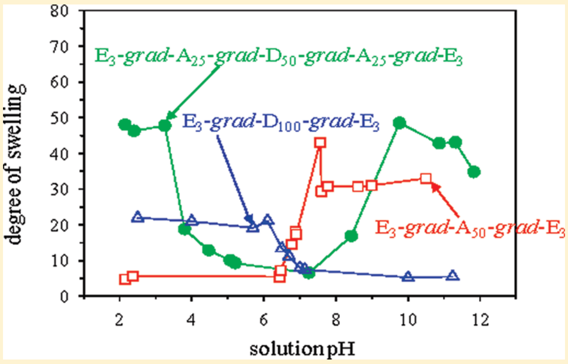

ABSTRACT: Four well-defined end-linked triblock polyampholyte conetworks composed of positively ionizable 2-(dimethylamino)ethyl methacrylate (DMAEMA) repeating units and negatively ionizable methacrylic acid (MAA) repeating units were synthesized using one-pot, sequential reversible addition−fragmentation chain transfer (RAFT) polymerization, by employing 1,4-bis[2-(thiobenzoylthio)prop-2-yl]-benzene (1,4-BTBTPB) as the chain transfer agent, and ethylene glycol dimethacrylate (EGDMA) as the cross-linker. From the four end-linked conetworks, three were based on ABA triblock polyampholytes with polyDMAEMA midblocks with a constant degree of polymerization (DP) and polyMAA end-blocks of different DPs. The fourth end-linked polyampholytic conetwork was based on an equimolar BAB triblock polyampholyte with a polyMAA midblock. Furthermore, two polyampholyte networks were also prepared: one based on an end-linked equimolar statistical polyampholyte, and one with a randomly cross-linked, rather than an end-linked, architecture. Finally, the two homopolymer networks based on the DMAEMA and the MAA monomers were also synthesized. The MAA units were introduced in the (co)networks via the polymerization of 2-tetrahydropyranyl methacrylate (THPMA) followed by its acid hydrolysis after (co)network formation. The linear precursors to the (co)networks were found to have molecular weights and compositions close to the expected values, whereas the extractables from the (co)networks were determined to be lower than 30%. In water, the degrees of swelling (DS) of all the polyampholyte (co)networks presented a characteristic minimum at intermediate pH values, around the (co)network isoelectric point (p*I*), while they increased at acidic and basic pHs. The p*I* values of the ampholytic (co)networks were estimated as the midpoints of the regions of reduced swelling and ranged between 5.3 and 6.8, decreasing with the increase of the MAA content in the (co)networks. Finally, small-angle neutron scattering (SANS) studies of the polyampholyte (co)networks swollen in D_2O provided SANS profiles without any peaks but broad shoulders whose location was consistent with the spacing of the cross-linking cores.

INTRODUCTION

Polyampholyte[1−5] networks[6−12] are cross-linked polymers bearing both acidic and basic units which are usually randomly distributed. When these units are weakly acidic or weakly basic, the polyampholyte networks display a great pH-responsiveness, with large aqueous degrees of swelling and high chain extensions at extreme pH values, and minimum swelling and chain contraction at an intermediate pH range around the isoelectric point, p*I*, the pH of zero net change. These materials have found applications in medicine,[6−8] most notably for drug release[9] and DNA adsorption,[10] and in metal-ion adsorption and removal.[11]

Despite the large number of studies on polyampholyte networks,[6−12] the structure of most of these materials is poorly defined, with the chains between the network junctions (so-called elastic chains) displaying broad molecular weight distributions, a result of the simultaneous free radical cross-linking copolymerization of the monomers and the cross-linker. Availability of better-defined polyampholyte networks[13] would enable the derivation of accurate structure−property relationships and may broaden their applications horizon.

Control over the length and composition of the network polyampholyte chains can most conveniently be achieved by the use of "living" polymerization techniques, such as anionic polymerization.[14] To date, the only reports on the preparation of well-defined polyampholyte (co)networks made use of sequential group transfer polymerization (GTP),[15] a controlled, "quasiliving"[16] anionic polymerization method best-suited for methacrylates, for the one-pot synthesis of end-linked ABA triblock polyampholytes,[17] and end-linked star polyampholytes.[18] As the acidic and basic units were placed in separate segments, these well-defined

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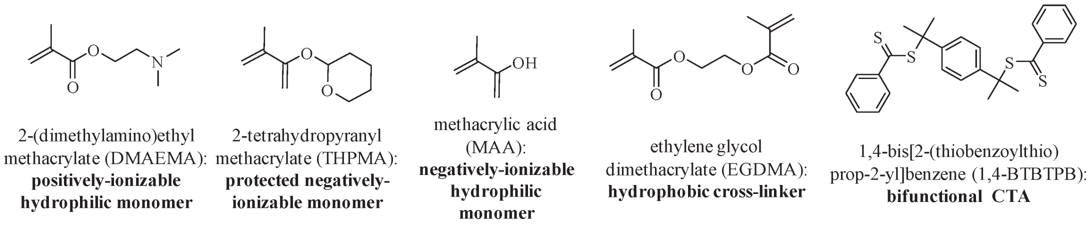

Figure 1. Chemical structures and names of the main reagents used for the (co)network synthesis.

materials are called polyampholyte "conetworks" rather than just "networks".

Controlled radical polymerization (CRP) methods represent a modern and powerful synthetic tool for the preparation of well-defined polymers. Among them is reversible addition−fragmentation chain transfer (RAFT) polymerization,[19] which can be applied to a great range of monomers, including acrylates, methacrylates, styrenics and acrylamides. This method has extensively been used for the preparation of various types of copolymers, including block, graft, and star copolymers. However, there are only a small number of reports on the application of RAFT polymerization for the synthesis of well-defined conetworks, all of which concern amphiphilic rather than ampholytic systems.[20,21] The aim in this investigation is to extend previous work on well-defined polyampholyte conetworks synthesized by GTP[17,18] and prepare well-defined end-linked polyampholyte conetworks using RAFT polymerization. This extension proved to be *nonstraightforward* as certain challenges had to be addressed, including the protection of the acidic monomer and the compatibility of this protected monomer with the RAFT process. After these issues were resolved, the synthesis of several well-defined polyampholyte (co)networks was accomplished. These materials covered a range of compositions and architectures, and were thoroughly characterized in terms of their aqueous swelling properties as a function of pH gravimetrically and also in terms of their structure in water using small-angle neutron scattering (SANS).

EXPERIMENTAL SECTION

Materials. The monomers 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%) and methacrylic acid (MAA, 99%), the cross-linker ethylene glycol dimethacrylate (EGDMA, 98%), basic alumina, calcium hydride (CaH_2, 90−95%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%), magnesium (98%), silica gel (60 Å, 70−230 mesh), *n*-hexane (≥96%), diethyl ether (≥99.7%), and 1,4-dioxane (99%) were purchased from Aldrich, Germany. The monomer 2-tetrahydropyranyl methacrylate (THPMA) was synthesized in our laboratory as detailed in a following section. Bromobenzene (≥99.5%) was purchased from Fluka, Germany. 1,4-Diisopropenyl benzene (97%) was purchased from TCI Europe, Belgium. 2,2′-Azobis(isobutyronitrile) (AIBN, 95%), carbon disulfide (purity ≥99.5%), ethanol (99.9%) and deuterated chloroform ($CDCl_3$) were purchased from Merck, Germany. Tetrahydrofuran (THF, 99.8%, both HPLC and reagent grade) was purchased from Scharlau, Spain.

Methods. Inhibitors and acidic impurities were removed from the DMAEMA monomer and the EGDMA cross-linker by passing these materials through basic alumina columns. This was followed by stirring DMAEMA and EGDMA over CaH_2, in the presence of the free radical inhibitor DPPH, for 72 h to neutralize the last traces of moisture, and a vacuum distillation. The AIBN radical initiator was recrystallized twice from ethanol. The polymerization solvent 1,4-dioxane was dried over CaH_2 and vacuum distilled prior to use.

