

Synthesis and Characterization of Anionic Amphiphilic Model Conetworks of 2-Butyl-1-Octyl-Methacrylate and Methacrylic Acid: Effects of Polymer Composition and Architecture

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Seven amphiphilic conetworks of methacrylic acid (MAA) and a new hydrophobic monomer, 2-butyl-1-octyl-methacrylate (BOMA), were synthesized using group transfer polymerization. The MAA units were introduced via the polymerization of tetrahydropyranyl methacrylate (THPMA) followed by the removal of the protecting tetrahydropyranyl group by acid hydrolysis after network formation. Both THPMA and BOMA were in-house synthesized. Ethylene glycol dimethacrylate (EGDMA) was used as the cross-linker. Six of the conetworks were model conetworks, containing copolymer chains between cross-links of precise molecular weight and composition. The prepared conetwork series covered a wide range of compositions and architectures. In particular, the MAA content was varied from 67 to 94 mol %, and three different conetwork architectures were constructed: ABA triblock copolymer-based, statistical copolymer-based, and randomly cross-linked. The linear conetwork precursors were analyzed by gel permeation chromatography and ¹H NMR spectroscopy in terms of their molecular weight and composition, both of which were found to be close to the theoretically calculated values. The degrees of swelling (DS) of all the amphiphilic conetworks were measured in water and in THF over the whole range of ionization of the MAA units. The DSs in water increased with the degree of ionization (DI) and the content of the hydrophilic MAA units in the conetwork, while the DSs in THF increased with the degree of polymerization of the chains between the cross-links and by reducing the DI of the MAA units. Finally, the nanophase behavior of the conetworks was probed using small-angle neutron scattering and atomic force microscopy.

Introduction

Amphiphilic polymer conetworks (APCN)^{1–40} represent an emerging class of materials with unique properties and great application potential. These materials comprise covalently bonded hydrophilic and hydrophobic polymer chains, which can swell in both aqueous and organic media, and may adsorb both polar and nonpolar solutes. Moreover, the immiscibility of their hydrophilic and hydrophobic components leads to phase separation at the nanoscale.^{3–11} Possible applications of APCNs include

uses as supports for enzymes,⁹ antifouling surfaces,¹² promoted release hosts,¹³ matrices for the preparation of inorganic nanoparticles⁶ and for drug delivery,^{14–17} and scaffolds for tissue engineering^{18–20} and for implantation²¹ and use in soft contact lenses.²²

Most of the APCNs reported in the literature have limited structural control as they have been prepared using free radical cross-linking polymerization.^{1–9,12–34} Thus, the chains between the cross-linking points have a wide distribution of molecular

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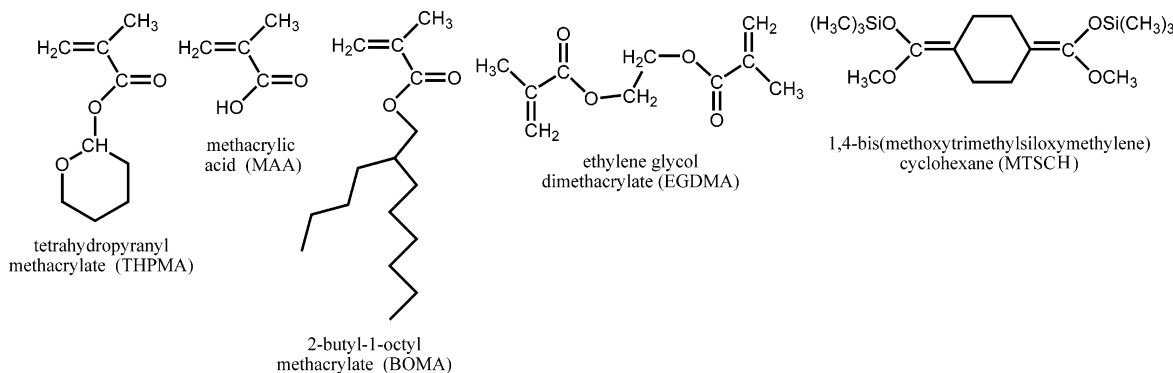


Figure 1. Chemical structures and names of the monomers, the cross-linker, and the initiator used for the conetwork synthesis.

weights and composition, not allowing the derivation of accurate structure–property relationships. In the past 7 years, one of our research teams has been using a controlled polymerization technique and prepared APCNs of improved structure.^{35–40} In particular, we have been using group transfer polymerization (GTP)^{41–46} to prepare APCNs based on chains with well-defined molecular weight and composition. We have named the produced materials “quasi-model” networks³⁵ to signify the improved structural control but also to distinguish them from perfect or “model” networks⁴⁷ possessing a precisely known number of arms at the cross-linking nodes.

Most of our previously reported quasi-model APCNs comprised tertiary amine hydrophilic units and glassy hydrophobic units such as methyl methacrylate³⁶ and benzyl methacrylate.³⁹ The aim of the present investigation is to expand the compositional scope by preparing APCNs based on carboxylic acid hydrophilic units and rubbery hydrophobic units. Thus, the materials of this study should have different swelling and mechanical properties. Regarding the former, they should present increasing swelling at high rather than at low pH, and regarding the latter, they should be softer and less fragile. The resulting materials were characterized thoroughly in terms of their swelling behavior in water and tetrahydrofuran. Moreover, their mechanical properties were studied using dynamical mechanical analysis (DMA). Finally, the nanophase behavior of the conetworks was investigated using small-angle neutron scattering (SANS) and atomic force microscopy (AFM).

Experimental Section

Materials and Methods. Methacrylic acid (MAA, hydrophilic and negatively ionizable, 98%), 2-ethylhexyl methacrylate (EHMA, 98%), ethylene glycol dimethacrylate (EGDMA, 98%), 3,4-dihydro-2H-pyran (DHP, 97%), methacryloyl chloride (MACl, 98+%), 2-butyl-1-octanol (BuOA, 95%), 3,5,5-trimethyl-1-hexanol (TMHA, 85%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, free radical inhibitor, 95%), calcium hydride (CaH₂, 90–95%), basic alumina, potassium metal (98%), and tetrabutylammonium hydroxide (40% in water) were all purchased from Aldrich, Germany. Triethylamine (Et₃N) and benzoic acid (99.9%) were purchased from Merck. Sodium metal was purchased from Fluka, Germany. Tetrahydrofuran (THF, 99.8%) was purchased from Labscan, Ireland, and was used both as the polymerization solvent (reagent grade) and as the mobile phase in chromatography (HPLC grade). Prior to its use as polymerization solvent, THF was dried by refluxing it over a potassium/sodium alloy for 3 days and was freshly distilled before the polymerization.

