

Synthesis and characterization of amphiphilic conetworks based on multiblock copolymers

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Received 13 January 2007; received in revised form 10 September 2007; accepted 23 September 2007
Available online 29 September 2007

Abstract

Model amphiphilic conetworks based on cross-linked block copolymers of the hydrophilic ionizable 2-(dimethylamino)ethyl methacrylate (DMAEMA, 25 nominal units per block) and the hydrophobic *n*-butyl methacrylate (BuMA, 5 nominal units per block) bearing three, five, seven and nine blocks were synthesized using group transfer polymerization. 1,4-Bis(methoxytrimethylsiloxymethylene)cyclohexane and ethylene glycol dimethacrylate were used as the bifunctional initiator and the cross-linker, respectively. Network synthesis was performed by sequential monomer/cross-linker additions to the reaction flask, which was pre-loaded with tetrabutylammonium bibenzoate (polymerization catalyst), tetrahydrofuran (THF, solvent), and initiator. All linear conetwork precursors were characterized using gel permeation chromatography and proton nuclear magnetic resonance spectroscopy and found to have molecular weights (MWs) and compositions reasonably close to the theoretically expected values. All polymer conetworks were characterized in terms of their degree of swelling (DS) in THF, in neutral water, and in aqueous media as a function of the solution pH. It was found that the DSs were highest in acidic pH due to the repulsive forces and the osmotic pressure developed by the ionization of the DMAEMA units. Intermediate values of the DSs were observed in THF, whereas the lowest DSs were measured in neutral water. In THF, the DSs increased with the MWs of the (final) linear (co)polymer precursors, while in acidic water the DSs increased with the DMAEMA content in the (co)networks.

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Keywords: Amphiphilic conetworks; Multiblock copolymers; Group transfer polymerization

1. Introduction

Amphiphilic polymer conetworks (APCN) [1,2] represent an emerging class of materials, composed of covalently-linked hydrophilic and hydrophobic segments, that combine the properties of hydrogels and surfactants. Regarding the former, APCNs can absorb water, but not as extensively as conventional hydrogels due to the presence of the hydrophobic segments, which enable swelling also in organic solvents. Regarding the latter, when APCNs are placed in a selective solvent, either aqueous or non-polar, the incompatible

segments are organized in micelle-like structures, leading to microphase separation [3].

The study of the properties and the exploration of potential applications of these materials constitute the objectives of several research groups worldwide [4–17]. However, most of the reports on APCNs involve poorly-defined materials, as the chains between the cross-links are greatly inhomogeneous in terms of molecular weight (MW) and composition [4–15]. This is a direct consequence of the synthetic procedure, which is usually free-radical cross-linking polymerization. During the past seven years, our research team has developed a synthetic strategy to prepare APCNs of improved structure, called model [18] APCNs, based on well-defined chains between the cross-links [16,17,19–22]. In particular, we have been using group transfer polymerization (GTP) [23] and reversible addition–fragmentation chain transfer (RAFT) polymerization

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[24] to prepare APCNs comprising either end-linked amphiphilic ABA triblock copolymers or interconnected amphiphilic star copolymers. In a more recent study, we presented examples of APCNs, consisting of end-linked amphiphilic ABCBA pentablock terpolymers with one hydrophobic and two different types of hydrophilic units [22].

The aim of the present investigation is to further expand on the structural complexity of the materials, by constructing model APCNs based on amphiphilic multiblock copolymers. Such APCNs have not yet been reported in the literature. In particular, in this study, we used a bifunctional GTP initiator and up to five sequential monomer additions to prepare copolymers with up to nine blocks. These copolymers were end-linked *in situ* by a final addition of cross-linker, which provided the desired multiblock APCNs. These materials were characterized in terms of their swelling properties in aqueous and organic media.

2. Experimental section

2.1. Materials

n-Butyl methacrylate (BuMA, purity >99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), basic alumina, calcium hydride (CaH₂, 90–95%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%) were all purchased from Aldrich. Deuterated chloroform (CDCl₃) was purchased from Merck. Tetrahydrofuran (THF, 99.8%, both HPLC and reagent grade) was purchased from Labscan.

