Amphiphilic Model Conetworks of Polyisobutylene Methacrylate and 2-(Dimethylamino)ethyl Methacrylate Prepared by the Combination of Quasiliving Carbocationic and Group Transfer Polymerizations

Theoni K. Georgiou[†] **and Costas S. Patrickios***[,‡]

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

Peter Werner Groh[§] **and Béla Iván***[,||]

Department of Polymer Chemistry and Material Science, Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences,
P. O. Box 17, Pusztaszeri u. 59-67, H-1525 Budapest, Hungary

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ABSTRACT: A series of amphiphilic polymer conetworks (APCN) of the hydrophobic polyisobutylene methacrylate macromonomer (PIBMA) and the ionizable hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA) were synthesized by combining, for the first time, two controlled polymerization methods, quasiliving carbocationic polymerization (QLCCP) and group transfer polymerization (GTP). First, isobutylene (IB) was polymerized by QLCCP, and the resulting IB 7-mer (PIB) was modified to yield PIBMA with exact chain end-functionality of 1.0. Subsequently, PIBMA was successfully polymerized sequentially by GTP with DMAEMA (comonomer) and ethylene glycol dimethacrylate (EGDMA, cross-linker) using a bifunctional GTP initiator, 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane. Amphiphilic conetworks with linear segments of well-defined molecular weights (model conetworks) and a randomly cross-linked conetwork with linear segments characterized by a broad size distribution between the cross-links were prepared. Four of the model conetworks were based on poly(PIBMA-*b*-DMAEMA-*b*-PIBMA) triblock copolymers and two were based on poly(DMAEMA-*b*-PIBMA-*b*-DMAEMA) triblock copolymers of different degrees of polymerization (DP). Another conetwork was prepared from statistical copolymer chains. For comparison, four more networks, two of them based on DMAEMA homopolymers and two others based on copolymers of DMAEMA and methyl methacrylate, were also synthesized in the course of this study. Gel permeation chromatography and ^{1}H NMR analyses indicated that the precursors to all the networks had the desired molecular weights and compositions. The degrees of swelling (DS) of the conetworks in tetrahydrofuran, *n*-hexane, and acidic water depended on the DP and the composition of the polymer chains between the EGDMA cross-links, while the DSs in neutral water were very low and almost constant because of the low degree of ionization of DMAEMA units in the conetworks in this solvent. These results show that the swelling behavior of the DMAEMA-PIBMA and DMAEMA-MMA conetworks can be controlled by the length and the composition of the chains between the cross-links, by the solvent polarity and the pH in a broad range.

Introduction

Amphiphilic polymer conetworks (APCN), composed of covalently bonded, otherwise immiscible hydrophilic and hydrophobic polymer chains, represent a new class of cross-linked polymers with a unique structure and, consequently, with unique properties.[1−32] The amphiphilic nature of these materials enables their swelling in both aqueous and hydrocarbon environments. Moreover, the arrangement of the conetwork hydrophilic and hydrophobic units into separate and sufficiently long segments leads to microphase separation.[33,34] These novel nanostructured[20,21] materials have great potential for their utilization in several specialty applications, such as nanotemplates for organic−inorganic nanohybrids,[26] pervaporation membranes,[23] supports for high efficiency enzyme catalysis,[27] antifouling coatings,[32] biomaterials, including controlled drug release matrices,[5,6,24,25] and scaffolds for tissue engineering.[22,28,29]

Most of the APCNs reported until now were prepared by the macromonomer method via radical polymerization of a telechelic macromonomer containing at least two polymerizable groups with a selected low molecular weight monomer leading to polymer chains with opposite philicity.[1,2,5−8,20,21,23,24,26,27] This process results in conetworks with polymer chains between the cross-linking points characterized by a broad molecular weight distribution. In order to obtain conetworks with a more controlled structure (“model” or “quasi-model” conetworks) the synthesis of APCNs by cross-linking polymer chains with well-defined lengths was recently investigated.[9−14] This mainly involved the preparation of block copolymers by group transfer polymerization (GTP),[35−39] followed by their endlinking using a difunctional monomer leading to a cross-linking core.[9−13]

The aim of the present work is to investigate the preparation and properties of model conetworks consisting of hydrophilic ionizable 2-(dimethylamino)ethyl methacrylate (DMAEMA) and polyisobutylene methacrylate (PIBMA) macromonomer segments coupled with ethylene glycol dimethacrylate (EGDMA). The PIBMA macromonomer was synthesized via quasiliving carbocationic polymerization (QLCCP).[40] This was followed by GTP copolymerization of DMAEMA and PIBMA, and subsequently conetwork formation by EGDMA addition to the GTP system. This work contains two novelties. First, on the synthetic side, this is the first approach to synthesize APCNs by

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* Authors to whom correspondence should be addressed.
[†] E-mail: chpgtg1@ucy.ac.cy.
[‡] E-mail: costasp@ucy.ac.cy.
[§] E-mail: groh@chemres.hu.
[||] E-mail: bi@chemres.hu.

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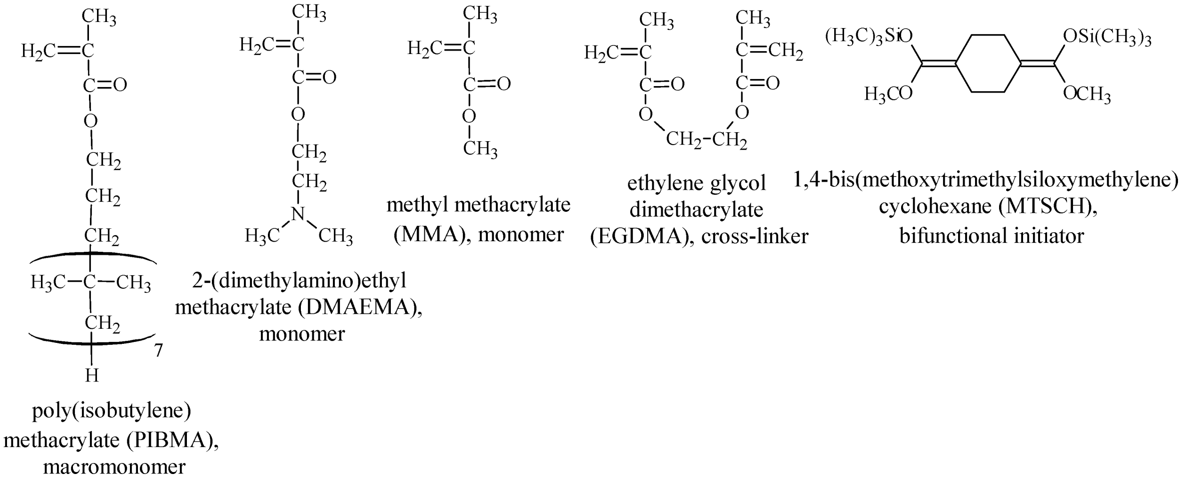


Figure 1. Chemical structures and names of the main reagents used for the conetwork synthesis.

combining two quasiliving polymerization techniques, in this case QLCCP and GTP. Second, the resulting conetworks are structurally different from all others reported so far, since one of the components, PIBMA, yields precursor copolymer chains with pendent hydrophobic PIB segments. The swelling behavior of these unique model conetworks is also reported in this work.