Initiator Synthesis. The bifunctional GTP initiator, 1,4-bis(methoxytrimethylsilyloxymethylene)cyclohexane (MTSCH), was synthesized according to the literature⁴⁸ and was distilled twice before use.

Catalyst Synthesis. The tetrabutylammonium bibenzoate (TBABB) catalyst was prepared by the method of Dicker et al.,⁴⁴ and was stored under vacuum until use.

Synthesis of the Tetrahydropyranyl Methacrylate (THPMA) Monomer. Tetrahydropyranyl methacrylate (THPMA) was in-house synthesized by the catalytic esterification of MAA with 100% excess DHP at 55 °C,⁴⁹ using a modification of the procedure reported by Hertler.⁵⁰ Thus, sulfuric acid, rather than cross-linked poly(4-vinylpyridine hydrochloride), was used as the acid catalyst.

Synthesis of Monomers 2-Butyl-1-octyl-methacrylate (BOMA) and 3,5,5-Trimethyl-1-hexyl methacrylate (TMHMA). The two hydrophobic monomers 2-butyl-1-octyl-methacrylate (BOMA) and 3,5,5-trimethyl-1-hexyl methacrylate (TMHMA) were prepared by the esterification of MACl with the corresponding alcohols, BuOA and TMHA. The reaction was carried out under a dry nitrogen atmosphere at 0 °C, in THF solution, in the presence of Et₃N. The resulting insoluble salt of Et₃N·HCl was removed from the monomers by filtration.

Figure 1 shows the chemical structures and names of the monomers, the cross-linker, and the initiator that were used to synthesize the quasi-model APCNs of this study.

Monomer and Cross-Linker Purification. All monomers and the cross-linker were purified by passage through basic aluminum oxide columns (THPMA required 2–3 passages) to remove the acidic impurities. Subsequently, they were stirred over CaH₂, in the presence of the DPPH free-radical inhibitor (to avoid undesirable thermal polymerization), to remove all moisture and the last traces of acidic impurities, and they were stored at 5 °C. Finally, the monomers and the cross-linker were vacuum distilled just prior to the polymerization and kept under a dry nitrogen atmosphere until use.

Polymerizations. All the conetworks in this study were synthesized by GTP.^{35–39,51,52} The reactions were carried out in 250-mL

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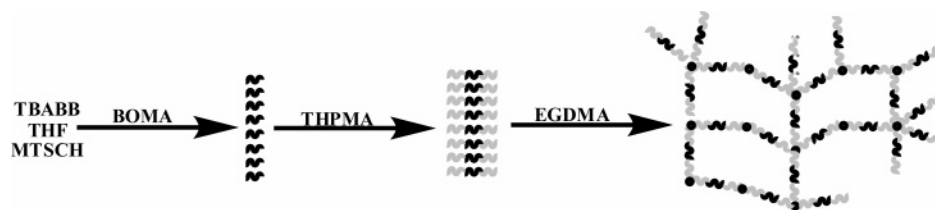


Figure 2. Schematic representation of the synthetic procedure for the preparation of the conetwork based on the THPMA₁₀-*b*-BOMA₁₀-*b*-THPMA₁₀ triblock copolymer. The BOMA and EGDMA units are black, while the THPMA units are gray. The number of arms at the cross-links is not 3–5 (as the Figure indicates) but around 30.^{36c}

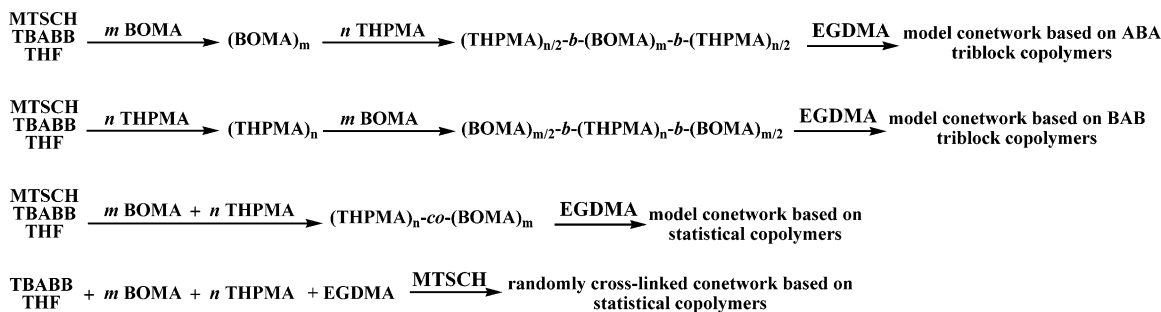


Figure 3. Synthetic routes followed for the preparation of the four different conetwork architectures.

round-bottom flasks at room temperature. The polymerization exotherm was monitored by a digital thermometer to follow the progress of the reaction.

The polymerization procedure for the synthesis of one of the quasi-model APCNs (Network 5) is detailed below and is illustrated schematically in Figure 2. Freshly distilled THF (27 mL), MTSCH initiator (0.33 mL, 0.40 g, 1.15 mmol), and BOMA (3.66 mL, 3.11 g, 11.5 mmol) were added in this order via a syringe to the polymerization flask, fitted with a rubber septum, kept under a dry nitrogen atmosphere, and containing a small amount (~10 mg, 20 μ mol) of TBABB catalyst. The polymerization exotherm (22–26 °C) abated within 5 min, samples were extracted and then, the second monomer, THPMA (2.50 mL, 2.34 g, 23.4 mmol), was added slowly giving an exotherm (23–37 °C). After sampling, EGDMA (1.75 mL, 1.84 g, 9.28 mmol) was added, leading to network formation within seconds. During the cross-linking reaction, the temperature increased from 27 to 34 °C.

Conetworks of different compositions and architectures were prepared by varying the comonomer ratio and the order of reagent addition, respectively. The synthetic sequences used for the preparation of the conetworks are summarized in Figure 3.

Characterization of the Conetwork Precursors. Gel Permeation Chromatography. The molecular weights (MWs) and the molecular

weight distributions (MWDs) of the linear homopolymer and the copolymer precursors to the conetworks were determined by gel permeation chromatography (GPC) before conetwork formation. GPC was performed on a Polymer Laboratories chromatograph equipped with an ERC-7515A refractive index detector and a PL mixed “D” column. The mobile phase was THF, delivered at a flow rate of 1 mL min⁻¹ using a Waters 515 isocratic pump. The MW calibration curve was based on eight narrow MW (630, 2600, 4250, 13000, 28900, 50000, 128000, and 260000 g mol⁻¹) linear poly-(methyl methacrylate) standards from Polymer Laboratories.