2.2. Methods

The monomers used, BuMA and DMAEMA, and the cross-linker were passed through basic alumina columns to remove protic impurities, were stirred over CaH₂ in the presence of the free radical inhibitor DPPH, and were freshly distilled prior to use. The bifunctional initiator, 1,4-bis(methoxytrimethylsilyloxymethylene)cyclohexane (MTSCH), was synthesized according to the literature [25]. Briefly, it was prepared in a two-step procedure. First, by treatment of dimethyl 1,4-cyclohexanedicarboxylate with diisopropylamine and *n*-butyl lithium and, second, by the silylation of the resulting product using

trimethylsilyl chloride. Tetrahydrofuran (THF) was dried by refluxing it over a sodium/potassium alloy for three days and it was freshly distilled. The catalyst was tetrabutylammonium bibenzoate (TBABB), prepared as described by Dicker and co-workers [23c] and stored under vacuum. Fig. 1 shows the chemical structures and names of the monomers, the cross-linker and the bifunctional initiator used for the polymer synthesis.

2.3. Network synthesis

All the (co)networks of this study were prepared by GTP. The number of moles of the cross-linker used for (co)network synthesis was eight times the number of moles of the MTSCH initiator to optimize inter-chain connection and network formation according to previous studies [26]. In total, five (co)networks were synthesized which were based on the homopolymer of DMAEMA, and on the block copolymers of DMAEMA and BuMA, bearing three, five, seven and nine blocks. All DMAEMA blocks had a nominal (targeted) degree of polymerization (DP) equal to 25 and all BuMA blocks had a DP equal to 5. A typical polymerization procedure yielding the conetwork based on the BuMA₅-*b*-DMAEMA₂₅-*b*-BuMA₅ triblock copolymer is detailed below. To a 100 mL flask containing a small amount of TBABB were added using glass syringes 30 mL of freshly distilled THF and 0.3 mL (0.36 g, 1.05 mmol) of MTSCH initiator, in this order. Then, 4.4 mL of DMAEMA (4.11 g, 26.11 mmol) was slowly added under stirring. The polymerization exotherm (26.8–40.4 °C) abated within 5 min, a sample for gel permeation chromatography (GPC) and ¹H NMR was extracted, and 1.7 mL of BuMA (1.52 g, 10.69 mmol) was added which produced an exotherm (34.3–36.8 °C). After extraction of a sample of the formed BuMA₅-*b*-DMAEMA₂₅-*b*-BuMA₅ triblock copolymer for GPC and ¹H NMR, 1.6 mL of the EGDMA cross-linker (1.68 g, 8.48 mmol) was added and led to the gelation of the solution within seconds. The other four block copolymer-based model conetworks were prepared by further sequential monomer additions before the cross-linker addition.

2.4. Characterization of the linear precursors

Samples of the linear polymer precursors were obtained before cross-linking and were characterized in terms of their

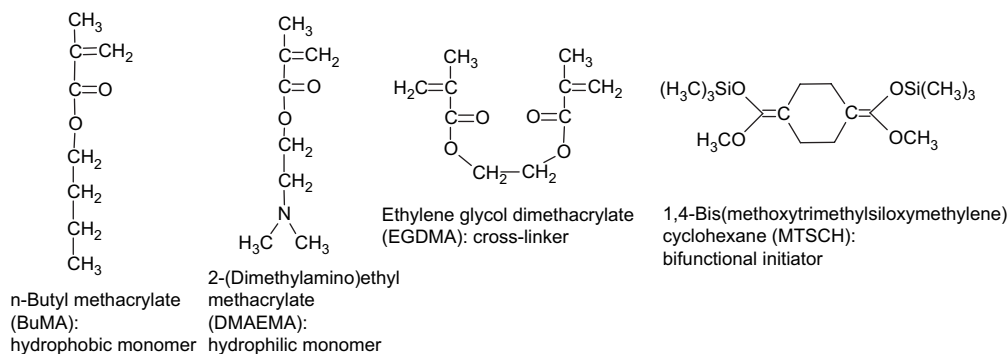


Fig. 1. Chemical structures and names of the main reagents used for the conetwork synthesis.