Synthesis of THPMA. The THPMA monomer was synthesized based on a modification of the procedure reported by Hertler.[22] In particular, THPMA was prepared by the esterification reaction of MAA with a 150% excess of 3,4-dihydro-2*H*-pyran at 65 °C over a 48 h period. In the mixture, a small amount of the free radical inhibitor DPPH was added to protect THPMA and MAA from undesired thermal polymerization.

Synthesis of the Chain Transfer Agent. The bifunctional chain transfer agent (CTA) 1,4-bis[2-(thiobenzoylthio)prop-2-yl]benzene (1,4-BTBTPB) was prepared by the reaction of 2 g of dithiobenzoic acid (DTBA) (13.0 mmol) with 0.98 g of 1,4-diisopropenyl benzene (6.20 mmol) in the presence of a catalytic amount (0.1 g) of *p*-toluenesulfonic acid (0.5 mmol) as described in the literature.[23] The required DTBA was prepared following the procedure given by Jayalakshmi et al.[24] Briefly, 1.1 g of Mg (45.8 mmol) and 127 mL of THF were transferred into a three-necked round-bottom flask, and then, 4.8 mL of bromobenzene (7.1 g, 45.5 mmol) was added dropwise into the reaction mixture. The reaction was carried out at 40 °C until the Mg was completely consumed and disappeared. Then, 2.7 mL of carbon disulfide (3.5 g, 45.4 mmol) was added dropwise over 20 min and left to react for 1 h at −5 °C. The successful synthesis of the CTA was confirmed by ^1H and ^{13}C NMR spectroscopies.

(Co)network Preparation. Figure 1 displays the chemical structures and names of the monomers, the cross-linker, and the bifunctional CTA used for the synthesis of the polyampholyte (co)networks.

The synthesis of the (co)networks was accomplished by a one-pot, sequential monomer, and cross-linker RAFT polymerization in Schlenk tubes, without isolation of the intermediate polymer precursors. A 6 : 1 molar ratio of EGDMA : CTA was used, following the conclusions of a previous study[21] in which the synthesis of DMAEMA homopolymer networks was optimized. (Co)networks of different compositions and different architectures were prepared. Composition variation was accomplished through the variation of the polyTHPMA end-block lengths at a constant polyDMAEMA middle block length, whereas architecture variation was achieved by the variation the order of addition of the reagents. End-linked conetwork synthesis required the sequential addition of monomers (in the appropriate order) and the cross-linker, while for the synthesis of randomly cross-linked polyampholyte network all the reagents were simultaneously terpolymerized. The THPMA units in the (co)networks were converted to MAA units by acid hydrolysis after (co)network formation and washing.

This paragraph details the procedure followed for the synthesis of one of the conetworks based on an end-linked ABA triblock copolymer. In particular, we describe the preparation of the equimolar ABA triblock copolymer-based end-linked conetwork with the structure $EGDMA_3$-*grad*-$THPMA_{25}$-*grad*-$DMAEMA_{50}$-*grad*-$THPMA_{25}$-*grad*-$EGDMA_3$. Note that the sequential rather than stepwise (which would have involved polymer precipitation and isolation after each synthetic step) polymerizations, employed to enhance the "livingness" of the system (to secure the preservation of more active polymerization sites), resulted in gradient rather than pure block copolymer structures. A 25 mL Schlenk tube containing a magnetic stirring bar was loaded with 83.0 mg of the bifunctional CTA 1,4-BTBTPB (0.178 mmol), 18.3 mg of AIBN (0.1 mmol), 1.5 mL of freshly distilled DMAEMA (1.4 g, 8.9 mmol), and 1.5 mL of freshly distilled 1,4-dioxane. The contents of the tube were subsequently degassed by three freeze−vacuum−thaw cycles, were placed under an inert nitrogen atmosphere, and were heated in an oil bath at 70 °C for 12 h. The produced DMAEMA homopolymer was sampled for gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy analyses (monomer conversion by ^{1}H NMR spectroscopy = 87.5%; GPC number-average molecular weight = M_n = 9150 g mol^{-1}; theoretical molecular weight (MW) = 8000 g mol^{-1}; M_w/M_n = polydispersity index (PDI) = 1.5; M_w is the weight-average molecular weight). Afterward, 1.5 mL of THPMA (1.5 g, 8.8 mmol) was added and was left to polymerize for 12 h. A sample of the synthesized ABA triblock copolymer was also obtained for GPC and ^{1}H NMR spectroscopy analyses (THPMA conversion by ^{1}H NMR spectroscopy = 83.4%; GPC M_n = 16000 g mol^{-1}; MW theory = 16500 g mol^{-1}; PDI = 1.5; THPMA/DMAEMA molar ratio in copolymer by ^{1}H NMR spectroscopy = 0.95), EGDMA cross-linker (0.2 mL, 0.2 g, 1.1 mmol) was added, resulting in gel formation within 24 h. Before the addition of EGDMA, 1 mL of 1,4-dioxane was added into the polymerization mixture to reduce the viscosity of the mixture.

For the preparation of the BAB triblock (with a THPMA midblock) copolymer-based end-linked conetwork, the addition of the two comonomers was reversed, with THPMA polymerized first. However, during its RAFT homopolymerization, THPMA was partially (45%) hydrolyzed to MAA units. This observation was consistent in all three repetitions of this synthesis. This problem was overcome by the addition of triethylamine to the polymerization solvent, which protected THPMA from hydrolysis. The idea of adding a tertiary amine to protect THPMA from hydrolysis was the result of the observation that THPMA always smoothly polymerized, without hydrolysis, when this was added as the second monomer, in the presence of the homopolymer of DMAEMA, a tertiary amine itself. Thus, rather than using 1.5 mL of 1,4-dioxane as polymerization solvent, a mixture composed of 0.75 mL of triethylamine and 0.75 mL of 1,4-dioxane was used instead. The same procedure with triethylamine addition was also employed for the synthesis of the THPMA homopolymer-based end-linked network.

Finally, the statistical copolymer end-linked polyampholyte network was synthesized by the simultaneous copolymerization of the two comonomers followed by the addition of cross-linker, while the randomly cross-linked network based on statistical polyampholytes was prepared by the simultaneous terpolymerization of the two comonomers and the cross-linker, without addition of triethylamine.

Characterization of the Linear Precursors by GPC and ^{1}H NMR Spectroscopy. Samples of linear homopolymers and linear copolymers extracted from the polymerization flask before cross-linking were characterized in terms of their MW and composition using GPC and ^{1}H NMR spectroscopy. A Polymer Laboratories system, equipped with an ERC−7515A Polymer Laboratories refractive index (RI) detector and a PL Mixed "D" column was employed for the GPC measurements, using THF as the eluent which was delivered at 1 mL min^{-1} by a Waters 515 isocratic pump. MW calibration was performed using poly(methyl methacrylate) (PMMA) standards supplied by Polymer Laboratories. The ^{1}H NMR spectra of the polymer solutions in deuterated chloroform ($CDCl_3$) were recorded using a 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet, and calibration was performed using the signal from residual protonated ($CHCl_3$) solvent (peak at 7.26 ppm). The copolymer composition was found from the ratio of the relative areas of the peak due to the two oxymethylene protons in polyDMAEMA at 3.96 ppm and that due to the methinic proton of polyTHPMA at 5.89 ppm. Furthermore, the conversion of the two monomers to polymer was also calculated from ^{1}H NMR spectroscopy as follows. For DMAEMA, monomer conversion was calculated from the ratio of the area of the peak due to the oxymethylene protons of the DMAEMA monomer at 4.1 ppm divided by the area of the oxymethylene protons of polyDMAEMA at 3.96 ppm, while, for THPMA, monomer conversion was calculated from the ratio of the area of the peak due the methinic proton of THPMA at 5.98 ppm divided by the area of the methinic proton of polyTHPMA at 5.89 ppm.