¹H NMR Spectroscopy. The synthesized monomers THPMA, BOMA, and TMHMA were characterized by ¹H NMR spectroscopy using a 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet. The solvent was CDCl₃ containing traces of tetramethylsilane (TMS), which was used as an internal reference. ¹H NMR was also used to characterize the precursors to and the extractables from the conetworks.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) was performed on a Q100 TA Instruments calorimeter to determine the glass transition temperatures (*T*_g's) of the linear homopolymers of BOMA, TMHMA, and EHMA in the temperature range between –150 and 150 °C. The heating rate was 10 °C/min. Each sample was run twice, and the second heat was used for the analysis.

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Determination of the Sol Fraction in the Conetworks. The prepared conetworks were taken out of the polymerization flasks and were washed in 200 mL of THF for two weeks to remove the sol fraction. Next, the THF solution was recovered by filtration. The extraction procedure was repeated once more after two weeks, and the solvent from the combined extracts was evaporated using a rotary evaporator. The recovered polymer was further dried overnight in a vacuum oven at room temperature. The sol fraction was calculated as the ratio of the dried mass of the extracted polymer divided by the theoretical mass of the polymer in the conetwork. The latter was calculated from the polymerization stoichiometry as the sum of the masses of the monomers, the cross-linker, and the initiator. The dried extractables were subsequently characterized in terms of their MW and composition by GPC and ^1H NMR spectroscopy, respectively.

Hydrolysis of the THPMA Units in the Conetworks. After the extraction, a part of each conetwork was transferred to a solution composed of 100 mL of THF and 34 mL of a 2 M HCl aqueous solution whose number of HCl moles was more than twice the number of THPMA equivalents in the conetwork. The system was allowed to hydrolyze for 3 weeks, followed by washing with distilled water for another 2 weeks to remove THF, DHP, and the excess HCl. The water was changed every day. A small sample from each conetwork was cut and dried under vacuum, and its FTIR spectrum was recorded.

Characterization of the Hydrolyzed Networks. Fourier Transform Infrared Spectroscopy. The Fourier transform infrared (FTIR) spectra of the conetworks (before and after hydrolysis) were recorded using a Shimadzu FT IR-NIR Prestige-21 spectrometer bearing an attenuated total reflection (ATR) accessory.

Dynamic Mechanical Analysis. The mechanical behavior of the conetworks (hydrolyzed and uncharged) was investigated using a Tritec2000 Triton Technologies DMA. The measurements were performed in the compression mode at a single frequency of 1 Hz. The experiments were carried out at 25 °C and, during the measurements, the samples were immersed in water (pH \approx 8).

Measurements of the Degree of Swelling (DS). The hydrolyzed conetworks were cut into small pieces (1–2 cm³) and dried under vacuum for 76 h. The dry conetwork mass was determined gravimetrically, followed by the transfer of the networks in THF or in water. One sample from each conetwork was allowed to equilibrate in THF, and 12 other samples were allowed to equilibrate in basic, neutral, and acidic milli-Q (deionized) water for two weeks. In nine of the twelve samples, a precalculated volume of base (0.5 M NaOH standard solution) was added, such that degrees of ionization between 10% and 100% were achieved. The calculation was based on the measured dry mass of each sample, from which the number of equivalents of MAA units was estimated (granting that no MAA units were ionized before the addition of NaOH). The pH of these nine samples covered the range between 8 and 13. One sample remained neutral (no acid or base was added) and had a pH of 5–7. Two samples became acidified by the addition of small volumes of a 0.5 M HCl standard solution. The samples were allowed to equilibrate for 3 weeks. The degrees of swelling (DSs) were calculated as the ratio of the swollen conetwork mass divided by the dry conetwork mass. All DSs were determined five times, and the averages of the measurements are presented along with their 95% confidence intervals. After the measurements of the DSs in water as a function of pH, the water-swollen samples were dried in a vacuum oven at room temperature for 3 days. A volume of 5 mL of THF was transferred into the glass vials containing the dried conetwork samples, which were allowed to equilibrate for 3 weeks. The THF-swollen mass of each conetwork was determined gravimetrically, from which the DS in THF was calculated.

Calculation of the Degrees of Ionization (DI) and the Effective pK. The degree of ionization (DI) of each sample was calculated as the number of NaOH equivalents added divided by the number of MAA unit equivalents present in the sample. The hydrogen ion titration curves were obtained by plotting the calculated DIs against the measured solution pH. The effective pK of the MAA units in each conetwork was estimated from the hydrogen ion titration curve as the pH (of the supernatant solution) at 50% ionization.

Small-Angle Neutron Scattering (SANS). All the (hydrolyzed) conetworks of this study were characterized using SANS in D₂O. The samples were in the uncharged state (pH \approx 8). 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). The incident wavelength was $\lambda = 6 \text{ \AA}$. Three sample-to-detector distances, 1.00, 4.00, and 15.30 m, were employed, covering a q -range [$q = 4\pi/\lambda \sin(\theta/2)$] from 0.003 to 0.60 \AA^{-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. The distance between the scattering centers was estimated from the position of the intensity maximum, q_{max} , as $2\pi/q_{\text{max}}$.

Atomic Force Microscopy (AFM). The surfaces of the dried samples (hydrolyzed and uncharged) were microtomed at room temperature with a diamond knife from Diatome and a Microtom ULTRACUT UCT from Leica, removing about 100 nm of the surface. AFM images of the microtomed samples were recorded with a Nanoscope III scanning probe microscope from Digital Instruments using Si cantilevers (tip radius about 5 nm) with a fundamental resonance frequency of approximately 200 kHz.

Results and Discussion

Copolymer Design. The aim of this study was to synthesize quasi-model APCNs using a new combination of monomers and to extensively characterize their properties. The hydrophilic monomer would be a weak acid rather than a weak base, so that aqueous swelling would increase with increasing pH. MAA could not be polymerized by GTP in its free form because its labile protons would cause termination of the polymerization. Thus, a chemically protected form was necessary. To this end, THPMA was selected. This monomer is reasonably stable for the polymerization, and it can be readily hydrolyzed under acidic conditions after the polymerization to MAA units. However, THPMA is not commercially available, and it had to be synthesized in the laboratory.

The hydrophobic monomer should give rubbery units (corresponding to homopolymers with a low T_g). This, in turn, required a relatively large number of carbon atoms and branching in the pendant group in the monomer. To this end, three hydrophobic monomers were tested. One of them, EHMA, was commercially available, while the other two, TMHMA and BOMA, were not and were therefore synthesized in the laboratory. To the best of our knowledge, there are no previous reports on their preparation. The ^1H NMR spectra of these two novel monomers are shown in Figure 4.