MW and composition using GPC and ^1H NMR, respectively. GPC was performed on a Polymer Laboratories system equipped with a Waters 515 isocratic pump, an ERC-7515A Polymer Laboratories refractive index detector and a PL Mixed “D” column. The eluent was THF, pumped at 1 mL min^{-1} . The instrumentation was calibrated using poly(methyl methacrylate) (PMMA) standards supplied by Polymer Laboratories. The ^1H NMR spectra of the polymer precursors in CDCl_3 were recorded using a 300 MHz Avance Bruker spectrometer equipped with an Ultrashield magnet. The copolymer composition was calculated from the ratio of the peak area due to the two azamethylene protons in DMAEMA at 2.6 ppm to the peak area due to the two oxymethylene protons of BuMA at 3.9 ppm.

2.5. Recovery and characterization of the extractables

First, the (co)networks were taken out of the polymerization flasks by breaking the flasks. Subsequently, they were placed in excess THF and left there for three weeks to extract the polymer not incorporated in the (co)network. The THF solution of the extracted material was dried in a rotary evaporator followed by vacuum-drying at room temperature for three days, and the mass of the polymer was determined. Samples of the extractables were characterized by GPC in THF and ^1H NMR in CDCl_3 using the equipment described in the previous paragraph.

2.6. Measurement of the degree of swelling

The degrees of swelling (DSs) of the (co)networks were measured in THF, in neutral water and in aqueous solutions covering the pH range between 3 and 12. After the equilibration in excess THF and the removal of the extractables (described in the preceding paragraph), 10 pieces were cut from each (co)network. Each piece was weighed and subsequently dried in a vacuum oven (at room temperature) for four days and weighed again. The DSs in THF were calculated as the ratio of the swollen divided by the dry mass and their values were averaged over the 10 samples of each (co)network. In order to measure the DSs in aqueous media at different pHs, 5 mL of deionized water was added to each sample of the dried (co)networks, followed by the addition of the appropriate number of drops of a 0.5 M HCl solution to adjust the pH within the range between 3 and 7, corresponding to degrees of ionization between 100% and 0%. The required number of moles of HCl in each case was calculated as the product of the desired degree of ionization times the number of moles of DMAEMA units present in the sample. One sample of each (co)network remained neutral. One and two drops of a 0.5 M NaOH solution were added to the two remaining samples of each (co)network to adjust the pH to alkaline values.

2.7. Calculation of the degree of ionization and the effective pK

The degree of ionization of each sample was calculated as the number of HCl equivalents added divided by the number

of DMAEMA unit equivalents (calculated from the (co)network dry mass and composition) present in the sample. The acid titration curves were obtained by plotting the calculated degrees of ionization against the measured solution pH. The effective pK of the DMAEMA units of each (co)network was estimated from its acid titration curve as the pH (of the supernatant solution) at 50% ionization.

3. Results and discussion

3.1. Polymerization methodology

This is the first synthesis of APCNs based on amphiphilic multiblock copolymers of well-defined MW and composition and regular alternation of the hydrophobic and hydrophilic blocks. The synthesis [27] and characterization [28] of multiblock copolymer APCNs have also been reported by Erdődi and Kennedy. These authors accomplished the synthesis of multiblock copolymers by the condensation reaction (by hydrosilylation) between α,ω -divinyl poly(ethylene glycol) (PEG) and α,ω -divinyl poly(dimethyl siloxane) (PDMSO), which secured neither the PEG/PDMSO block alternation nor the MW homogeneity of the chains between cross-links. However, defects are also present in the system described in this investigation. These non-idealities arise mainly from the use of the EGDMA cross-linker for network formation, and include loops, dangling chains and chain entanglements.