Characterization of the (Co)networks. *Determination of the Sol Fraction (Extractables).* Upon (co)network formation, a small piece was cut from each (co)network, placed in a small volume of $CDCl_3$ overnight, and the thus-extracted material was promptly characterized using ^{1}H NMR spectroscopy in terms of its composition, and, in particular, the final monomer and cross-linker conversions based on the signal from the unreacted olefinic protons. These extractables were called "early" extractables.

The rest of each (co)network was placed in a large (1-L) glass-jar, and left to equilibrate in THF for 2 weeks to remove all the extractables. Subsequently, the extractables solution was separated from the THF-swollen conetwork pieces by filtration, and was dried by evaporating off the solvent using a rotary evaporator. This was followed by the complete drying of the thus-predried extractables by placing them in a vacuum oven at room temperature for 72 h. The sol fraction was calculated as the ratio of the dried mass of the extracted polymer divided by the theoretical mass of the gel which was estimated as the sum of the masses of the monomers, the cross-linker and the CTA. Finally, the extractables were characterized using GPC and ^{1}H NMR spectroscopy analyses.

Measurement of the Degree of Swelling (DS) in THF. All (co)networks were characterized before their hydrolysis in terms of their degrees of swelling (DSs) in THF. The (co)networks were cut in small pieces and were weighed to determine their THF-swollen mass. The pieces were dried in a vacuum oven at room temperature for 72 h and their dry mass was, subsequently, determined. The DSs were calculated as the ratio of the average swollen (co)network mass (determined three times) divided by the dry (co)network mass.

Hydrolysis of the THPMA Units. After the extraction of the sol fraction and the measurement of the DS in THF, each THF-swollen (co)network was transferred to a 1-L glass jar, which contained approximately 400 mL of pure water plus a volume of a 10 M HCl solution. The number of moles of HCl was three times the number of moles of THPMA plus DMAEMA (DMAEMA is not hydrolyzed but captures HCl to get ionized). The system was allowed to hydrolyze for 1 week, followed by washing with distilled water for another 2 weeks to remove the excess of HCl. The water was changed every day. Before each water change, the pH of the supernatant solution was measured. The pH of the supernatant solution of the (co)networks immediately after the hydrolysis was approximately 1.5, but after the washings for 2 weeks, it rose to 3.5−4.0. This hydrolysis step converted the THPMA−DMAEMA amphiphilic (co)networks to MAA−DMAEMA ampholytic (co)networks.

Measurement of the DSs in Water. After their hydrolysis and washing with water, all the (co)networks were characterized in terms of their aqueous DSs within the pH range between 1.5 and 13 without added salt. To this end, several pieces from each (co)network were first cut and weighed to determine their swollen mass in water at a pH ∼3.5−4.0. Then, these pieces were dried under vacuum for 72 h at room temperature and were, again, weighed to determine their dry mass. Their aqueous DSs were calculated as the ratio of the water-swollen mass divided by the dry mass. Subsequently, the dried ampholytic (co)network pieces were transferred in a volume of water where the appropriate volume of 0.5 M NaOH (pH range from 3.5 to 13) or 0.5 M HCl (pH range from 1.5 to 3.5) standard solutions had been added to adjust the pH within the range between 1.5 and 13. The number of moles of NaOH required for each sample was calculated as the product of the desired degree of deprotonation times the total number of moles of DMAEMA plus MAA units contained in the sample. The latter was calculated from the (co)network dry mass, and the polymerization stoichiometry. For these calculations, a linear hydrogen ion titration curve was assumed, in which the degree of

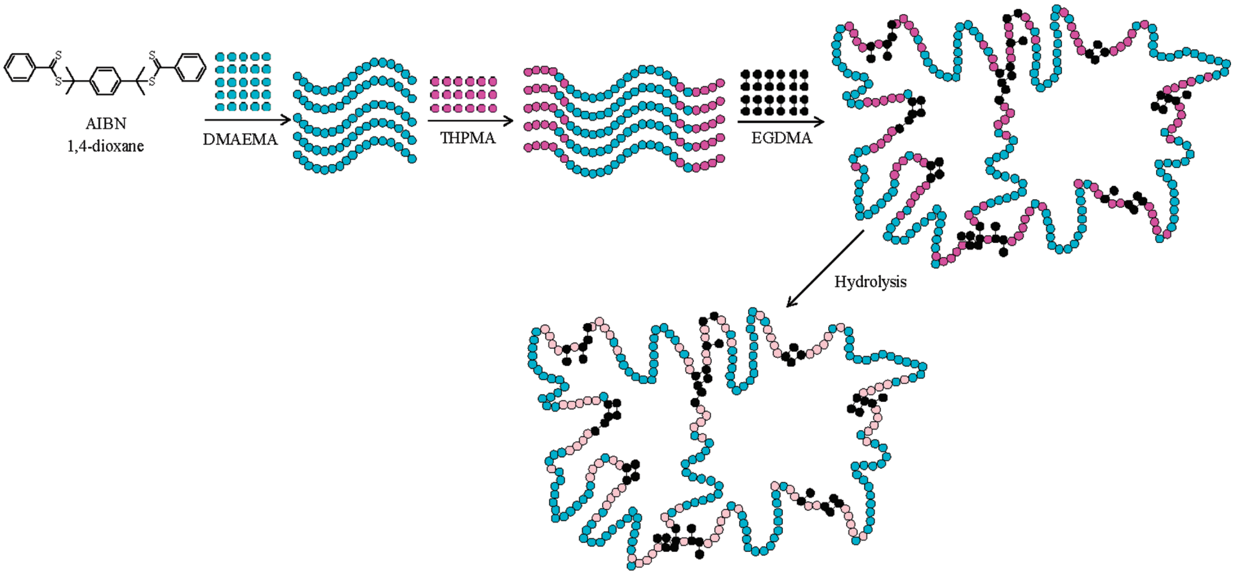

Figure 2. Schematic representation of the synthetic procedure followed for the preparation of the end-linked conetwork based on the gradient triblock copolymer THPMA$_{25}$-*grad*-DMAEMA$_{50}$-*grad*-THPMA$_{25}$. The DMAEMA units are shown in light blue, the THPMA units are painted purple and the MAA units are shown in light pink. Black dumbbells represent the EGDMA cross-linker units.

protonation or deprotonation varied from 0 to 1 within the pH range from 1.5 to 13. Although the assumption for linearity in the hydrogen ion titration may sound too simplistic, experimental hydrogen ion titration curves of linear block polyampholytes are almost linear,[25] a result of the strong electrostatic interactions in these highly charged systems. In any case, this simplification did not adversely affect our data, because the actual equilibrium pH value was always measured experimentally. The above calculation simply aimed at securing samples with various pH values, with the adjacent samples having degrees of ionization differing roughly by the same value. To adjust the pH within the range between 1.5 and 3.5, one and two drops of the 0.5 M HCl standard solution were added to two pieces of each (co)network. The samples were equilibrated for 3 weeks and the swollen masses were measured. The DSs of all samples were again calculated by dividing the average value of the swollen mass by the dry mass for the different samples of each (co)network.

Determination of the Isoelectric pH (pI) of the Polyampholyte (Co)networks. The p*I* of the polyampholyte (co)networks was taken as the pH where the (co)network presented a minimum DS. In some cases, however, the (co)networks did not present a clear minimum in their swelling profile but they formed a plateau. In these cases, the p*I* was estimated as the middle point of this plateau region.

Small-Angle Neutron Scattering (SANS). SANS measurements were performed on the 30 m NG7 instrument at the Center for Neutron Research of the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland. The incident wavelength λ was 6 Å. Three sample-to-detector distances of 1, 4.5, and 13.5 m were employed, covering a q-range $[q = 4\pi/\lambda \sin(\theta/2)]$ from 0.0335 to 5.715 nm^{-1}. The samples were loaded in quartz cells. The scattering patterns were isotropic, and therefore, the measured counts were circularly averaged. The averaged data were corrected for empty cell and background.