These three monomers were polymerized by GTP to produce linear homopolymers of degrees of polymerization (DP) around 30, whose T_g 's were measured using DSC. The monomer whose homopolymer exhibited the lowest T_g from the three was BOMA. In particular, the T_g 's of polyEHMA and polyTMHMA were around 0 °C, while that of polyBOMA was around -50 °C, which is slightly lower than the T_g 's of the homopolymers of the most common and commercially available methacrylates, even lower than that of poly(lauryl methacrylate)—the lauryl methacrylate monomer is an isomer of BOMA—which presents a T_g between -48 °C⁵³ and -43 °C.⁵⁴ Therefore, the BOMA monomer was chosen for the synthesis of the quasi-model APCNs in this study. It is noteworthy that BuOA, the alcohol from which BOMA was prepared, is naturally found in fish oil⁵⁵ and honey,⁵⁶ contributing to the rheological properties of these fluids.

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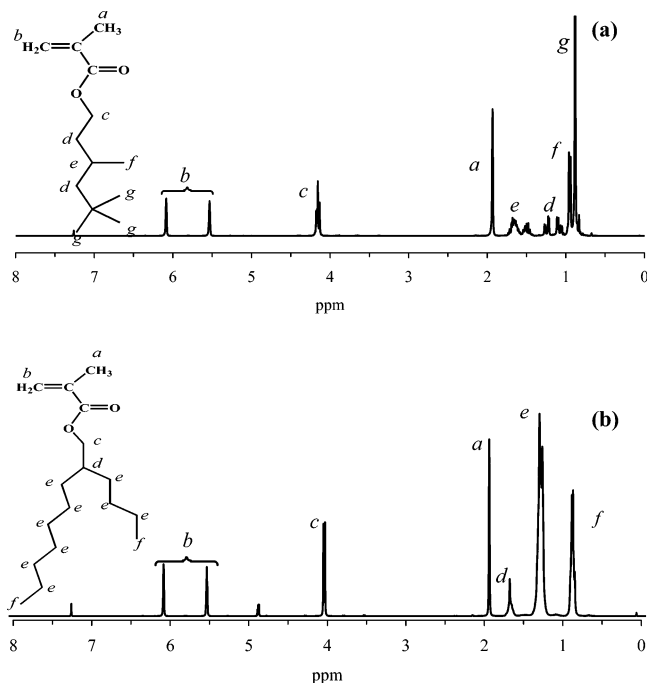


Figure 4. The ^1H NMR spectra of (a) the TMHMA and (b) the BOMA monomers.

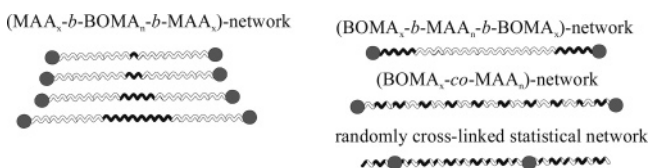


Figure 5. Schematic representations of the structures of the segments between the cross-links of the conetworks of this study. The white and black colors represent the MAA and the BOMA units, respectively. The EGDMA cross-links are shown as gray circles. Conetworks of different architecture and the same composition are shown in the right-hand-side column, while conetworks of the same architecture but different composition are shown on the left.

Polymerization Methodology. The structures of the linear precursors to the APCNs are shown in Figure 5. Conetworks of different compositions and architectures were prepared by varying the comonomer ratio and the order of reagent addition, respectively (see Figure 3). In particular, for the two triblock copolymer-based architectures, shown in the left-hand-side column of Figure 5 and the first structure in the right column, the two monomers were added sequentially to the THF solution of the initiator and catalyst, and then the EGDMA cross-linker was introduced to the system. For the second conetwork structure in the right-hand-side column, the two monomers were added simultaneously to form a statistical copolymer before the addition of the cross-linker. Finally, upon the addition of the initiator into a solution of the monomers and the cross-linker, a randomly cross-linked conetwork was prepared (third structure in the right-hand-side column).

Molecular Weights and Compositions. Table 1 lists the number-average molecular weights (M_n 's), the polydispersity indices (PDIs, M_w/M_n) and the compositions of the precursors to the conetworks as measured by GPC and ^1H NMR, respectively. The M_n 's of the precursors to the conetworks were higher than the theoretically calculated MWs, also shown in the table, probably

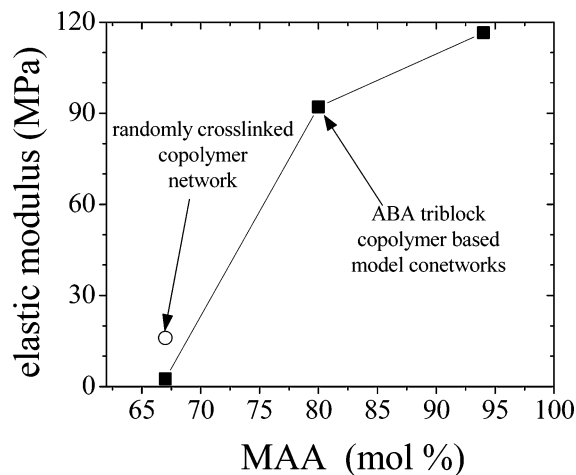


Figure 6. Dependence of the elastic moduli of the hydrolyzed and uncharged $\text{MAA}_{10}\text{-}b\text{-BOMA}_m\text{-}b\text{-MAA}_{10}$ conetworks in water ($\text{pH} \approx 8$) on the MAA content.

Table 1. Molecular Weights, Polydispersity Indices and Compositions of the Linear Precursors to the MAA–BOMA Conetworks

net. no.	chemical structure ^a	theoretical MW	M_n by GPC	M_w/M_n by GPC	% mol THPMA	
					theoretical	^1H NMR
1	$\text{B}_{1.25}$	338	962	1.25	—	—
	$\text{T}_{10}\text{-}b\text{-B}_{1.25}\text{-}b\text{-T}_{10}$	3740	6190	1.13	94	95
2	$\text{B}_{2.5}$	676	1570	1.24	—	—
	$\text{T}_{10}\text{-}b\text{-B}_{2.5}\text{-}b\text{-T}_{10}$	4080	7180	1.14	89	83
3	B_5	1353	3440	1.13	—	—
	$\text{T}_{10}\text{-}b\text{-B}_5\text{-}b\text{-T}_{10}$	4750	10030	1.18	80	81
4	T_{20}	3400	5960	1.13	—	—
	$\text{B}_5\text{-}b\text{-T}_{20}\text{-}b\text{-B}_5$	6100	6680	1.23	67	67
5	B_{10}	2704	5900	1.09	—	—
	$\text{T}_{10}\text{-}b\text{-B}_{10}\text{-}b\text{-T}_{10}$	6100	15330	1.25	67	74
6	$\text{T}_{20}\text{-}co\text{-B}_{10}$	6100	16520	1.15	67	83
7	random–random	6100	—	—	67	—