Experimental Section

Network Synthesis. Materials and Methods. The monomers, methyl methacrylate (MMA, hydrophobic, 99%) and DMAEMA (hydrophilic and ionizable, 98%), the cross-linker, EGDMA (98%), tetrabutylammonium hydroxide (40% in water), benzoic acid (99.5%), calcium hydride (CaH_2, 90−95%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, free radical inhibitor, 95%), basic alumina, potassium metal (98%), methacryloyl chloride (97%, MACl), dimethyl 1,4-cyclohexanedicarboxylate (97%) diisopropylamine (99.95%), *n*-butyllithium (2.5 M in hexane), titanium tetrachloride (99.9%), 1,1,4,4-tetramethylethylenediamine (99.5%, TMEDA), 2,4,4-trimethyl-1-pentene (99%), borane (BH_3, 1.0 M solution in tetrahydrofuran, THF), and hydrogen peroxide (35% solution in water) were all purchased from Aldrich, Germany. Hexane (96%) and dichloromethane (99.5%) were purchased from Scharlau S.A., Spain. Isobutylene (IB, 99.8%) was obtained from Messer Griessheim, Germany. Triethylamine (Et_3N, 99%), potassium hydroxide (98%), and sulfuric acid (96%) (all from Merck) were used as received. Sodium metal and allyltrimethylsilane (ATMS, 97%) were products of Fluka, Germany. THF (99.8%) was purchased from Labscan, Ireland, and was used as the mobile phase in chromatography (HPLC grade); it was also used as a solvent (reagent grade), both in the reaction for the synthesis of the macromonomer and for the polymerizations.

Figure 1 shows the chemical structures and names of the monomers, including those of the PIBMA macromonomer, the cross-linker and the initiator that were used for the conetwork synthesis.

Purification of Solvents, Monomers, and Other Reagents. THF was dried by refluxing it over a potassium/sodium alloy for 3 days and was distilled prior to use. *n*-Hexane was stored over concentrated H_2SO_4 for several weeks or refluxed over concentrated H_2SO_4 for 24 h in order to remove impurities containing double bonds. The acidic remnants and impurities were removed by filtration in a column filled with basic alumina. The filtrate was refluxed and distilled over CaH_2 under an inert nitrogen atmosphere prior to use. Dichloromethane was also refluxed over CaH_2 under inert atmosphere for several hours and was then distilled prior to use. IB was condensed at the reaction temperature (−78 °C) separately after passing it through an Aldrich Drierite gas-drying unit. The DMAEMA and MMA monomers and the EGDMA cross-linker were passed twice through basic alumina columns to remove inhibitors and protic impurities. They were subsequently stirred over CaH_2 in the presence of the DPPH free radical inhibitor and were stored at 5 °C until they were freshly distilled under vacuum, and then kept under a dry nitrogen atmosphere until use. Et_3N was dried by stirring it over CaH_2 for 3 days, followed by vacuum distillation just before use. MACl was freshly distilled under vacuum just before use, and it was kept under a dry nitrogen atmosphere.

Preparation of Initiators and Catalyst. The QLCCP monofunctional initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), was obtained by hydrochlorination of 2,4,4-trimethyl-1-pentene in CH_2Cl_2 followed by a vacuum distillation.[41] The 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane (MTSCH) bifunctional GTP initiator was synthesized by the silylation of dimethyl 1,4-cyclohexanedicarboxylate, accomplished in a two-step procedure: the reaction of dimethyl 1,4-cyclohexanedicarboxylate with diisopropylamine and *n*-butyllithium in absolute THF at −78 °C, followed by the reaction of the mixture with trimethylsilyl chloride under the same conditions.[42] The TBABB catalyst for GTP was prepared from the reaction of tetrabutylammonium hydroxide with benzoic acid, following the method of Dicker et al.[37] and was stored as a dried powder in a round-bottom flask under vacuum until use.

Synthesis of PIBMA by QLCCP and End Group Modifications. All glassware was dried at 120 °C overnight and was subsequently cooled to room-temperature prior to use. IB was polymerized by QLCCP. In particular, a 60:40 v/v *n*-hexane−dichloromethane solvent mixture (2900 mL), the TMPCl initiator (21.22 g, 0.14 mol), the catalyst system consisting of titanium tetrachloride/TMEDA (62.7 mL, 108.3 g, 0.57 mol/21.5 mL, 16.6 g, 0.14 mol), and the IB monomer (37.0 mL, 26 g, 0.46 mol) were added via syringes in this order to a 5000 mL round-bottom flask, under an inert dry nitrogen atmosphere at −80 °C.[43] The polymerization was terminated by ATMS (45.4 mL, 32.6, 0.28 mol), leading to the formation of an allyl chain end. The allyl-PIB was then purified with three extractions (one with hexane/methanol−ammonia and two with hexane/water) and by filtration through a neutral Al_2O_3 column. Subsequently, the allyl-PIB was modified to hydroxy-PIB (PIBOH) by a one-pot two-step reaction. The first step was the hydroboration of allyl-PIB (40 g, 0.091 mol in THF) by the addition of borane (293 mL, 1 M in THF).[44] The second step involved oxidation by the addition of a 25% w/w KOH solution in methanol (0.94 mol, 52.5 g, 210 mL), followed by the dropwise addition of a 30% w/w H_2O_2 solution in water (0.35 mol, 12.0 g, 36 mL) at 0 °C. The resulting PIBOH was esterified using MACl to give PIBMA. In particular, freshly distilled THF (160 mL) and Et_3N (0.27 mol, 12.9 g, 39.0 mL) were added in this order to a 500 mL round-bottom flask fitted with a rubber septum, kept under an inert dry nitrogen atmosphere and containing the PIBOH (0.088 mol, 40 g). Finally, MACl (0.16 mol, 9.12 g, 16.0 mL) was added dropwise at 0 °C. The resulting PIBMA was purified by filtration (of the Et_3NHCl salt), rotary evaporation and treatment with basic Al_2O_3, so that the remaining (excess) MACl would be completely