The synthetic procedure for the preparation of all the (co)networks of the present work is illustrated schematically in Fig. 2. The synthesis involved sequential monomer and cross-linker additions. The first step resulted in the preparation of the linear DMAEMA₂₅ homopolymer with both active ends (indicated by asterisks) due to the use of the bifunctional initiator. The second step led to the synthesis of the BuMA₅-*b*-DMAEMA₂₅-*b*-BuMA₅ triblock copolymer with two active ends. Further sequential monomer additions provided the other multiblock copolymers with greater number of blocks. The synthesis for each (co)network was completed by the addition of the EGDMA cross-linker, which effected the interconnection of the (co)polymer active ends, providing a three-dimensional network. The number of arms at the cross-links is not 3, as indicated in Fig. 2, but higher, between 20 and 50, as determined by static light scattering experiments on star polymers prepared by the same synthetic method but using a monofunctional rather than a bifunctional GTP initiator [26c].

3.2. Molecular weights and composition of the precursors

Table 1 shows the number-average MWs, M_n s, the peak MWs (MWs at the peak maximum), M_p s, and the compositions of the linear (co)polymer precursors to the (co)networks as measured by GPC and ^1H NMR. As the different (co)networks were based on linear (co)polymers containing a different number of blocks, a different number of linear precursors corresponded to each (co)network: five to the nonablock copolymer conetwork (the nonablock, the heptablock, the

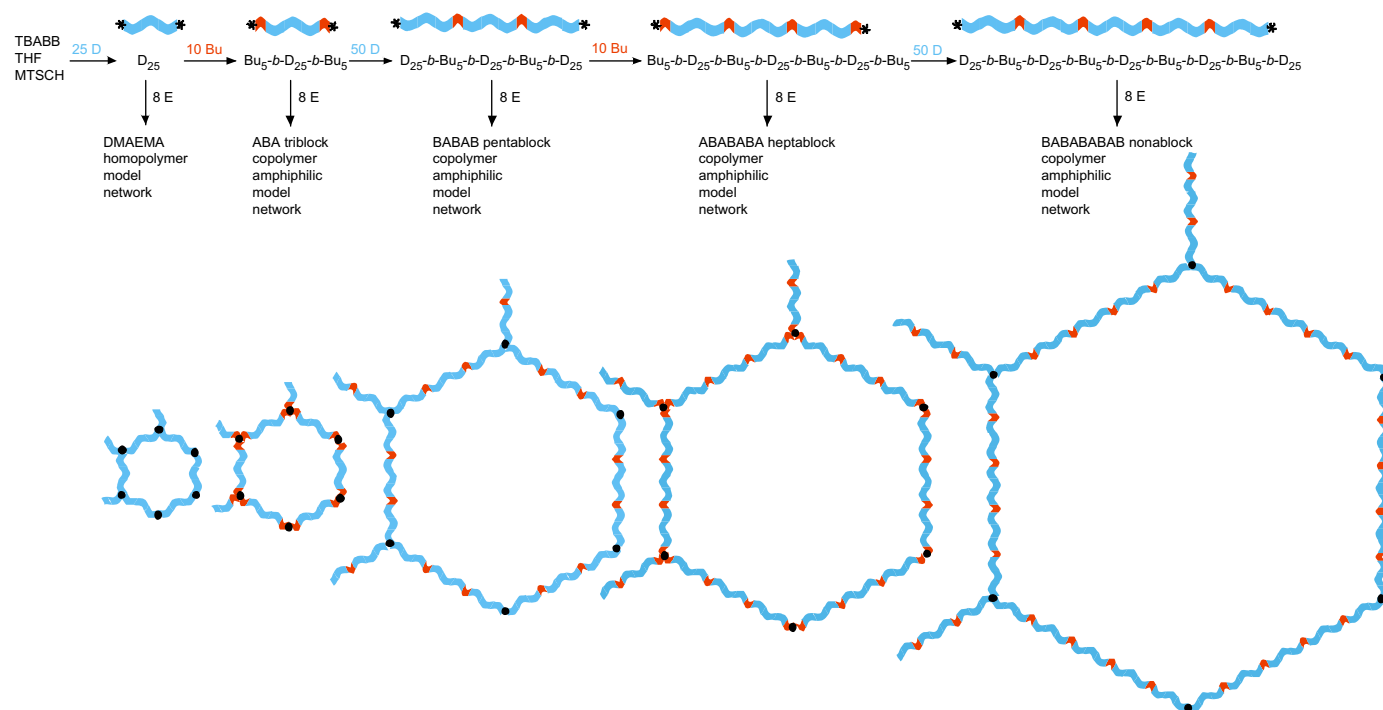


Fig. 2. Synthetic procedure and structures of the five (co)networks of this study. D, Bu and E are further abbreviations for DMAEMA, BuMA and EGDMA, respectively. The number of arms at the cross-links is not 3, as indicated in the figure, but between 20 and 50.