RESULTS AND DISCUSSION

Selection of Monomers. DMAEMA and MAA were selected as the most common methacrylate weak base and weak acid monomers, respectively. For the MAA protection, we elected the tetrahydropyranyl group which can be readily removed under mildly acidic conditions after the polymerizations and (co)network formation. *tert*-Butyl protection was avoided due to the harsher reagents and more extreme conditions required for hydrolysis (trifluoroacetic acid at room temperature or hydrochloric acid under reflux conditions). Likewise, the very labile trimethylsilyl group was also avoided as its detachment spontaneously occurs even with atmospheric moisture. It is noteworthy, however, that trimethylsilyl-protected (meth)acrylic acid has been successfully incorporated in amphiphilic conetworks via conventional free radial copolymerization for the introduction of carboxylic acid groups (after its deprotection).[26−31]

Synthesis of the End-Linked (Co)networks. In the present work, four end-linked triblock polyampholyte conetworks, one end-linked statistical and one randomly cross-linked polyampholyte networks, as well as two homopolymer end-linked networks, were synthesized by sequential RAFT polymerization using AIBN as the initiator, 1,4-BTBTPB as the chain transfer agent, 1,4-dioxane as the solvent, DMAEMA as the basic monomer, THPMA as the protected acid (MAA) monomer, and EGDMA as the cross-linker. The synthetic procedure for the preparation of an ABA triblock copolymer-based end-linked conetwork by sequential monomer and cross-linker additions, followed by the acid hydrolysis of the THPMA units, is presented schematically in Figure 2. In this figure, the DMAEMA units are shown in light blue, the THPMA units are shown in purple, and the MAA units, obtained upon the hydrolysis of the THPMA units, are shown in light pink. The black dumbbells in the conetwork represent the EGDMA cross-linker units. As is shown in the figure, the synthesis of the linear DMAEMA homopolymer with both active ends (due to the use of the bifunctional CTA) was accomplished first, followed by the addition of the THPMA monomer which resulted in chain growth and formation of the THPMA-*grad*-DMAEMA-*grad*-THPMA (gradient) triblock copolymer, again with two active ends. Finally, the addition of the cross-linker led to the formation of a three-dimensional conetwork via the interconnection of the active copolymer chain ends. As already explained, the synthesis of the conetworks involved sequential rather than stepwise monomer and cross-linker additions to enhance the

Table 1. Monomer and Cross-Linker Conversions, Molecular Weight, and Composition Characteristics of the Linear Precursors to the (Co)networks Synthesized

no.	polymer structure[a]	conversion (mol %)				gelation time (min)	theor MW[d]	GPC results		% mol T	
		T	D	E	time (min)			M_n	M_w/M_n	theor	^{1}H NMR
1	D_{100}	---	85.7[b]	---	710		16 000	14900[b]	1.5[b]	0	
	E_3-*grad*-D_{100}-*grad*-E_3	---	91.7[c]	95.6[c]	1440	180	---	---	---	---	---
2	T_{50}	99.0[b]	---	---	1150		9000	12300[b]	1.3[b]	100	100[b]
	E_3-*grad*-T_{50}-*grad*-E_3	99.0[c]	---	99.1[c]	1440	≤540	---	---	---	---	---
3	D_{50}	---	96.2[b]	---	668		8000	8830[b]	1.5[b]	0	0[b]
	$T_{12.5}$-*grad*-D_{50}-*grad*-$T_{12.5}$	85.3[b]	99.3[b]	---	690		12 500	13300[b]	1.5[b]	33.0	46.1[b]
	E_3-*grad*-$T_{12.5}$-*grad*-D_{50}-*grad*-$T_{12.5}$-*grad*- E_3	89.2[c]	100[c]	86.0[c]	1440	610	---	---	---	---	---
4	D_{50}	---	87.5[b]	---	660		8000	9150[b]	1.5[b]	0	0[b]
	T_{25}-*grad*-D_{50}-*grad*-T_{25}	83.4[b]	96.7[b]	---	675		16 500	16000[b]	1.5[b]	50.0	47.9[b]
	E_3-*grad*-T_{25}-*grad*-D_{50}-*grad*-T_{25}-*grad*-E_3	95.7[c]	99.9[c]	88.6[c]	1440	505	---	---	---	---	---
5	T_{50}	98.0[b]	---	---	705		9000	9500[b]	1.6[b]	100	100[b]
	D_{25}-*grad*-T_{50}-*grad*-D_{25}	100[b]	66.3[b]	---	750		16 500	14200[b]	1.9[b]	50.0	60.3[b]
	E_3-*grad*-D_{25}-*grad*-T_{50}-*grad*-D_{25}-*grad*-E_3	99.0[c]	98.5[c]	100[c]	1440	≤540	---	---	---	---	---
6	D_{50}	---	94.5[b]	---	660		8000	9310[b]	1.4[b]	0	0[b]
	$T_{37.5}$-*grad*-D_{50}-*grad*-$T_{37.5}$	81.8[b]	100[b]	---	690		21 000	16400[b]	1.5[b]	60.0	55.3[b]
	E_3-*grad*-$T_{37.5}$-*grad*-D_{50}-*grad*-$T_{37.5}$-*grad*- E_3	88.5[c]	100[c]	82.3[c]	1440	625	---	---	---	---	---
7	D_{50}-*co*-T_{50}	92.6[b]	87.2[b]	---	740		16 500	15300[b]	1.4[b]	50.0	48.5[b]
	E_3-*grad*-(D_{50}-*co*-T_{50})-*grad*-E_3	100[c]	99.6[c]	99.7[c]	1440	540	---	---	---	---	---
8	D_{50}-*co*-T_{50}-*co*-E_6	100[c]	100[c]	100[c]	1440	75	---	---	---	---	---

[a] D: 2-(dimethylamino)ethyl methacrylate. T: 2-tetrahydropyranyl methacrylate. E: ethylene glycol dimethacrylate. [b] From the analysis of the ^{1}H NMR spectra or the GPC traces of the linear precursors. [c] From the analysis of the ^{1}H NMR spectra of the "early" extractables. [d] $MW_{theor} = [M]/[CTA] \times (\text{monomer conversion}) \times MW_{monomer} + MW_{CTA}$.

"livingness" of the polymerization (to preserve a greater number of active polymerization sites) and enable facile conetwork formation. In initial experiments, the conetwork preparation was accomplished by stepwise additions of the monomers and the cross-linker. After the formation of each polymer, the polymerization was stopped and the polymer was recovered. In those experiments, a 6 : 1 EGDMA : CTA molar ratio was again used where it was observed that this ratio was insufficient to effect conetwork formation and, thus, a higher cross-linker loading was necessary for gelation.

Molecular Weights and Composition of the Linear Precursors and Monomer Conversion. Table 1 lists the theoretical chemical structures of all the (co)networks and their linear precursors, the MWs and compositions of the linear precursors, and the monomer and cross-linker conversions as determined by GPC and ^{1}H NMR spectroscopy. Note that the final comonomer and cross-linker conversions in the (co)networks were calculated from the ^{1}H NMR spectra of the "early" extractables. Figure 3 shows the GPC traces of the homopolymer and triblock copolymer linear precursors to all (co)networks. The M_n and PDI values for all linear homopolymer and copolymer precursors were calculated from these GPC traces and are listed in Table 1. The M_n values of the triblock copolymers were higher than those of their parent homopolymers, as expected. Furthermore, all M_n values, both of the homopolymers and the copolymers, were very close, within 20%, to those expected from theory, with the exception that of the largest triblock copolymer, $THPMA_{37.5}$-*grad*-$DMAEMA_{50}$-*grad*-$THPMA_{37.5}$. The PDIs were relatively high (≥1.3) but comparable with those in other studies[20b,21] for polymers synthesized using the same CTA.