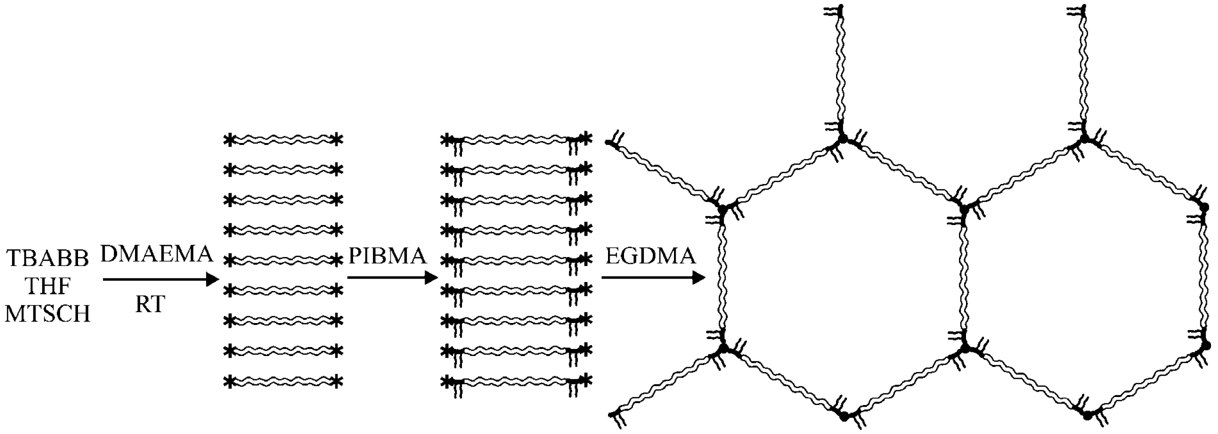


Figure 2. Schematic representation of the synthetic procedure followed for the preparation of the ABA triblock copolymer-based network 7 (Table 1): ($PIBMA_2$-*b*-$DMAEMA_{20}$-*b*-$PIBMA_2$)-*network*. The number of arms is not 3 as indicated in the figure, but much higher, around 30.[15,16] The black and white colors indicate poly(isobutylene methacrylate) (PIBMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) segments, respectively, while the asterisks denote active polymerization sites. TBABB: tetrabutylammonium bibenzoate. THF: tetrahydrofuran. MTSCH: 1,4-bis-(methoxytrimethylsiloxymethylene)cyclohexane. EGDMA: ethylene glycol dimethacrylate.

removed. Finally, the purified PIBMA macromonomer was dissolved in THF to obtain a 50% w/v solution. After the addition of DPPH and CaH_2, the macromonomer solution was stirred overnight, before being filtered directly into the reaction flask of the GTP polymerization using a 0.45 μm syringe filter. The allyl, hydroxyl, and methacrylated end-functional PIBs were analyzed in every step by ^{1}H NMR spectroscopy, indicating 100% functionality of the polymer. The number-average degree of polymerization (DP_n) of PIBOH was determined by ^{1}H NMR to be around 7, by calculating the ratio of the area of the signals due to the two methyl groups of isobutylene at 1.0 ppm and that of the oxymethylene protons at 3.6 ppm, corresponding to a number-average molecular weight (M_n) of 425 g mol^{-1}. Thus, the M_n of the resulting PIBMA was 520 g mol^{-1}.

GTP Polymerizations. The procedure established for conetwork preparation via GTP was followed.[11−13] The reactions were carried out in 250 mL 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 Network 7 based on ABA triblock copolymers, with a central block bearing 20 DMAEMA units and two PIBMA end-blocks bearing 2 PIBMA units each, is detailed below and is illustrated schematically in Figure 2. Freshly distilled THF (17 mL), MTSCH initiator (0.33 mL, 0.40 g, 1.15 mmol), and DMAEMA (3.9 mL, 3.6 g, 23 mmol) were added via syringes in this order to a 250 mL round-bottom flask fitted with a rubber septum, kept under an inert dry nitrogen atmosphere and containing a small amount (~10 mg, 20 μmol) of TBABB catalyst. The polymerization exotherm (22.6 − 43 °C) abated within 5 min, and then a sample was withdrawn for gel permeation chromatography (GPC) analysis (full monomer conversion, number-average molecular weight $M_n = 3800$ g mol^{-1}, $M_w/M_n = 1.18$; M_w is the weight-average molecular weight), and PIBMA (4.8 mL of 50% v/v solution in THF, 2.4 g or 4.6 mmol of neat macromonomer) was added slowly giving an exotherm (25.5 − 26.1 °C). After sample withdrawal for GPC and ^{1}H NMR analyses (full monomer conversion, $M_n = 6000$ g mol^{-1}, $M_w/M_n = 1.17$; copolymer composition 86 mol % DMAEMA), EGDMA (1.7 mL, 1.8 g, 9.2 mmol) was added, which promoted gelation within minutes and produced an exotherm (23.4−32.8 °C).

Characterization of the Conetwork Precursors. Gel Permeation Chromatography. The molecular weights (MW) and the molecular weight distributions (MWD) of all the linear precursors to the conetworks as well as of PIBOH were determined by GPC analyses. For PIBOH, a Waters 510 GPC chromatograph and a MicroStyragel column series with $10^3-10^2-10^1-5$ nm pore sizes supplied by Waters Associates was used. The detection was carried out by a dual Viscotek differential refractometer/viscometer detector at room temperature. THF was the mobile phase with a flow rate of 1.5 mL min^{-1}. The collection and the analysis of the data were carried out by Viscotek Trisec GPC 3.01 software, using the universal calibration method. The MWs and the MWDs of the linear precursors to the model conetworks prepared by GTP were determined by GPC using a single high MW range PL-Mixed “D” Polymer Laboratories column. The mobile phase was THF with a flow rate of 1 mL min^{-1} using a Waters 515 isocratic pump. The refractive index signal was measured using an ERC-7515A refractive index detector also supplied by Polymer Laboratories. The calibration curve was based on eight narrow MW (630, 2600, 4250, 13000, 28900, 50000, 128000, and 260000 g mol^{-1}) linear PMMA standards.

^{1}H NMR Spectroscopy. The allyl and hydroxyl end-functionalized PIBs were characterized by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a 200 MHz VXR Varian spectrometer. PIBMA was characterized using a 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet. The latter NMR spectrometer was also used to determine the compositions of the conetwork precursors and the extractables from the conetworks. The solvent was in all cases $CDCl_3$ containing traces of tetramethylsilane (TMS) which was used as an internal reference.