^a B, T, and b are (further) abbreviations for BOMA, THPMA (MAA), and block, respectively.

due to partial deactivation of the initiator. The MWDs of the homopolymer precursors were found to be narrow, with PDIs lower than 1.16, with the exception of the two BOMA homopolymer precursors with the lowest DP. The GPC traces of the copolymer precursors were monodisperse, without any traces of the corresponding homopolymer precursor, with reasonably low (< 1.25) PDIs. The compositions of the copolymer precursors were determined from the ^1H NMR spectra (not shown) by ratioing the signal from the two esteric methylene protons of BOMA at 4.0 ppm to that from the one ester acetal proton of THPMA at 5.9 ppm and were found to be satisfactorily close to the theoretically calculated compositions.

Percentage, MW, and Composition of the Sol Fraction of the Conetworks. Table 2 shows the mass percentage, the M_n 's, the PDIs, and the composition of the extractables from each conetwork as measured by gravimetry, GPC, and ^1H NMR. With the exception of Network 4, the sol fractions of the conetworks were lower than 25%. Network 4 was the only conetwork with BAB architecture (BOMA- b -THPMA- b -BOMA triblock copolymer linear precursor), and its high sol fraction was probably due to a cross-reactivity of the BOMA–EGDMA pair lower than that of the THPMA–EGDMA pair. From the M_n 's and the PDIs of the extractables, the step where the highest deactivation occurred during synthesis could be inferred. For all the conetworks, the extractables contained more of the monomer

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Table 2. Mass Percentage, Molecular Weights, and Compositions of the Sol Fractions Extracted from the Networks, as Measured by Gravimetry, GPC, and ^1H NMR

net. no	theoretical chemical structure ^a	extractables (w/w %)	GPC results		% mol THPMA		
			M_n	M_w/M_n	theoretical of precursor	precursor	extractables
1	$T_{10}\text{-}b\text{-}B_{1.25}\text{-}b\text{-}T_{10}$	25.3	5970	1.26	94	95	64
2	$T_{10}\text{-}b\text{-}B_{2.5}\text{-}b\text{-}T_{10}$	20.5	6690	1.27	89	83	44
3	$T_{10}\text{-}b\text{-}B_5\text{-}b\text{-}T_{10}$	23.3	9250	1.31	80	81	33
4	$B_5\text{-}b\text{-}T_{20}\text{-}b\text{-}B_5$	39.3	6280	1.92	67	67	53
5	$T_{10}\text{-}b\text{-}B_{10}\text{-}b\text{-}T_{10}$	18.9	25360	1.01	67	74	39
6	$T_{20}\text{-}co\text{-}B_{10}$	24.6	16840	1.21	67	83	61
7	random-random	7.2	—	—	67	—	30

^a B, T, and *b* are (further) abbreviations for BOMA, THPMA (MAA), and *block*, respectively.

units of the middle block of the linear precursor, indicating that most of the deactivation occurred at the beginning of the copolymerization.

Yields of Cross-Linker Polymerization and THPMA Hydrolysis. To convert the THPMA units to MAA units, acid hydrolysis rather than thermolysis was used.^{49,52a,57} Acid hydrolysis provides a cleaner route to deprotection than thermolysis^{49,58} due to the tendency of the latter to lead to partial anhydride formation.^{59,60} The hydrolysis was carried out using a 2 M HCl solution containing a 100% excess of HCl relative to the THPMA units. The conversion to MAA units was confirmed qualitatively by FTIR from the appearance of a double peak at 2940–2860 cm^{-1} due to the stretching vibration of the OH group of MAA. The ATR-FTIR spectra also indicated full conversion of the vinyl groups of the cross linker due to the absence of the signal at 1637 cm^{-1} .

Mechanical Properties of the Conetworks. The elastic moduli in compression of the hydrolyzed and washed conetworks in water at $\text{pH} \approx 7\text{--}8$ were determined using DMA and are plotted against the MAA content in Figure 6. The elastic moduli of the conetworks based on $\text{MAA}_{10}\text{-}b\text{-}\text{BOMA}_m\text{-}b\text{-}\text{MAA}_{10}$ triblock copolymers ranged between 2.5 and 110 MPa and increased with the MAA content because of the concomitant decrease in the BOMA soft component. The modulus of the randomly cross-linked conetwork (also shown in the figure) was much lower than those of the MAA-rich triblock copolymer conetworks, and higher than that of its ABA triblock copolymer isomer. The latter difference may be attributed to the greater density of elastic chains in the randomly cross-linked conetwork, resulting from the random distribution of the cross-linker in the conetwork.⁶² In contrast, in the triblock copolymer-based conetworks, the cross-linkers were concentrated at the chain ends (four cross-linker residues per chain end), leading to fewer elastic chains of higher MW.

Degrees of Swelling and Ionization. The experimentally measured DSs in water and in THF and the DIs of all the conetworks are plotted against pH (the aqueous pH; for the samples in THF the pH reported is that measured in water prior to drying and transfer to THF) in Figure 7. The DSs in the two solvents followed exactly the opposite pH dependencies, with

those in water following closely the DI curves. In water, the conetworks started to swell above pH 7 due to the ionization of the weakly acidic MAA units. There were two driving forces for the swelling of the conetworks: the osmotic pressure in the conetworks caused by the presence of the sodium counterions to the carboxylate groups,⁶³ and the electrostatic repulsive forces between the backbones caused by the presence of the negative charge on the MAA blocks.¹⁰ The DSs presented a maximum around pH 11, followed by a small decrease at higher pH values, which was probably due to the increase in the ionic strength effected by the relatively high concentration of NaOH under these conditions.⁶³ The degree of ionization (DI) vs pH curves followed the respective DS vs pH curves, confirming the importance of electrostatics in swelling.

In THF, the conetworks showed the opposite behavior. In particular, the DSs in THF decreased as the ionization of the MAA units in the conetworks (and the aqueous pH) increased. This was due to the incompatibility of THF with the ionized MAA units. The incompatibility of charged units with organic solvents of low dielectric constant is referred to as the ionomer effect, which has already been reported for networks with ionized carboxylic acid units equilibrated in various organic solvents and solvent mixtures.^{64–68}

The plots in Figure 7 were used to extract the pKs and the DSs in water and in THF in the uncharged and the fully charged states of the conetworks, which are presented and discussed in the following sections.