Figure 4 displays the ^{1}H NMR spectrum of the ABA triblock copolymer $THPMA_{25}$-*grad*-$DMAEMA_{50}$-*grad*-$THPMA_{25}$ and that of its homopolymer precursor. The spectrum of the triblock copolymer presents the characteristic methinic proton peak f of the tetrahydropyranyl ring at 5.89 ppm in the polyTHPMA blocks, indicating the incorporation of THPMA units in the end-blocks. Note that peak k at 5.98 ppm in the same spectrum is due to the methinic proton of the THPMA monomer. Comparison of the areas of peaks f and k allowed the calculation of the conversion of THPMA monomer to polymer in the triblock. Similarly, the conversion of the DMAEMA monomer to polymer (in the DMAEMA homopolymer and in the triblock) was calculated from the areas of the peaks of the oxymethylene protons of polyDMAEMA and DMAEMA monomer at 3.96 and 4.1 ppm, respectively. The monomer conversions in the linear homopolymer and copolymer precursors to the (co)networks

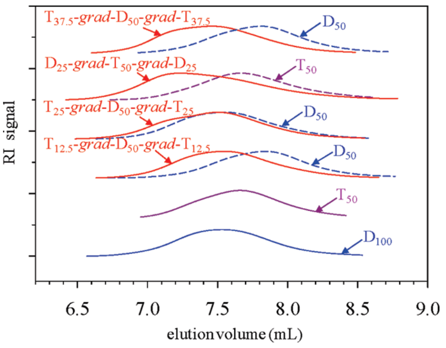

Figure 3. GPC traces of the homopolymers and the triblock copolymer linear precursors to all the (co)networks. D: 2-(dimethylamino)ethyl methacrylate. T: 2-tetrahydropyranyl methacrylate.

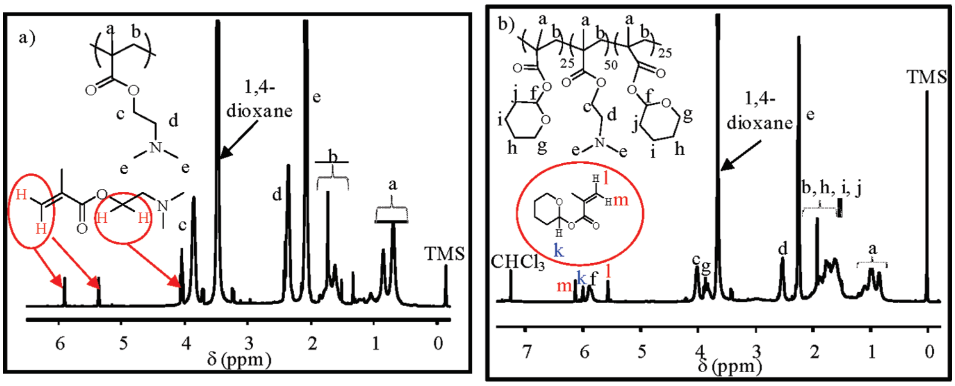

Figure 4. ^{1}H NMR spectra of (a) the DMAEMA$_{50}$ homopolymer precursor and (b) the THPMA$_{25}$-*grad*-DMAEMA$_{50}$-*grad*-HPMA$_{25}$ triblock copolymer.

are listed under the “Conversions” heading in Table 1, in the corresponding row (of homopolymer or copolymer). The monomer conversions in the homopolymers were always high, ranging from 85.7 to 96.2% for DMAEMA, and 98.0 to 99.0% for THPMA. The monomer conversions in the copolymers were also fairly high, ranging from 66.3 to 100.0% for DMAEMA, and 81.8 to 100.0% for THPMA. The lowest value for the DMAEMA conversion of 66.3% might be attributed to the polymerization of this monomer after the polymerization of THPMA as first block; even some partial hydrolysis of THPMA would delay the polymerization of the second comonomer. Also note that in all cases, the conversion of the monomer in the first block of a copolymer was higher in the copolymer compared to the parent homopolymer, indicating further progress of the polymerization, as expected. Finally, the compositions of the linear precursors were calculated from the normalized areas due to the peaks of the characteristic protons of polyTHPMA (peak f) and polyDMAEMA (peak c). The thus-calculated composition is also given in the last column of Table 1 as the THPMA % mol, and, in all cases, this was close to the theoretically expected composition.

The final conversions of the DMAEMA and the THPMA monomers in the (co)networks were calculated from the ^{1}H NMR spectra of the “early” extractables using the same peaks as those used for the calculations for the linear copolymers mentioned above. The ^{1}H NMR spectra of the “early” extractables were also used to estimate the conversion of the EGDMA cross-linker in the (co)networks from the peak of the oxymethylene protons of (nonpolymerized) EGDMA at 4.40 ppm. These three conversions are also listed in Table 1 under the “Conversions” heading for the rows corresponding to (co)networks. The conversions of the three components in the (co)networks were high, between 98.5 and 100.0% for DMAEMA, between 88.5 and 100.0% for THPMA, and between 82.3 and 100.0% for EGDMA. The lowest EGDMA conversion of 82.3% corresponded to the end-linked ABA triblock copolymer conetwork with the longest chains (overall DP of 125), whereas somewhat higher EGDMA conversions of ca. 87% were measured for the end-linked ABA triblock copolymers with shorter chains (DPs of 75 and 100). The EGDMA conversion in the remaining (co)networks were 95% or higher. Note that these differences in the cross-linker conversion will be reflected in the DSs of the (co)networks, which will be presented and discussed later in the manuscript.

Properties of the Sol Fraction. The extracted material (sol fraction; final extractables rather than “early”extractables) was characterized in terms of its percentage, M_n, and PDI values. The results are listed in Table 2. The percentage of the extractables was moderate (<30%), indicating sufficient incorporation of linear precursors into the (co)network. Reduction of the extractables via the use of a greater charge of cross-linker was avoided because of the risk of the formation of a second network totally based on cross-linker.[32] The lowest percentages of extractables were presented by the network based on the end-linked statistical polyampholyte and the randomly cross-linked polyampholyte network. This can be attributed to the fewer polymerization steps until cross-linking in these two networks, one and zero, respectively, as compared to two steps in the case of the ABA and BAB triblock copolymer end-linked conetworks. Note that the end-linked statistical polyampholyte network and the randomly cross-linked polyampholyte network also presented quantitative EGDMA polymerization conversions (Table 1).

From the ^{1}H NMR spectra of the extractables, it was observed that these mainly consisted of linear chains (polyDMAEMA, polyTHPMA or poly(DMAEMA-*grad*-THPMA)) which were probably deactivated before the addition of the cross-linker. In particular, the composition of the extractables was richer in the polymer of the midblock, as this participated in the polymerization from the beginning and was, therefore, subjected to deactivation longer. The extractables also contained THPMA monomer and EGDMA cross-linker, while only in one case (E$_3$-*grad*-D$_{100}$-*grad*-E$_3$) did they contain DMAEMA monomer.

The M_n value of the main peak of the extractables, determined by GPC, is also shown in Table 2. For (co)networks E$_3$-*grad*-T$_{50}$-*grad*-E$_3$, E$_3$-*grad*-T$_{12.5}$-*grad*-D$_{50}$-*grad*-T$_{12.5}$-*grad*-E$_3$, E$_3$-*grad*-T$_{25}$-*grad*-D$_{50}$-*grad*-T$_{25}$-*grad*-E$_3$ and E$_3$-*grad*-T$_{37.5}$-*grad*-D$_{50}$-*grad*-T$_{37.5}$-*grad*-E$_3$, the M_n values of the extractables were lower compared to that determined by GPC for their corresponding linear precursors (Table 1), probably due to the early deactivation of the active centers of the linear precursors. In contrast, in the cases of (co)networks E$_3$-*grad*-D$_{100}$-*grad*-E$_3$ and E$_3$-*grad*-D$_{25}$-*grad*-T$_{50}$-*grad*-D$_{25}$-*grad*-E$_3$, the M_n values of their extractables were higher than that determined by GPC for their linear precursors (Table 1), suggesting possible interconnection of the free polymer chains during the extraction procedure.