Characterization of the Conetworks. Determination of the Sol Fraction. The prepared conetworks were removed from the polymerization flasks and were washed in 200 mL THF for 1 week to remove the sol fraction. Next, the THF solution was recovered by filtration. The extraction procedure was repeated once more after 1 week and the solvent from the combined extracts was evaporated using a rotary evaporator. The recovered polymer was further dried for 24 h under vacuum 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 ^{1}H NMR spectroscopy, respectively.

Measurement of the Degree of Swelling. The washed conetworks were cut into small cubes with edge dimensions of ~10 mm. The mass of the THF-swollen cubes was measured gravimetrically before drying under vacuum for 72 h at room temperature, and then the mass of the dried conetworks was determined. The dried conetworks were subsequently transferred in water or THF. One sample from each conetwork was allowed to equilibrate in THF and 12 other samples were allowed to equilibrate in acidic, neutral and alkaline milli-Q (deionized) water for 3 weeks. Nine from the 12 samples were acidified by the addition of a calculated volume of a 0.5 M HCl standard solution, such that degrees of ionization between 12% and 100% were achieved. The calculation

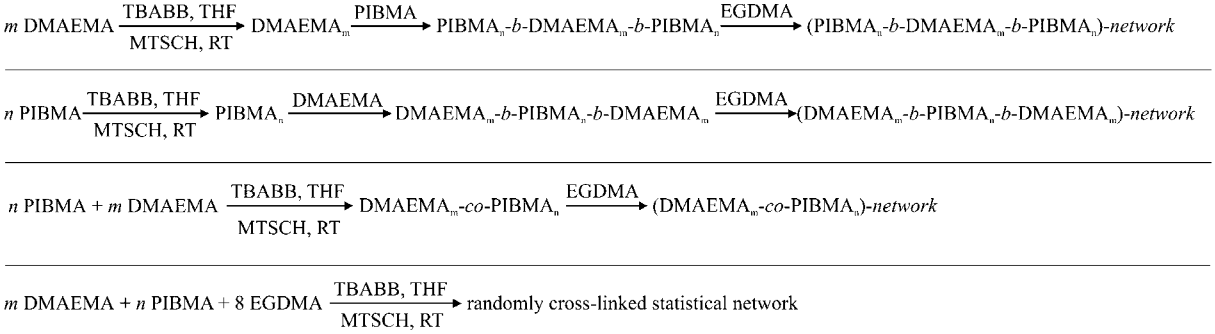


Figure 3. Synthetic sequences employed for the preparation of the different conetwork architectures. DMAEMA: 2-(dimethylamino)ethyl methacrylate. TBABB: tetrabutylammonium bibenzoate. THF: tetrahydrofuran. MTSCH: 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane. PIBMA: polyisobutylene methacrylate. EGDMA: ethylene glycol dimethacrylate.

was based on the measured dry mass of each sample, from which the number of equivalents of the DMAEMA units was estimated (granting that all DMAEMA units were not ionized before the addition of HCl). The pH of these nine samples covered the range between 2 and 7. One sample remained neutral (no acid or base was added) and had a pH 6−8. Two samples became alkaline by the addition of small volumes of a 0.5 M NaOH standard solution. The samples were allowed to equilibrate for 3 weeks. The degrees of swelling (DS) 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.

Calculation of the Degree of Ionization and the Effective p*K*. The degree of ionization (DI) of each sample was calculated as the number of HCl equivalents added divided by the number of DMAEMA unit equivalents present in the sample. This calculation is based on two assumptions. First, all the DMAEMA units were uncharged in the prepared conetworks, as uncharged DMAEMA monomer was used for the polymerizations, and water itself cannot cause ionization of the DMAEMA units in the conetworks. The second assumption is that all added HCl partitions almost exclusively into the gel phase rather than the supernatant solution phase, provided that the volume of supernatant solution is not much larger than the gel volume, as dictated by Donnan equilibrium for intermediate pH values ($\sim 3 - 11$). The hydrogen ion titration curves were obtained by plotting the calculated DI against the measured solution pH. The effective p*K* of the DMAEMA units in each conetwork was estimated from the hydrogen ion titration curve as the pH (of the supernatant solution) at 50% ionization.

Results and Discussion

Synthesis and Structure of the Conetworks. The conetworks were synthesized via the combination of two quasiliving polymerization techniques, QLCCP and GTP. To the best of our knowledge, this is the first report where these two polymerization methods were combined together to give conetworks and also the first time that an IB containing macromonomer was polymerized by GTP. However, there is one study by Takács and Faust where QLCCP and GTP were used to produce diblock copolymers, but that study involved the coupling reaction of the two homopolymers.[45] In the present study, the macromonomer methodology was used. In particular, after IB was polymerized using QLCCP and after quantitative chain end modifications of the resulting polymer, a methacrylate macromonomer, PIBMA, was produced. PIBMA characterization by ^{1}H NMR indicated a DP$_n$ of around 7, which corresponded to an M_n of 520 g mol^{-1}, and a complete chain end-functionality. The PIBMA macromonomer was then polymerized by GTP.

The main synthetic sequences employed for the preparation of the conetworks of this study are shown in Figure 3. They comprised successful multi- (two- or three-) step sequential additions in one-pot preparations. The linear (co)polymers produced via the (sequential) addition of methacrylate monomer(s) to a solution containing the bifunctional GTP initiator (MTSCH) and the GTP catalyst (TBABB) were converted to conetworks upon the sequential addition of the dimethacrylate cross-linker, EGDMA. The preparation of networks 3, 5, 4, and 8 (BAB triblock-copolymer based conetworks, Table 1) required the sequential addition of two different monomers before the EGDMA addition, with the DMAEMA monomer added second, while for the synthesis of the reverse structure (ABA triblock copolymer based conetworks), networks 2, 7, 10 and 11, the DMAEMA monomer was added first. The statistical copolymer conetwork, network 9, required the simultaneous addition of the two monomers, PIBMA and DMAEMA, before the cross-linker addition. The homopolymer networks, networks 1 and 6, were prepared by the DMAEMA/cross-linker sequential additions. Finally, for the preparation of the randomly cross-linked statistical conetwork, the two monomers and the cross-linker were added before the addition of the bifunctional initiator.