Effective pKs of the MAA Units. The dependence of the effective pKs of the MAA units in the conetworks on the MAA content of the conetworks is shown in Figure 8. The percentage of MAA content does not seem to influence the effective pK values of the MAA units in the conetworks. This contradicts previous studies on DMAEMA–MMA conetworks where a weakening effect on the basic character of the DMAEMA units (decrease in the value of the effective pKs) was observed with an increase in the hydrophobicity because of the decrease in the dielectric constant.^{36b,63,69} The insensitivity of the effective pKs of the MAA units to the MAA content might be due to the high percentage of MAA in these conetworks, which varied within a relatively narrow range, between 67 and 94 mol %. No effect of the conetwork architecture on the effective pKs of the MAA

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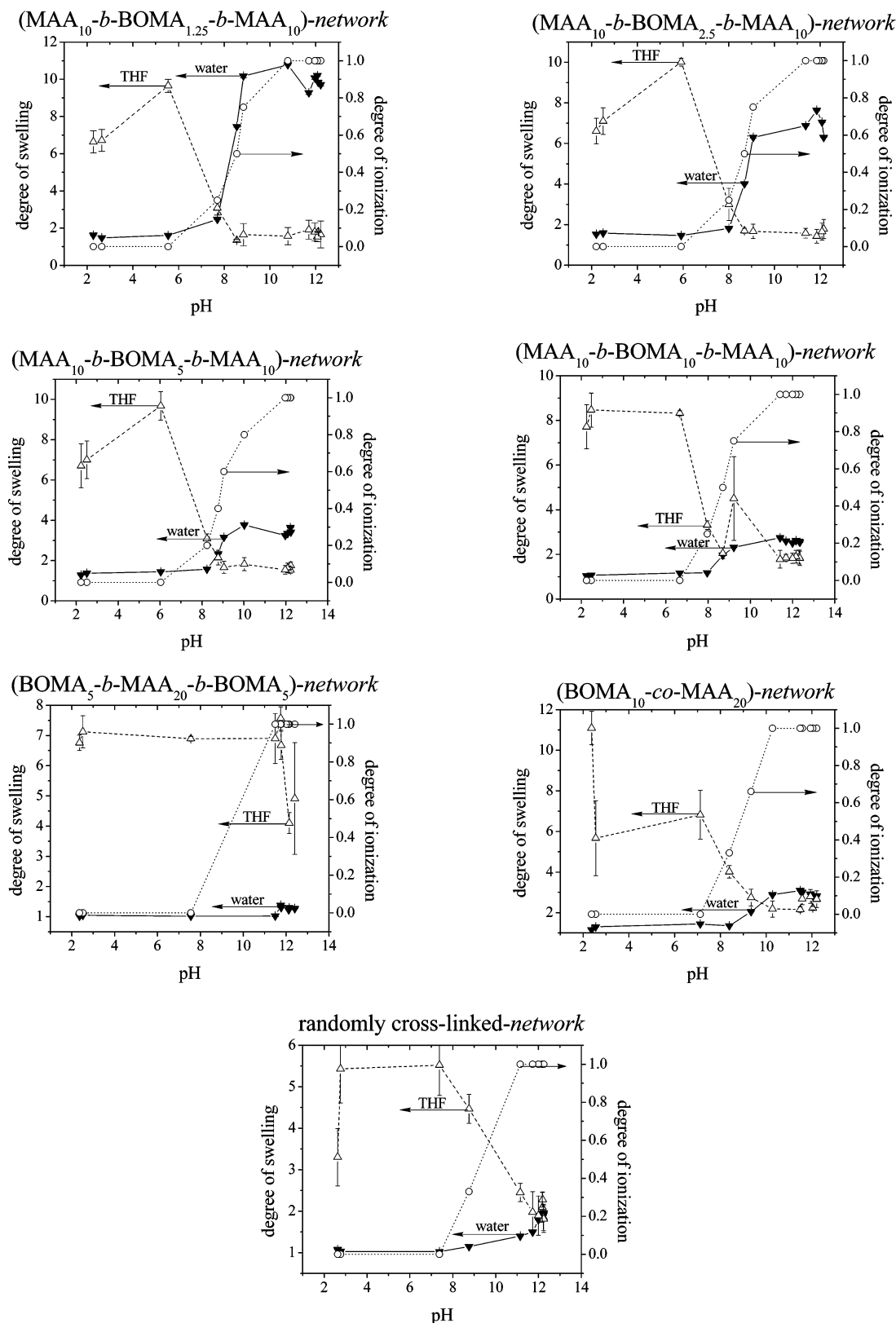


Figure 7. Degrees of swelling in water and in THF and degrees of ionization of all the conetworks as a function of pH.

units in the conetworks was observed, with the conetworks exhibiting quite similar pK values (8.7–9.5), in agreement with previous studies. The effective pK values of these conetworks were higher than those reported in the literature for MAA homopolymer networks of $pK = 6.8$, as expected.⁵⁷

DSs in Water and in THF in the Fully Charged and Uncharged States. The DSs of the conetworks in water and in

THF in the completely ionized ($pH \approx 11$) and the uncharged ($pH \approx 2$) states are shown in Figure 9. Figure 9a focuses on conetwork composition, while Figure 9b presents the effect of conetwork architecture. The DSs in high pH water were higher than the DSs in low pH water due to the ionization of the MAA units in the higher pH range. The DSs in THF in the uncharged state were higher than the DSs in (low pH) water in the uncharged state and

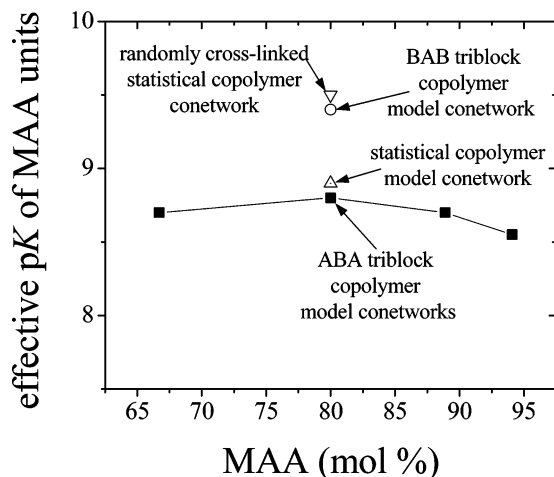


Figure 8. Dependence of the effective pKs of the MAA units in the conetworks on the MAA content and on the conetwork architecture.

in THF in the fully charged state for all the conetworks, because both the BOMA and the uncharged MAA units were compatible with THF, whereas BOMA and fully ionized MAA were incompatible with water and THF, respectively. The DSs of the uncharged conetworks in THF were also higher than the DSs in (high pH) water in the fully charged state for all the conetworks, with the exception of the two conetworks with the highest MAA content whose composition was very close to that of the MAA homopolymer (and high pH water was a better solvent for the MAA segments than THF).