pentablock, and the triblock copolymers as well as the homopolymer), four to the heptablock copolymer conetwork, three to the pentablock copolymer conetwork, two to the triblock copolymer conetwork, and one to the homopolymer. The MWs and compositions of all 15 of the above linear precursors are listed in the table. The M_n s of the precursors were close to, but systematically higher than, the theoretically expected MWs calculated from the monomer/initiator ratios. This indicates some initiator deactivation. The molecular weight distributions (MWDs) were narrow with polydispersity indices

(PDI, M_w/M_n) equal to or lower than 1.25 in all cases. This confirms the homogeneity of the lengths of the segments between cross-links (elastic chains) in the (co)networks.

Fig. 3 presents the GPC traces of the two linear precursors to the conetwork based on the triblock copolymer. The chromatogram of the triblock copolymer is shifted to shorter elution times (higher MWs) compared to its homopolymer precursor, as expected. Both chromatograms are unimodal. However, there is a shoulder on the lower MW side of the peak of the triblock copolymer, indicating the presence of

Table 1
Molecular weights and compositions of the linear precursors to the networks

No.	Polymer formula ^a	Theoretical MW ^b	GPC results			DMAEMA (mol%)	
			M_n	M_w/M_n	M_p	Theory	¹ H NMR
1	D ₂₅	4129	5960	1.06	6360	100.0	—
2	D ₂₅	4129	4660	1.15	5290	100.0	—
	Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅	5551	6380	1.15	7640	71.4	69.8
3	D ₂₅	4129	5600	1.14	6760	100.0	—
	Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅	5551	7170	1.15	9470	71.4	70.3
	D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅	13,412	17,900	1.18	15,900	88.2	85.3
4	D ₂₅	4129	7300	1.15	9760	100.0	—
	Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅	5551	9800	1.16	13,700	71.4	74.8
	D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅	13,412	28,100	1.15	26,030	88.2	84.7
	Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅	14,834	29,560	1.16	27,700	78.9	81.4
5	D ₂₅	4129	6080	1.13	7410	100.0	—
	Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅	5551	7830	1.14	10,100	71.4	77.4
	D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅	13,412	18,200	1.20	17,000	88.2	88.3
	Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅	14,834	20,300	1.18	18,000	78.9	81.8
	D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅ - <i>b</i> -Bu ₅ - <i>b</i> -D ₂₅	22,695	29,600	1.25	32,300	86.2	86.7

^a D: DMAEMA, Bu: BuMA.

^b The contribution from the initiator fragment of 198 g mol⁻¹ was included in the calculation.

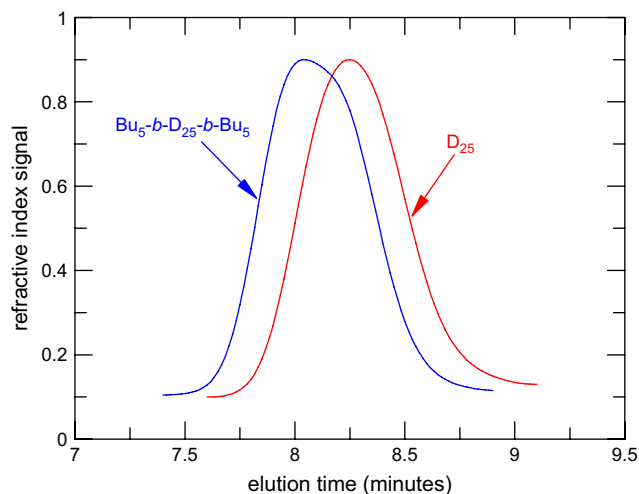


Fig. 3. GPC traces of the two linear precursors to the triblock copolymer conetwork.

some homopolymer, arising from some termination during the blocking reaction. Thus, the growth of the two end-blocks of the triblock occurred successfully, without significant termination.