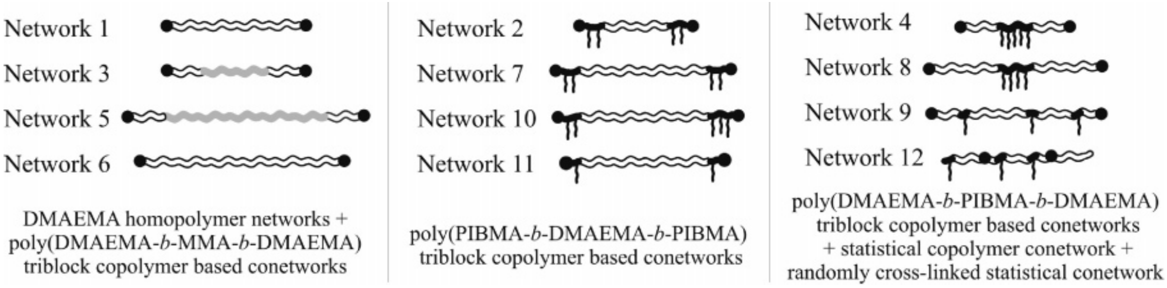
Figure 4 illustrates schematic representations of the architectures of all the networks prepared in the course of this study. The four structures in the first column from the left are of the two networks based on DMAEMA homopolymers of different DP and of the two conetworks based on poly(DMAEMA-*b*-MMA-*b*-DMAEMA) triblock copolymers of different DPs of the MMA units. In the second column, all the conetworks based on poly(PIBMA-*b*-DMAEMA-*b*-PIBMA) triblock copolymers with different DPs of PIBMA are shown. In the last column, conetworks of three different structures are illustrated: two based on poly(DMAEMA-*b*-PIBMA-*b*-DMAEMA) triblock copolymers of different DPs (networks 4 and 8), one based on the statistical copolymer (network 9) and the randomly cross-linked statistical conetwork. The last conetwork has the least controlled structure since the distribution of the DPs of the chains between the cross-links is broad, due to the random distribution of the cross-linker in this conetwork.

Molecular Weights. Figure 5 shows the GPC chromatograms of the two linear precursors (homopolymer and triblock copolymers) to two conetworks: network 7, (PIBMA$_2$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_2$)-*network*, and network 8, (DMAEMA$_{10}$-*b*-PIBMA$_4$-*b*-DMAEMA$_{10}$)-*network*. The MWDs of the first-generation precursors to the conetworks, i.e., the homopolymers DMAEMA$_{20}$ and PIBMA$_4$, were narrow and unimodal, as expected. The MWDs of the second-generation precursors to the conetworks, i.e., the triblock copolymers, were also narrow and unimodal, without any traces of the homopolymer precursors. No unreacted DMAEMA monomer or PIBMA macromonomer was present in any of the chromatograms. Thus,

Table 1. Gel Permeation Chromatography (GPC) and ^{1}H NMR Characterization of the Network Precursors

			GPC results		% mol DMAEMA	
network no.	precursor formula[a]	theoretical MW[b]	M_n[b]	M_w/M_n[b]	theory	^{1}H NMR
1	D_{10}	1770	2700	1.27		
	D_5-*b*-D_{10}-*b*-D_5	3342	5100	1.24	100	100
2	D_{10}	1770	2200	1.31		
	P_2-*b*-D_{10}-*b*-P_2	3850	4200	1.24	71	76
3	M_{10}	1198	3000	1.35		
	D_5-*b*-M_{10}-*b*-D_5	2768	7200	1.19	50	43
4	$P_{4.6}$	2590	4900	1.12		
	D_5-*b*-$P_{4.6}$-*b*-D_5	4160	7500	1.13	68	74
5	M_{26}	2798	6600	1.21		
	D_5-*b*-M_{26}-*b*-D_5	4370	9900	1.21	28	18
6	D_{20}	3342	3900	1.19		
	D_{10}-*b*-D_{20}-*b*-D_{10}	6486	7200	1.17	100	100
7	D_{20}	3342	3800	1.18		
	P_2-*b*-D_{20}-*b*-P_2	5422	6000	1.17	83	86
8	P_4	2278	3900	1.14		
	D_{10}-*b*-P_4-*b*-D_{10}	5422	8500	1.19	83	83
9	D_{20}-*co*-P_3	4902	6200	1.17	87	88
10	D_{20}	3342	5600	1.17		
	P_3-*b*-D_{20}-*b*-P_3	6462	6700	1.19	77	80
11	D_{20}	3342	3900	1.18		
	P_1-*b*-D_{20}-*b*-P_1	4382	4600	1.17	91	N.D.[c]
12	D_{20}-*co*-P_3-*co*-E_8					

[a] D, M, and P are (further) abbreviations for 2-(dimethylamino)ethyl methacrylate (DMAEMA), methyl methacrylate (MMA) and polyisobutylene methacrylate (PIBMA), respectively. [b] MW: molecular weight. M_n: number-average MW. M_w: weight-average MW. [c] N.D.: Not determined.



DMAEMA homopolymer networks + poly(DMAEMA-*b*-MMA-*b*-DMAEMA) triblock copolymer based conetworks

poly(PIBMA-*b*-DMAEMA-*b*-PIBMA) triblock copolymer based conetworks

poly(DMAEMA-*b*-PIBMA-*b*-DMAEMA) triblock copolymer based conetworks + statistical copolymer conetwork + randomly cross-linked statistical conetwork

Figure 4. Schematic representation of the architectures of the networks (see Table 1 for numbering) prepared in the course of this study. The 2-(dimethylamino)ethyl methacrylate (DMAEMA) units are colored white, the methyl methacrylate (MMA) units gray, and the polyisobutylene methacrylate (PIBMA) units black, and the cross-links are depicted as black circles.

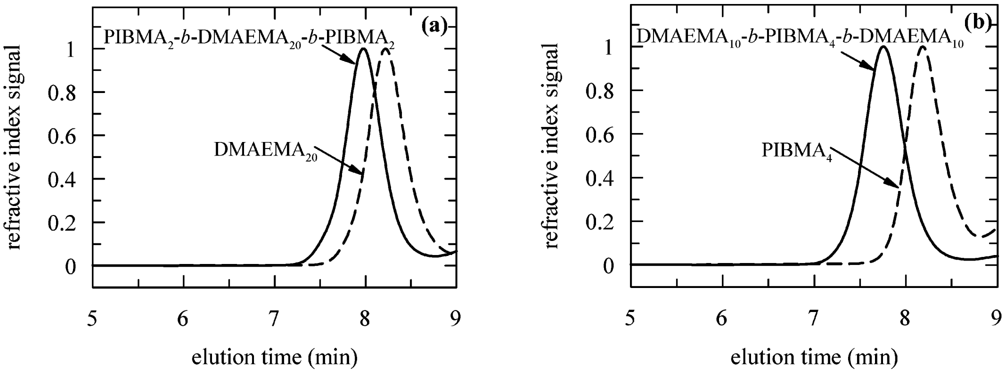


Figure 5. Gel permeation chromatograms of the two linear precursors to (a) network 7, (PIBMA$_2$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_2$)-*network*, and (b) network 8, (DMAEMA$_{10}$-*b*-PIBMA$_4$-*b*-DMAEMA$_{10}$)-*network*. Network numbers are from Table 1. PIBMA: polyisobutylene methacrylate. DMAEMA: 2-(dimethylamino)ethyl methacrylate.

the PIBMA macromonomer was successfully polymerized by GTP and copolymerized with DMAEMA both as a first and as a second monomer. The quality of the chromatograms of these PIBMA-DMAEMA copolymers was similar to those of the MMA−DMAEMA copolymers also prepared in the course of this study (Table 1). Moreover, the other PIBMA-DMAEMA copolymers also presented similarly narrow MWDs.