Figure 9a shows that the DSs in water of the fully charged conetworks (high pH water) increased with the percentage of MAA, as expected. In particular, the DSs increased from 2.5 to 11 as the MAA content increased from 67 to 94 mol %. This relatively large swelling was achieved despite the fact that the conetworks bore highly hydrophobic BOMA units. This indicated that the electrostatic repulsion constituted a strong driving force for conetwork swelling. In contrast, the DSs in water of the uncharged conetworks (low pH water) were very low and increased slightly, from 1 to 2, with the MAA content. This slight increase in the swelling was due to the small but finite compatibility of the protonated MAA units with water. However, the conetworks were almost collapsed due to the combination of the great incompatibility of the BOMA units with water and the marginal compatibility of the protonated MAA units with water. Similarly low were also the DSs in THF of the fully charged conetworks. In this case, however, there was a slight decrease of the DS with the MAA content. This was due to the concomitant decrease of the content in BOMA, which was THF compatible. The conetworks were almost collapsed in this solvent because of the great incompatibility of charged MAA units with THF. Finally, Figure 9a displays the DSs in THF of the uncharged conetworks. These DSs were rather high due to the compatibility of THF with both the BOMA and the uncharged MAA units (nonselective solvent), and decreased slightly from 8 to 7 as the MAA content increased due to the accompanying decrease of the DP of the chains between cross-links from 30 to 21.

Figure 9b illustrates the effect of conetwork architecture on the DSs. At low pH, the DSs in water of all the (uncharged) conetworks were very low (as explained before) and similar, without presenting any architecture effect. The DSs in THF of the uncharged conetworks were highest (again as explained before). The values of the DSs in THF of the three uncharged quasi-model conetworks (the statistical copolymer-based and the two triblock copolymer-based) were between 7 and 8,

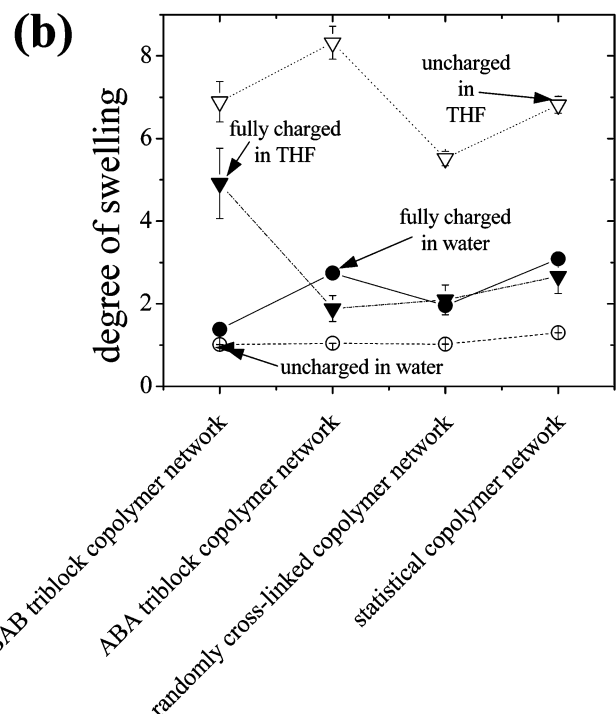
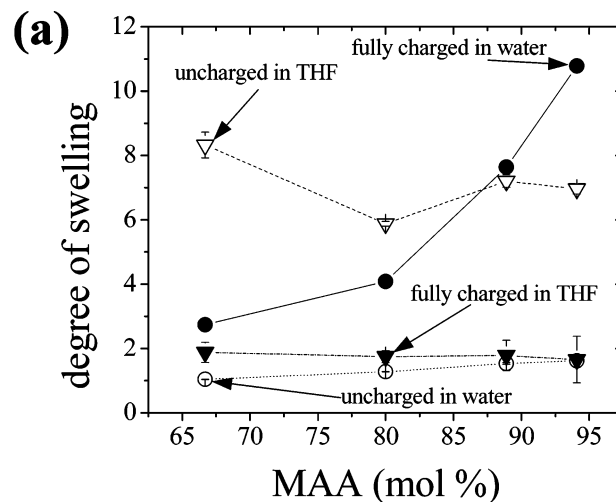


Figure 9. Degrees of swelling of the conetworks in water and in THF at their uncharged and fully charged states. Effects of (a) conetwork composition and (b) conetwork architecture.

reflecting their similar chain lengths between cross-linking points, whereas the DS of the randomly cross-linked conetwork was lower, around 5.5, manifesting the greater density of elastic chains, as explained in the section “Mechanical Properties of the Conetworks.” Stronger copolymer architecture effects were observed with the DSs of the fully charged conetworks in both solvents. For the triblock copolymer-based conetworks, lowest swelling was obtained when the solvent-incompatible blocks were end-blocks. This would lead to the formation of micelle-like structures around the cross-linking nodes, which would cooperatively reduce the effective chain lengths and lower swelling. Thus, the fully ionized ABA (MAA₁₀-*b*-BOMA₁₀-*b*-MAA₁₀) triblock copolymer-based conetwork exhibited lower swelling in THF than in water. The reverse was true for the fully ionized BAB (BOMA₅-*b*-MAA₂₀-*b*-BOMA₅) triblock copolymer-based conetwork which displayed lower swelling in water than in THF. Moreover, in this case, the DS in water was very low due to the additive effect of the hydrophobic EGDMA cross-