DSs in THF. The DSs in THF of all the (co)networks before their hydrolysis were also measured and are listed in Table 3. The DSs for the three ABA triblock copolymer-based end-linked conetworks increased as the EGDMA cross-linker conversion decreased (Table 1), leading to less compact materials. This DS increase followed also the increase of the overall chain DP from 75 to 125 (THF is a nonselective solvent for DMAEMA and THPMA), but we believe that the effect of cross-linker conversion was more pronounced. From the three isomeric equimolar

Table 2. Percentage, Compositions, and Molecular Weights of the Extractables from the (Co)networks

			^{1}H NMR results (mol %)					GPC results	
no.	network structure[a]	% w/w extract.	PD[b]	PT[c]	D	T	E	M_n	PDI
1	E_3-*grad*-D_{100}-*grad*-E_3	24.2	88.1	0	9.4	---	2.5	19 000	1.8
								240	1.1
2	E_3-*grad*-T_{50}-*grad*-E_3	22.3	0	97.2	---	0	2.8	9500	1.5
								230	1.1
3	E_3-*grad*-$T_{12.5}$-*grad*-D_{50}-*grad*-$T_{12.5}$-*grad*-E_3	29.8	56.8	29.9	0	7.4	5.9	7400	1.6
								220	1.1
4	E_3-*grad*-T_{25}-*grad*-D_{50}-*grad*-T_{25}-*grad*-E_3	24.3	55.9	25.0	0	9.9	9.2	8000	1.4
								200	1.1
5	E_3-*grad*-D_{25}-*grad*-T_{50}-*grad*-D_{25}-*grad*-E_3	25.1	37.4	60.8	0	1.8	0	17 400	1.3
								351	1.1
6	E_3-*grad*-$T_{37.5}$-*grad*-D_{50}-*grad*-$T_{37.5}$-*grad*-E_3	25.0	42.8	43.4	0	9.9	3.9	10 200	2.2
								230	1.1
7	E_3-*grad*-(D_{50}-*co*-T_{50})-*grad*-E_3	4.4	0	0	0	0	0	210	1.1
8	D_{50}-*co*-T_{50}-*co*-E_6	11.1	55.8	44.2	0	0	0	9560	1.1
								220	1.1

[a] D: 2-(dimethylamino)ethyl methacrylate. T: 2-tetrahydropyranyl methacrylate. E: ethylene glycol dimethacrylate. [b] PD: poly(2-(dimethylamino)ethyl methacrylate). [c] PT: poly(2-tetrahydropyranyl methacrylate).

Table 3. Degrees of Swelling in THF, in Water at the Conditions of Hydrolysis Following Washing (pH ~ 3.5) and at the Isoelectric Points (p*I*) of all the (Co)networks, and p*I* Values

		degree of swelling			
			DS in water after hydrolysis		
no.	network structure[a]	DS in THF before hydrolysis	at pH = 3.5−4.0	at p*I*	p*I*
1	E_3-*grad*-D_{100}-*grad*-E_3	21.0	24.0	---	---
2	E_3-*grad*-A_{50}-*grad*-E_3	---	19.6	---	---
3	E_3-*grad*-$A_{12.5}$-*grad*-D_{50}-*grad*-$A_{12.5}$-*grad*-E_3	54.0	39.6	6.0	5.5
4	E_3-*grad*-A_{25}-*grad*-D_{50}-*grad*-A_{25}-*grad*-E_3	56.4	47.7	7.9	6.1
5	E_3-*grad*-D_{25}-*grad*-A_{50}-*grad*-D_{25}-*grad*-E_3	---	22.7	3.7	6.3
6	E_3-*grad*-$A_{37.5}$-*grad*-D_{50}-*grad*-$A_{37.5}$-*grad*-E_3	62.7	54.9	7.9	5.4
7	E_3-*grad*-(D_{50}-*co*-A_{50})-*grad*-E_3	5.60	23.9	9.2	6.8
8	D_{50}-*co*-A_{50}-*co*-E_6	20.5	22.0	7.9	5.3

[a] D: 2-(dimethylamino)ethyl methacrylate. A: methacrylic acid. E: ethylene glycol dimethacrylate.

(co)networks, the end-linked statistical polyampholyte network and the randomly cross-linked polyampholyte network presented the lowest DSs in THF, which was consistent with the complete polymerization of EGDMA in these two polyampholyte networks and the minimum percentage of extractables.

DSs in Water at pH ~ 3.5−4.0. The DSs in water, without added salt (to maximize electrostatic interactions), of all the (co)networks after their hydrolysis and washings (pH between 3.5 and 4.0) are also shown in Table 3. The trends for these DSs followed the same ones for the DSs in THF discussed in the previous paragraph. In particular, (co)networks where the EGDMA was polymerized to a higher conversion (Table 1) presented lower DSs. For example, polyampholyte conetwork 6 with the lowest EGDMA conversion exhibited the highest DS also at pH ~ 3.5.

pH-Dependence of the Aqueous Degrees of Swelling of the Polyampholyte (Co)networks. The experimentally measured aqueous DSs of all the polyampholyte (co)networks as well as those of the two homopolymer polyelectrolyte networks are plotted against the pH of the supernatant solution in Figure 5, while, Table 3 lists the p*I* values of the polyampholyte (co)networks. The aqueous DSs of the DMAEMA homopolymer end-linked network increased at pH < 7 due to the ionization of the DMAEMA units in this pH range. Similarly, the aqueous DSs of the MAA homopolymer end-linked network also increased upon the ionization of the MAA units. However, with MAA being a weak acid rather than a weak base, ionization occurred upon increasing the pH, and the swelling increased at pH > 6. On the other hand, the aqueous DSs of all the polyampholyte (co)networks presented a characteristic minimum at intermediate pH values, while they increased at acidic and basic pHs. This behavior is typical of polyampholyte (co)networks, due to the existence of the isoelectric point, p*I*, which is the pH of zero net charge.[25,33] At and around the p*I*, the net repulsive forces are zero, while the van der Waals and hydrophobic attractive forces dominate, leading to a reduced extension of the polyampholyte chains. The slight decrease in the DSs at very high or very low pH values was probably due to