Table 1 shows the GPC characterization data for all the precursors to the networks prepared in this study. At this point it must be clarified that the non-integer values of the DPs of PIBMA are average values. Moreover, although these DPs values are low, they represent a relatively high weight fraction of PIBMA due to the high MW of PIBMA (520 g mol^{-1}). These GPC data shown in Table 1 include the M_ns and the polydispersity indices (PDI, M_w/M_n). The M_ns of all the homopolymers were higher than the theoretical MWs due to partial initiator deactivation, while their PDIs were reasonably low ($\leq$1.35). For the copolymers, the M_ns were also higher than the theoretical. All the M_ns of the copolymer precursors to the conetworks were higher than the respective homopolymer precursors, as expected, indicating that the polymerization of the second monomer was successful. The PDIs of the copolymers

Table 2. Mass Percentage, Number-Average Molecular Weights (M_n), and Compositions of the Sol Fractions Extracted from the Networks As Measured by Gravimetry, Gel Permeation Chromatography (GPC), and ^{1}H NMR

network no.	theoretical chemical structure[a]	extractables (w/w %)	GPC results[b]		% mol DMAEMA		
						by ^{1}H NMR	
			M_n	M_w/M_n	theoretical of precursor	precursor	extractables
1	(D$_5$-*b*-D$_{10}$-*b*-D$_5$)-*network*	9.9	4900	1.33	100	100	100
2	(P$_2$-*b*-D$_{10}$-*b*-P$_2$)-*network*	25.6	3800	1.23	71	76	86
3	(D$_5$-*b*-M$_{10}$-*b*-D$_5$)-*network*	10.1	2900	1.27	50	43	22
4	(D$_5$-*b*-P$_{4.6}$-*b*-D$_5$)-*network*	16.1	3800	1.12	68	74	36
5	(D$_5$-*b*-M$_{26}$-*b*-D$_5$)-*network*	17.0	4000	1.27	28	18	6
6	(D$_{10}$-*b*-D$_{20}$-*b*-D$_{10}$)-*network*	14.7	5100	1.27	100	100	100
7	(P$_2$-*b*-D$_{20}$-*b*-P$_2$)-*network*	24.1	5100	1.33	83	86	88
8	(D$_{10}$-*b*-P$_4$-*b*-D$_{10}$)-*network*	12.7	6000	1.30	83	83	69
9	(D$_{20}$-*co*-P$_3$)-*network*	13.0	5200	1.18	87	88	86
10	(P$_3$-*b*-D$_{20}$-*b*-P$_3$)-*network*	33.3	5100	1.33	77	80	86
11	(P$_1$-*b*-D$_{20}$-*b*-P$_1$)-*network*	23.3	3600	1.19	91	N.D.[c]	N.D.[c]
12	(D$_{20}$-*co*-P$_3$-*co*-*E*$_8$)-*network*	9.5	4000	1.35	-	-	49

[a] D, M, and P are (further) abbreviations for 2-(dimethylamino)ethyl methacrylate (DMAEMA), methyl methacrylate (MMA) and polyisobutylene methacrylate (PIBMA), respectively. [b] M_w: weight-average molecular weight. [c] N.D.: Not determined.

Table 3. Effective pKs of 2-(Dimethylamino)ethyl Methacrylate (DMAEMA) Units in the Networks Measured Using Hydrogen-Ion Titration

network no.	theoretical chemical structure[a]	effective p*K*
1	(DMAEMA$_5$-*b*-DMAEMA$_{10}$-*b*-DMAEMA$_5$)-*network*	5.0
2	(PIBMA$_2$-*b*-DMAEMA$_{10}$-*b*-PIBMA$_2$)-*network*	2.6
3	(DMAEMA$_5$-*b*-MMA$_{10}$- *b*-DMAEMA$_5$)- *network*	3.5
4	(DMAEMA5-*b*-PIBMA$_{4.6}$-*b*-DMAEMA$_5$)- *network*	2.5
5	(DMAEMA$_5$-*b*-MMA$_{26}$-*b*-DMAEMA$_5$)-*network*	2.5
6	(DMAEMA$_{10}$-*b*-DMAEMA$_{20}$-*b*-DMAEMA$_{10}$)- *network*	4.9
7	(PIBMA$_2$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_2$)- *network*	4.4
8	(DMAEMA$_{10}$-*b*-PIBMA$_4$-*b*-DMAEMA$_{10}$)- *network*	4.5
9	(DMAEMA20-co-PIBMA$_3$)- *network*	4.8
10	(PIBMA$_3$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_3$)- *network*	4.4
11	(PIBMA$_1$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_1$)- *network*	4.4
12	(DMAEMA$_{20}$-*co*-PIBMA$_3$-*co*-EGDMA$_8$)- *network*	4.0

[a] PIBMA: polyisobutylene methacrylate. MMA: methyl methacrylate. EGDMA: ethylene glycol dimethacrylate.

were also reasonably low ($\leq$1.24) and, in most cases, lower than the homopolymer precursors, as expected for a quasiliving polymerization technique.

The composition of each copolymer conetwork precursor (sampled right before the addition of the cross-linker) was determined from its ^{1}H NMR spectrum (Table 1). In particular, the ratios of the integral values of the signals of representative protons of the monomer units were calculated. These representative protons were the two oxymethylene protons of PIBMA at 3.8 ppm or the three methoxy protons of MMA at 3.6 ppm, and the six protons in the two azamethyl groups of DMAEMA at 2.3 ppm. The percentages of DMAEMA determined by ^{1}H NMR were found to be close to the theoretical values. This confirmed that the conetworks had the desired composition.