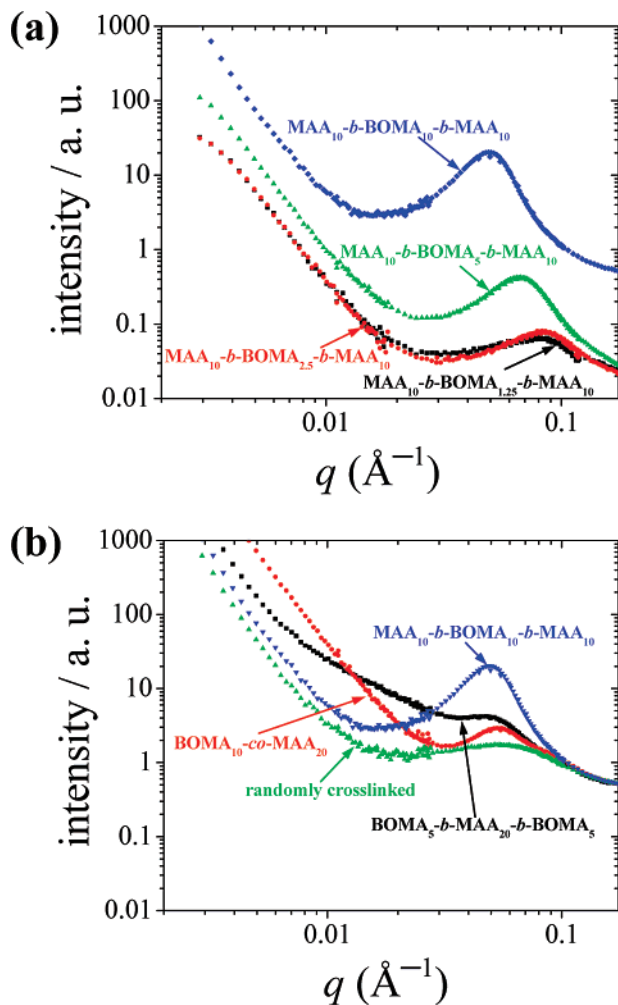


Figure 10. SANS profiles of all the APCNs in D₂O in the uncharged state.

linker units placed next to the BOMA end-blocks. The DSs of the ionized randomly cross-linked conetwork in water and THF were rather low (higher density of elastic chains) and equal, whereas those of the ionized statistical copolymer conetwork were slightly higher.

Nanophase Behavior. In the following, we provide the results of an investigation of the nanophase behavior of the conetworks, using both SANS and AFM.

SANS. Figure 10 shows the SANS profiles of all the APCNs in the uncharged state in D₂O. Figure 10a illustrates the effect of conetwork composition, while Figure 10b presents the effect of conetwork architecture. In Figure 10a, all SANS profiles exhibited single peaks, consistent with conetwork nanophase separation. The absence of higher harmonics could be attributed to the polydispersity of the scattering centers or/and to their short-range liquidlike order.^{70–72} As the BOMA content in the APCNs increased, the position of the peaks was shifted to lower q -values, and the peak scattering intensity increased. The latter was in agreement with more complete nanophase separation in the more hydrophobic conetworks (larger scattering centers), while the former indicated the greater separation between the scattering centers as the size of the conetwork elastic chains

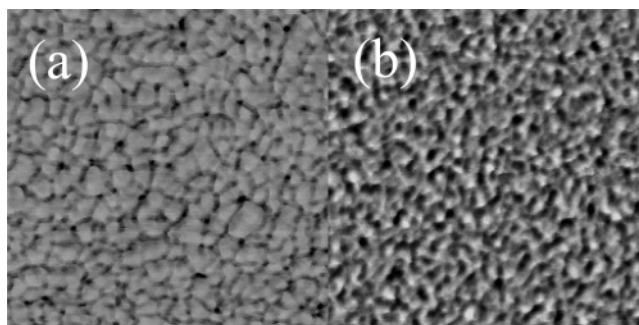


Figure 11. AFM phase mode images for (a) the PMAA–PBOMA–PMAA triblock copolymer-based and (b) the statistical copolymer-based quasi-model conetworks. Each image has dimensions of 500 nm \times 500 nm.

increased. In particular, the spacing between the scattering centers (calculated as $2\pi/q_{\max}$) varied from 7.7 to 7.6 nm, to 9.3 nm and to 12.8 nm as the M_n of the linear copolymer precursors to the conetworks increased from 6190 to 15330 g mol⁻¹ (see Table 1).

Figure 10b plots the SANS profiles of the four isomeric APCNs having different architectures. All curves presented a peak, manifesting the presence of scattering centers. However, the peak of the randomly cross-linked APCN was very weak, possibly reflecting some correlation between EGDMA cross-linker residues or BOMA unimolecular micelles. The peaks of the three other APCNs were located approximately at the same q -values, suggesting similar distances between the scattering centers. This could be understood considering the fact that these APCNs were isomeric. The scattering profile of the BOMA₅-*b*-MAA₂₀-*b*-BOMA₅ conetwork was different from that of the MAA₁₀-*b*-BOMA₁₀-*b*-MAA₁₀ conetwork, as the peak of the former was less pronounced (it was almost a shoulder), followed by a shallow tail to lower q -values. This may be attributed to a conetwork morphology different from those of its isomers.

AFM. Figure 11 displays AFM images for the quasi-model APCNs based on (a) the MAA₁₀-*b*-BOMA₁₀-*b*-MAA₁₀ triblock copolymer and (b) the statistical copolymer. The images were measured in phase mode, which distinguishes between hard (bright) and soft (dark) phases. The triblock copolymer MAA₁₀-*b*-BOMA₁₀-*b*-MAA₁₀-based APCN (Figure 11a) displayed large spherical domains of a size of approximately 40 nm (domain sizes ranged from 28 to 55 nm), whereas the statistical copolymer-based conetworks exhibited smaller and elongated domains of a broadly distributed size in a range of 4–20 nm with the average of some 10 nm. The domain size of 40 nm in the former conetwork is larger than the characteristic size of 13 nm determined by SANS. This indicates that the contrast difference between the phases was not high enough to see distinguishable morphologies in the higher resolution. Note that one polymer phase (the MAA) was below its T_g . It is possible that the large domains seen in Figure 11a were phase separated as well. Thus, the SANS measurements can give complementary information to AFM. The domain size of 10 nm in the statistical copolymer quasi-model conetwork corresponds to the EGDMA cores and is in good agreement with the SANS measurements (scattering center spacing of 12 nm).

Conclusions

Seven amphiphilic conetworks were successfully synthesized using GTP. These conetworks comprised a novel, rubbery hydrophobic monomer, BOMA, and the hydrophilic, negatively ionizable MAA. The prepared conetwork series covered a wide range of compositions and architectures. The DSs of the

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conetworks in water increased with the DI of the MAA units, whereas their DSs in THF exhibited exactly the opposite dependence on the DI. The effect of composition and architecture of the conetworks was studied as well. The DSs of the conetworks in water both in the uncharged and charged states increased with the MAA content, whereas the DSs in THF in either state decreased with the MAA content. SANS on uncharged conetworks in D₂O provided the average spacing between the scattering centers, which increased with the MW between the cross-links of the MAA–BOMA–MAA quasi-model conetworks, while AFM indicated the formation of large domains in the above-mentioned type of conetworks in the bulk.

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