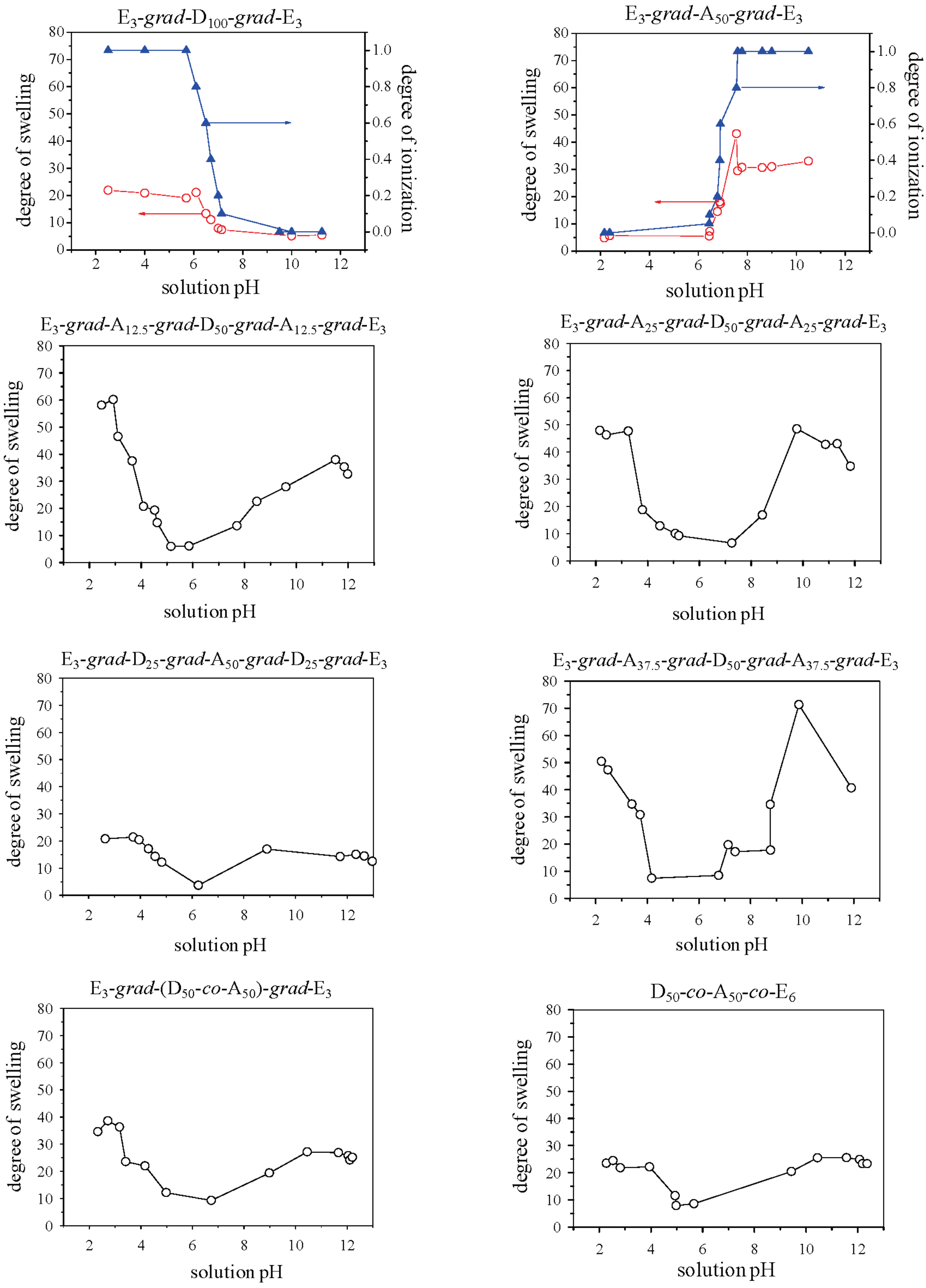

Figure 5. Degree of swelling as a function of the pH of the supernatant solution for all the polyampholyte (co)networks.

the increase of the ionic strength, effected by the relatively high concentration of NaOH or HCl under these conditions. Thus, the behavior of the polyampholyte (co)networks at extreme pH values was similar to that of simple polyelectrolyte networks,[34] in which the osmotic pressure established by the counterions to the ionized units and the electrostatic repulsive forces between the charged polymer chains both promoted network swelling.

The p*I*s of the polyampholyte (co)networks, estimated from the position of the swelling minimum, ranged from 5.3 to 6.8. The p*I*s of end-linked polyampholyte conetworks E_3-*grad*-A_{25}-*grad*-D_{50}-*grad*-A_{25}-*grad*-E_3 and E_3-*grad*-$A_{37.5}$-*grad*-D_{50}-*grad*-$A_{37.5}$-*grad*-E_3 were 6.1 and 5.4, respectively, decreasing with the MAA content, as expected. However, the most basic end-linked polyampholyte conetwork E_3-*grad*-$A_{12.5}$-*grad*-D_{50}-*grad*-$A_{12.5}$-*grad*-E_3

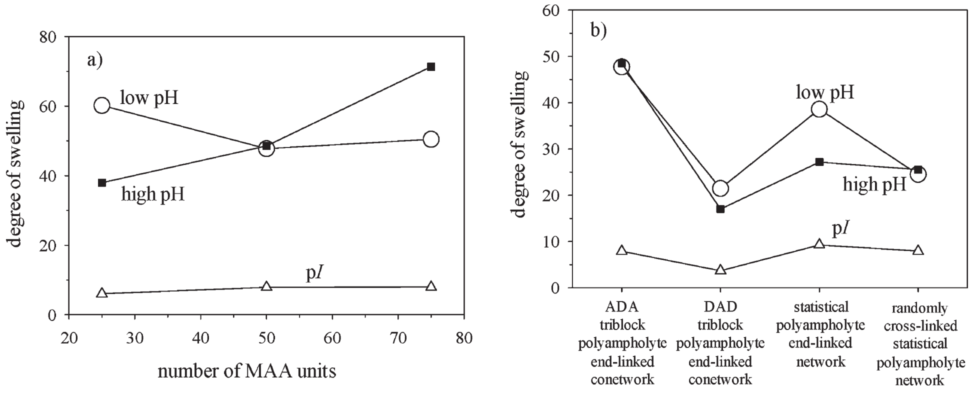

Figure 6. Degrees of swelling of the polyampholyte (co)networks at low, high and isoelectric pH. (a) Effect of polyampholyte composition. (b) Effect of polyampholyte architecture.

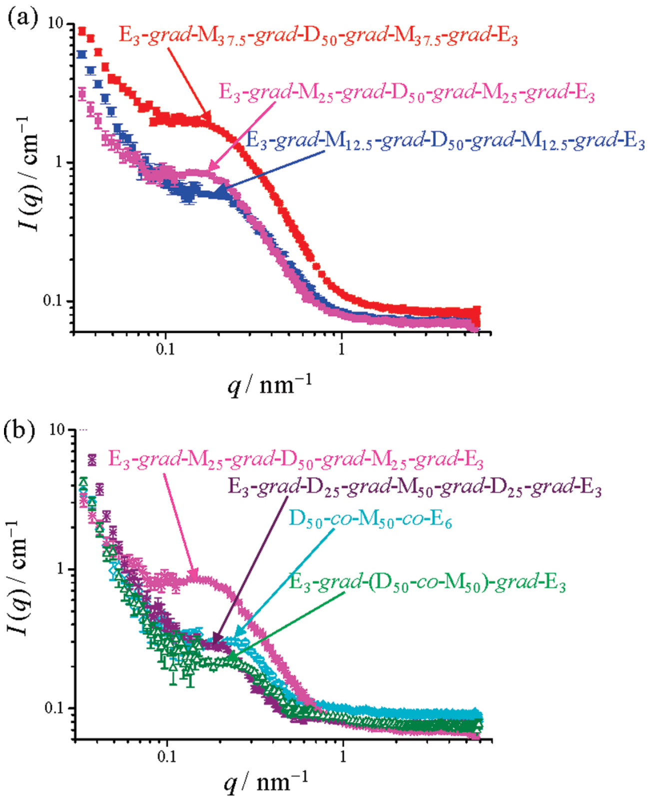

Figure 7. SANS profiles of all the (co)networks in D_2O at pH = 3.5. (a) Effect of polyampholyte composition. (b) Effect of polyampholyte architecture.

unexpectedly presented a relatively low p*I* value of around 5.5. This discrepancy might arise from the approximate method of estimation of the p*I* from the *DS* vs *solution pH* curve. For the particular polyampholyte conetwork, this curve is highly asymmetrical, with the branch at lower pH values being much steeper than the one on the alkaline side, which may render the p*I* estimation method less accurate. Note, however, that the maximum acidic DS of this polyampholyte conetwork was higher than the maximum alkaline DS, correctly reflecting the excess DMAEMA units relative to the MAA units. Also note that the reverse was true for the most acidic end-linked polyampholyte conetwork E_3-*grad*-$A_{37.5}$-*grad*-D_{50}-*grad*-$A_{37.5}$-*grad*-E_3, while for the equimolar polyampholyte conetwork the maximum acidic and maximum alkaline DSs were approximately equal, again in line with our expectations. In particular, at the pH extremes, the swelling behavior of the polyampholyte conetworks was expected to be dominated by the corresponding fully ionized units. Thus, at low pH values the high DSs were due to the ionization of the DMAEMA units, while at high pH values the high DSs were due to the ionization of the MAA units. The p*I*s of the three equimolar end-linked polyampholyte (co)networks span a range of values from 6.1 to 6.8. This variation is probably due to the sensitivity of p*I* to composition around the equimolar composition.[25,33,35]

Aqueous DSs at Low and High pH and at the p*I*.. The aqueous DSs of the polyampholyte (co)networks at low pH (pH ~ 3), at high pH (pH ~ 11) and at around the p*I* (pH ~ 5−7) were extracted from Figure 5 and are plotted in Figure 6. Figure 6a presents the effect of polyampholyte composition, while Figure 6b presents the effect of polyampholyte architecture.