Sol Fraction of the Conetworks. Table 2 shows the mass percentage, the M_ns, the PDIs, and the composition of the extractables from each conetwork as measured by gravimetry, GPC and ^{1}H NMR. Eight networks: the two DMAEMA homopolymer networks, the two DMAEMA-MMA conetworks, and four DMAEMA-PIBMA conetworks exhibited relatively low sol fractions, lower than 17%, while the four poly(PIBMA-*b*-DMAEMA-*b*-PIBMA) (ABA) triblock copolymer-based conetworks, where PIBMA was polymerized as second monomer of the sequence, contained 23−33% extractables. The higher extractables in the last case are probably due to the lower cross-reactivity of the PIBMA-EGDMA pair compared to the DMAEMA-EGDMA and MMA-EGDMA pairs. In turn, this is due to the steric effect of the PIBMA macromonomer on the apparent reactivity of the corresponding active polymer.[46,47] The composition of the extractables was similar to that of the corresponding triblock copolymer precursors, with the exception of the two conetworks based on poly(DMAEMA-*b*-PIBMA-*b*-DMAEMA) triblock copolymers, where PIBMA was polymerized first, and the extractables were richer in PIBMA. In general, the GPC and ^{1}H NMR data of the extractables and of the linear precursors indicated satisfactory control over the conetwork structure by the applied synthetic method, i.e., block copolymerization of DMAEMA with the PIBMA macromonomer.

Degrees of Swelling of the Conetworks. Effect of pH. The experimentally measured DSs and DIs of all the networks are plotted against the pH of the supernatant solution in Figure 6. The figure shows that the pH was an important factor that affected the DSs of all the conetworks. In particular, as the pH was decreased, the DSs of all the networks increased. This was due to the fact that all the conetworks contained ionizable DMAEMA units. DMAEMA is a weakly basic tertiary amine which is uncharged at high pH but becomes positively charged at low pH.[48−50] The electrostatic repulsion created by the network charges and the osmotic pressure due to the chloride counterions to the charges at low pH both promoted network swelling.

Notable was the fact that the networks did not start to swell at the same pH, but at different pH values that depended on their composition but not on their architecture, as also observed for DMAEMA-MMA conetworks.[11] These critical pH values will be further discussed later along with the effective p*K*s.

Effect of Conetwork Composition. Figure 7 shows the maximum aqueous DSs (at pH = 3), the aqueous DSs at neutral pH, and the DSs in THF and in *n*-hexane of the PIBMA$_x$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_x$ (where x = 1, 2 and 3) amphiphilic conetworks as a function of the conetwork % mol composition

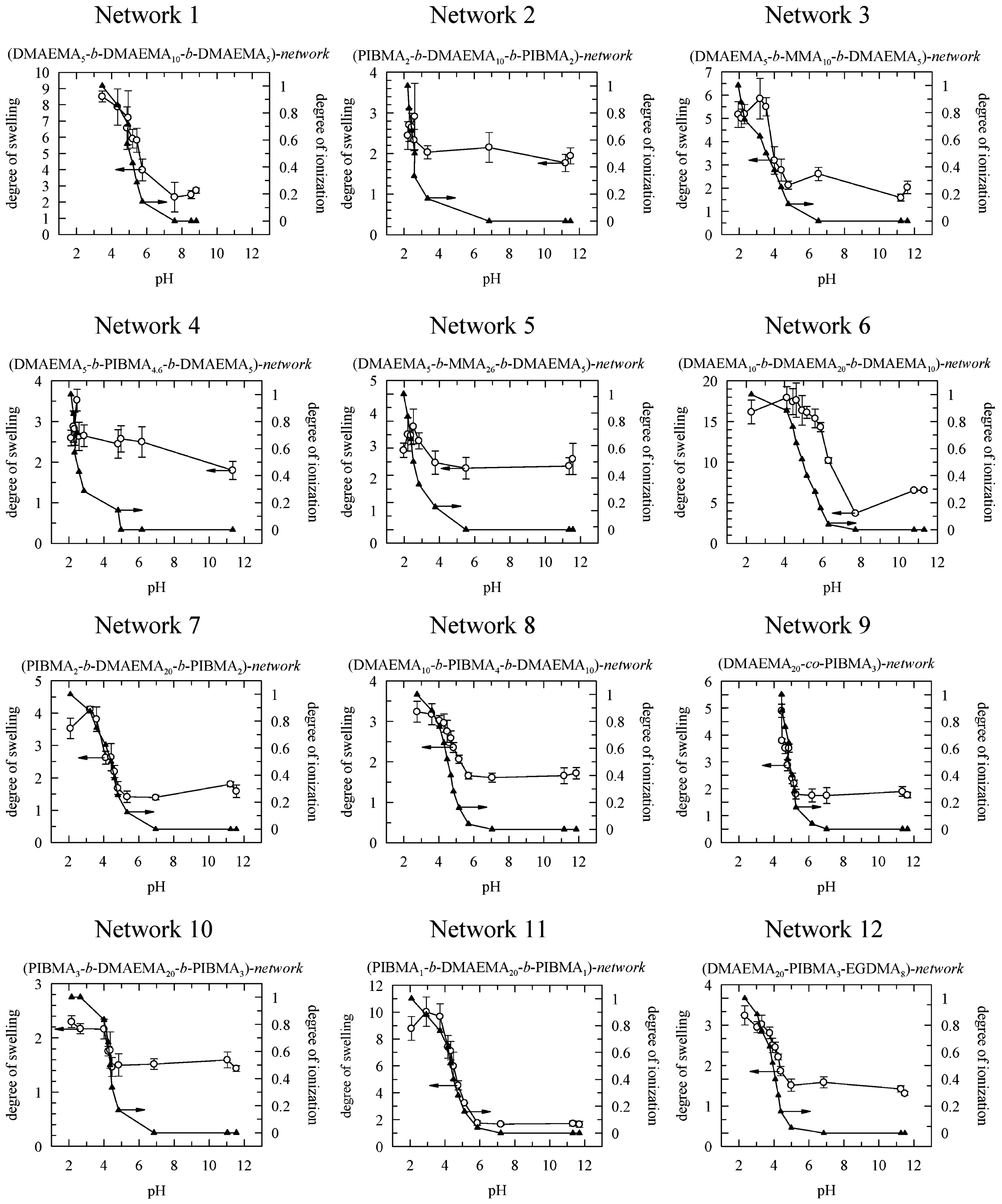


Figure 6. pH-dependence of the aqueous degrees of swelling and the degrees of ionization of the networks. DMAEMA: 2-(dimethylamino)ethyl methacrylate. PIBMA: polyisobutylene methacrylate. MMA: methyl methacrylate. EGDMA: ethylene glycol dimethacrylate.

in the hydrophobic PIBMA monomer (the MW of the copolymer chains increases as the PIBMA content increases). The DSs in water under acidic conditions (pH = 3) were higher than those at neutral conditions (pH = 7) for all the conetworks. The ionization of the DMAEMA units at low pH was responsible for this behavior. The very low values of the DSs in neutral water were due to the incompatibility of PIBMA with water and the low solubility of uncharged polyDMAEMA in water at room temperature. The DSs in THF were higher than those in neutral water and *n*-hexane because THF is a nonselective (good) solvent for the two types of monomer repeat units, DMAEMA and PIBMA, while water and *n*-hexane are selective solvents for the DMAEMA and PIBMA units, respectively.