The percentage compositions determined from ^1H NMR were close to those expected theoretically based on the comonomer feed ratio, confirming full monomer-to-polymer conversion during synthesis. The DMAEMA content in the copolymers was kept relatively high, at 70 mol% or higher, to secure conetwork water-compatibility (so that the corresponding linear copolymers were water-soluble, even when their DMAEMA units were neutral).

3.3. Percentage, molecular weights and composition of the extractables

The results of the characterization of the extractables are listed in Table 2, including their percentage, M_n and PDI. The percentage of the extractables (sol fraction) was found to be relatively low, equal to or lower than 17%, and in most cases around 10%, confirming the well-defined structure

of the (co)networks and indicating that the choice of a 8:1 cross-linker:initiator molar ratio [26,29] was appropriate for sufficient incorporation of the linear chains into the networks. The M_n s of the extractables, also listed in Table 2, were lower than those of the corresponding linear precursors. This was as expected because the extractables were composed of early-terminated polymers as well as “living” multiblock copolymers which could not approach the cross-links due to steric hindrances. Also, the lower M_n s confirmed that the inactivation (via termination or chain transfer) of the extractables occurred before the linear precursors were fully formed. The PDIs of the extractables are also shown in Table 2. These were similar to those of the corresponding linear copolymer precursors listed in Table 1. The ^1H NMR spectra of the extractables indicated similar compositions to those determined from the spectra of the linear copolymer precursors.

3.4. Degrees of swelling in water in dependence of pH

The experimentally measured DSs and degrees of ionization of all the (co)networks are plotted against pH in Fig. 4. The structure of each (co)network is indicated above each plot. A general feature of these plots is that each DS vs. pH curve followed the corresponding degree of ionization vs. pH curve, confirming the importance of charge on (co)network swelling. The (co)networks began to swell below pH 7 because of the presence of DMAEMA, a tertiary amine becoming ionized in that pH range. The ionization of the DMAEMA units resulted in electrostatic repulsions between the positively charged chains, and in the build-up of an osmotic pressure created by the counterions to the charges in the (co)networks [30]. The DSs presented a maximum at pH \sim 4–5, followed by a decrease at low pH values (pH \sim 2), which was probably due to the increase in ionic strength effected by the relatively high concentration of HCl under these conditions. At pH 7 and higher, the DSs were low and the conetworks were rather contracted because of the presence of the hydrophobic BuMA units, but not totally collapsed due to the presence of the marginally hydrophilic (at high pH) DMAEMA units as well [31]. Thus, the aqueous DSs in neutral and alkaline pHs ranged between 2 and 3.

Table 2

Percentage, molecular weights and composition of the extractables from the networks and comparison with the corresponding quantities of the linear polymer precursors

Polymer formula ^a	w/w% (extractables)	GPC results				DMAEMA (mol%)	
		Extractables		Precursors		Extractables	Precursors
		M_n	M_w/M_n	M_n	M_w/M_n		
D ₂₅	12	N.D. ^b	N.D.	5960	1.06	—	—
Bu ₅ -b-D ₂₅ -b-Bu ₅	8.0	4020	1.19	6380	1.15	83.3	69.8
D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅	11	9280	1.34	17,900	1.15	84.2	85.3
Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅	17	23,500	1.07	29,600	1.16	83.4	81.4
D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅	9.0	24,500	1.09	29,600	1.25	86.2	86.7

^a D: DMAEMA, Bu: BuMA.

^b N.D.: not determined.