Figure 6a shows that the isoelectric aqueous DSs of the end-linked ABA triblock polyampholyte-based conetworks were constant and around 8, indicating that the polyampholyte conetworks were in a less expanded state due to the absence of counterions and repulsive forces. The low pH aqueous DSs were highest for the DMAEMA-rich ABA triblock polyampholyte conetwork which bore the greatest number of positively charged units under these conditions (lowest number of MAA units). This was despite the higher EGDMA conversion (Table 1) upon the synthesis of this conetwork compared to that of its two homologues with higher MAA contents, plotted in the same figure, suggesting the dominance of the charge effect on swelling at this instance. In contrast, the fact that the low pH aqueous DS of the MAA-rich polyampholyte conetwork was not lower than but equal to that of the equimolar polyampholyte conetwork may be due to the lower EGDMA conversion upon the synthesis of the former conetwork. The high pH DSs plotted in the same figure were highest for the MAA-rich polyampholyte conetwork which bore the greatest number of carboxylate anions at alkaline conditions, although its greatest overall DP of the chains and the lowest EGDMA conversion must have also contributed. In fact, the high pH aqueous DSs of the three ABA triblock polyampholyte conetworks increased monotonically with the number of MAA units in the polyampholyte chain. Finally, it is noteworthy that the high and the low pH aqueous DSs of the equimolar polyampholyte conetwork were the same because of the same number of charged units per chain at the two pH extremes, leading to the same electrostatic repulsion and same driving force for swelling.

Table 4. Experimental (from DSs) and Maximum Theoretical Distances between the EGDMA Cores and DSs in H_2O (pH~3.5) of the Polyampholyte (Co)networks

no.	polymer structure[a]	core spacing (nm) maximum theoretical[b]	core spacing (nm) from DS	DS in H_2O (pH ~ 3.5)
1	E_3-*grad*-$A_{12.5}$-*grad*-D_{50}-*grad*-$A_{12.5}$-*grad*-E_3	19.0	23.2	39.6
2	E_3-*grad*-A_{25}-*grad*-D_{50}-*grad*-A_{25}-*grad*-E_3	25.4	25.4	47.7
3	E_3-*grad*-D_{25}-*grad*-A_{50}-*grad*-D_{25}-*grad*-E_3	25.4	19.0	22.7
4	E_3-*grad*-$A_{37.5}$-*grad*-D_{50}-*grad*-$A_{37.5}$-*grad*-E_3	31.8	26.2	54.9
5	E_3-*grad*-(D_{50}-*co*-A_{50})-*grad*-E_3	25.4	12.5	6.00
6	D_{50}-*co*-A_{50}-*co*-E_6	---	---	22.0

[a] D: 2-(dimethylamino)ethyl methacrylate. A: methacrylic acid. E: ethylene glycol dimethacrylate. [b] The spacing between the EGDMA cores was calculated as the sum of the DPs of the DMAEMA plus the MAA units in each (co)network chain multiplied by 0.254 nm which is the contribution of one monomer repeating unit to the contour length.

Figure 6b illustrates the effect of (co)network architecture on the aqueous DSs of the four equimolar polyampholyte (co)networks. At the p*I*s, all four isomeric polyampholyte (co)networks were less expanded, exhibiting approximately the same DSs, around 8. This is in agreement with previous studies[17,18] which indicated the independence of the DS at the p*I* on polyampholyte (co)network architecture. The low and high pH aqueous DSs of the polyampholyte (co)networks presented values that depended both on EGDMA conversion upon (co)network synthesis and on comonomer unit distribution along the chains. In particular, the equimolar ABA triblock polyampolyte-based end-linked conetwork presented the highest low and high pH DSs, which reflected the lowest conversion of EGDMA (88.6%, less compact conetwork). In contrast, the quantitative EGDMA conversion upon the synthesis of the BAB triblock polyampholyte-based end-linked conetwork exhibited the lowest high and low pH DSs (more compact conetwork). Finally, the other two equimolar polyampholyte networks, the statistical polyampholyte-based end-linked network and the randomly cross-linked polyampholyte network, had DSs closer to those of the BAB triblock polyampholyte-based end-linked conetwork, as EGDMA conversion in all three (co)networks was complete. The lower DSs of the randomly cross-linked polyampholyte network compared to those of its statistical polyampholyte-based end-linked counterpart might be attributed to the existence of a distribution of longer and shorter chains in the former network and the dominating effect of the shorter chains.

Structure of Swollen (Co)networks. All the (co)networks were also characterized in terms of their structure in D_2O using SANS. Figure 7 shows the SANS profiles of all the polympholyte (co)networks in D_2O at pH = 3.5. Figure 7a illustrates the effect of polyampholyte composition, while Figure 7b presents the effect of polyampholyte architecture. The scattering profiles from all polyampholyte (co)networks displayed an upturn of the intensity in the very low *q*-region, and a shoulder in the intermediate *q*-region, without exhibiting any distinct peak. Such a peak has previously been observed with end-linked *amphiphilic* conetworks in D_2O, prepared using a similar polymerization method,[21] and also with other amphiphilic conetworks in the bulk.[36] In the case of the amphiphilic conetworks, the peak was attributed to the micelle-like structures formed by the aqueous self-assembly of the ABA triblock copolymer amphiphilic chains. In the present *polyampholyte* (co)networks, the two hydrophilic comonomers, DMAEMA and MAA, were not as effective at driving microphase separation, and the peak was ***replaced*** by the **shoulder**. The shoulder was located in the *q*-range between 0.1−0.2 nm^{-1}, corresponding to a correlation length of $2\pi/q = 30-60$ nm, in reasonable agreement with the EGDMA core spacing of about 25 nm calculated from the experimentally measured DSs[37,38] in water at pH = 3.5 and assuming 20 chains[32] radiating out of each core. This calculation was also based on the GPC M_n values, after subtracting the molar mass loss associated with the removal of the protecting groups from the THPMA units, and an average polymer bulk density of 1.1 g cm^{-3}. Table 4 lists the values of the thus-calculated spacings between the cores, which were close to and slightly lower than the values of the maximum core spacings calculated for fully stretched polyampholyte chains, and are also listed in Table 4. The scattering observed in the very low *q*-region (<0.06 nm^{-1}) probably arises from large-scale inhomogeneities (>100 nm = $2\pi/q$) in the system, most likely caused by spatial variations in the concentration of the (co)network, such as existence of condensed areas separated by less dense regions. Note that these inhomogeneities are more than 1 order of magnitude larger than the (random coil) polymer chain dimensions (~5 nm). Thus, the SANS profiles might relate to the core−core distances within the polyampholyte (co)networks.

■ CONCLUSION

Four well-defined end-linked polyampholyte conetworks, one end-linked statistical polyampholyte network and one randomly cross-linked polyampholyte network, as well as two end-linked homopolymer networks, were synthesized using RAFT polymerization. The (co)networks contained positively ionizable DMAEMA units and negatively ionizable MAA units. The extractables from all the (co)networks were moderate, indicating successful (co)network formation. The aqueous DSs of all polyampholyte (co)networks presented a minimum around the isoelectric point (p*I*) where the net charge was zero, while they increased at alkaline and acidic pHs due to the ionization of the weakly acidic and the weakly basic monomer repeating units, respectively. Moreover, the low pH DSs were highest for the DMAEMA-rich ABA-triblock polyampholyte end-linked conetwork, and the high pH DSs were highest for the MAA-rich ABA triblock polyampholyte end-linked conetwork, while the equimolar ABA triblock polyampholyte end-linked conetwork presented more balanced low and high pH DSs. The DSs at the p*I* of all the polyampholyte (co)networks were around 8, and largely remained composition- and architecture-independent. The SANS profiles of the (co)networks did not show any distinct peaks but only shoulders, suggesting lack of microphase separation. However, the position of the shoulders in the SANS profiles was consistent with the spacing between the cross-linking cores.

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