The DSs in the nonselective THF increased with the PIBMA content because of the simultaneous increase of the copolymer chain MW with the PIBMA content (MW rather than composition effect). The dependence of the DSs in water, both at pH 3 and 7, on the increasing PIBMA content was the outcome of

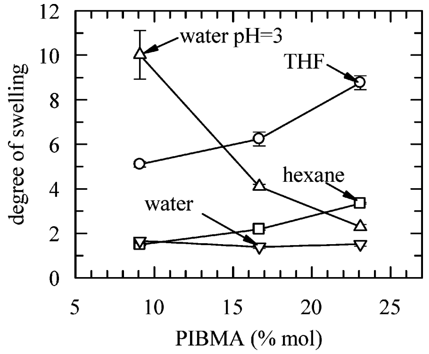


Figure 7. Degrees of swelling of the PIBMA$_x$-*b*-DMAEMA$_{20}$-*b*-PIBMA$_x$ amphiphilic conetworks as a function of the hydrophobic PIBMA content in water at low pH (pH = 3), at neutral pH, in *n*-hexane and in tetrahydrofuran (THF). PIBMA: polyisobutylene methacrylate. DMAEMA: 2-(dimethylamino)ethyl methacrylate.

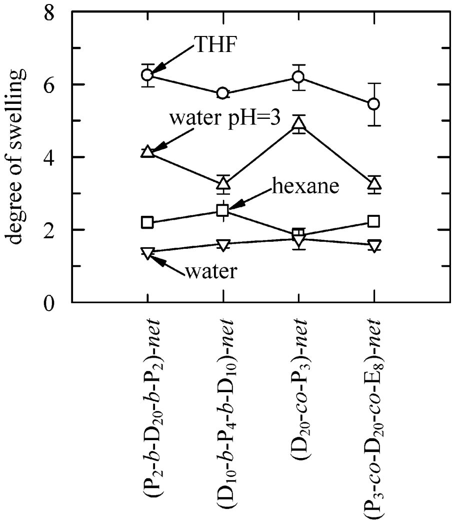


Figure 8. Degrees of swelling of the polyisobutylene methacrylate (PIBMA) - 2-(dimethylamino)ethyl methacrylate (DMAEMA) amphiphilic conetworks as a function of the conetwork architecture in water at low pH (pH = 3), at neutral pH, in *n*-hexane and in tetrahydrofuran (THF). P, D, E, and *net* are (further) abbreviations for PIBMA, DMAEMA, ethylene glycol dimethacrylate (EGDMA), and *network*, respectively.

the competition between the effects of PIBMA hydrophobicity, which opposed swelling in water, and the increasing polymer chain MW with PIBMA content, which would favor swelling in any solvent. In this case, the effect of PIBMA hydrophobicity dominated. In *n*-hexane, the increase of the DSs with the PIBMA content was due to the combined effects of *n*-hexane-PIBMA compatibility and the increasing polymer MW with the PIBMA content.

Effect of Conetwork Architecture. Figure 8 shows the DSs of all the isomeric PIBMA-DMAEMA amphiphilic conetworks of different architectures in water at low pH, at neutral pH, in *n*-hexane and in THF. The conetwork architecture did not seem to have a strong effect on the DSs in THF, in *n*-hexane and in neutral water. The DSs in water at pH = 3 indicated that they only slightly depended on network architecture. In particular, the statistical copolymer based conetwork presented a slightly higher DS than its isomers, while the randomly cross-linked conetwork presented the lowest DSs in THF and in acidic aqueous medium.

Effective p*K*s of the DMAEMA Units. Table 3 lists the effective p*K*s of the DMAEMA units in all the networks prepared in the course of this study: the DMAEMA homopolymer networks and the DMAEMA-MMA and the DMAEMA-PIBMA conetworks. The p*K*s of the networks were determined from the DI vs pH curves in Figure 6 as the pH at 50% ionization. The DMAEMA homopolymer networks, networks 1 and 6, had the highest effective p*K*s, close to 5.0, while the copolymer networks exhibited p*K* values between 2.5 and 4.8. The lower effective p*K*s of the amphiphilic conetworks were attributed to their greater hydrophobicity (due to the presence of PIBMA or MMA units), leading to the reduction of the dielectric constant, rendering ionization more difficult and reducing the p*K*.[51]

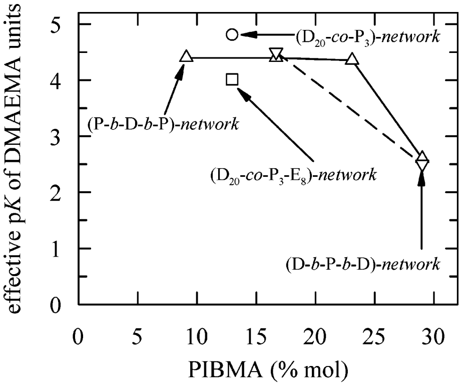


Figure 9. Dependence of the effective p*K*s of the 2-(dimethylamino)-ethyl methacrylate (DMAEMA or D) units within the DMAEMA−polyisobutylene methacrylate (PIBMA or P) polymer conetworks on their PIBMA content. E: ethylene glycol dimethacrylate (EGDMA).

The p*K*s of the amphiphilic DMAEMA-PIBMA polymer conetworks are plotted against the conetwork PIBMA content in Figure 9. These data suggest that the p*K* values decrease as the PIBMA content increases, as observed before for DMAEMA-MMA triblock copolymer based conetworks.[11] Another observation from Figure 9, also made with the DMAEMA-MMA copolymer conetworks,[11] is that networks with the same composition but with different architectures have almost the same p*K* values, indicating that the architecture of the conetworks does not affect significantly their dielectric constant.

Conclusions

For the first time, QLCCP and GTP were successfully combined to prepare amphiphilic polymer model conetworks. The combination was accomplished by the QLCCP of IB, followed by the modification of the resulting PIB to PIBMA, which was subsequently copolymerized by GTP with DMAEMA and EGDMA. A series of amphiphilic conetworks were prepared, with PIBMA being the hydrophobic and DMAEMA the hydrophilic, ionizable component, covering different DPs and architectures. Two DMAEMA−MMA amphiphilic conetworks and two DMAEMA homopolymer networks were also synthesized for comparison. The DS of all these networks was measured in THF, *n*-hexane, and acidic and neutral aqueous media. The DSs of the networks in all the solvents depended on the DP of the chains between cross-links and on the content in the hydrophobic PIBMA macromonomer, while the DSs of the conetworks at low pH also exhibited a slight dependence on architecture.

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