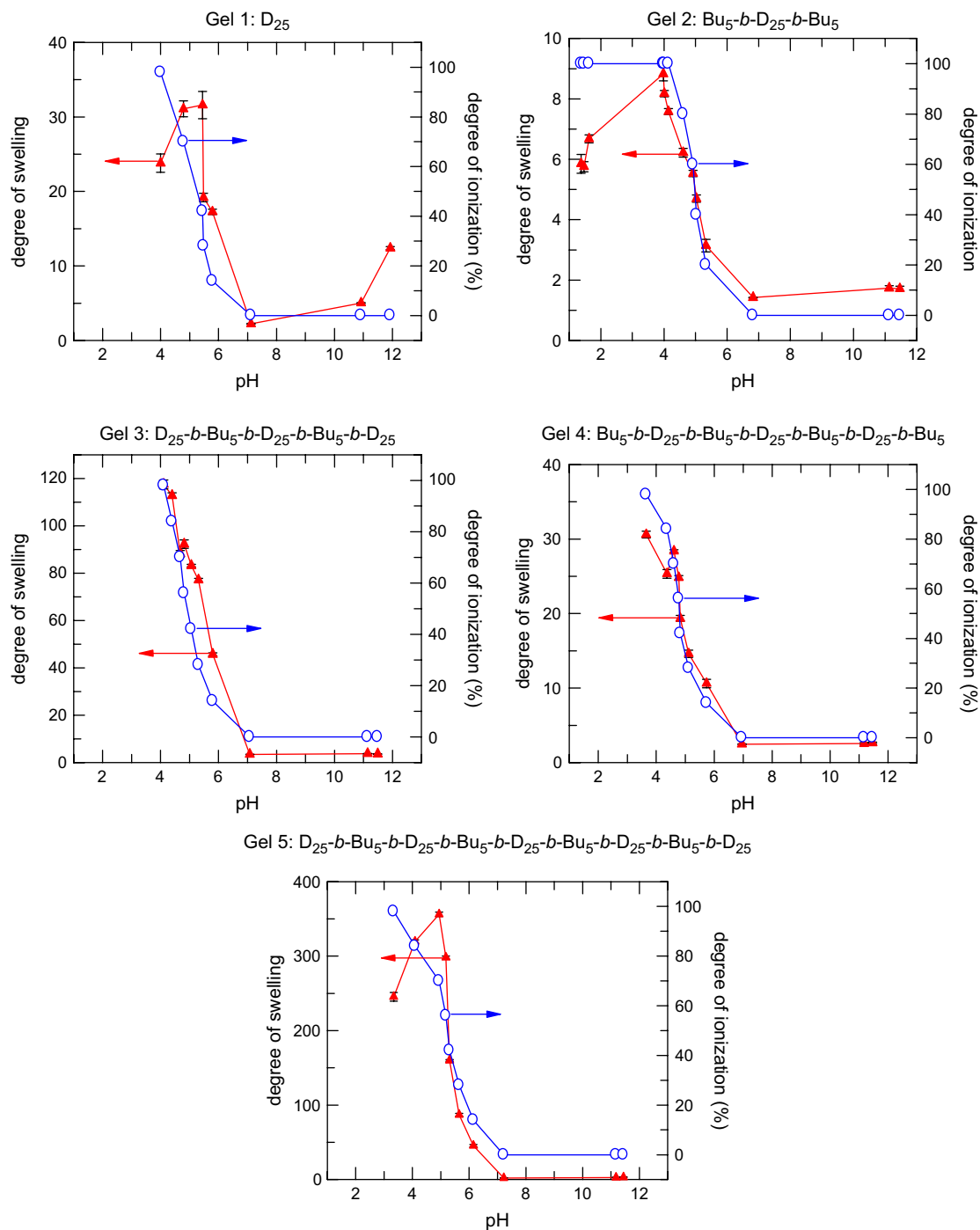


Fig. 4. Degrees of swelling and degrees of ionization of all the (co)networks as a function of pH.

3.5. Degrees of swelling in water and THF

The DSs in pure water (pH \sim 7) and in acidified water (pH \sim 4) were extracted from Fig. 4 for all the (co)networks and are plotted in Fig. 5 along with the corresponding DSs in THF (uncharged networks). Fig. 5(a) examines the effect of MW on swelling, while Fig. 5(b) explores the effect of composition on swelling. The effect of the number of blocks on swelling is not examined separately, as the number of blocks is dependent on MW and composition, already investigated in the afore-mentioned figures.

In both Fig. 5(a) and (b), the DSs of all (co)networks increased in the order:

neutral water < THF < acidic water.

THF is a non-selective solvent, solvating well both the DMAEMA and the BuMA units. In contrast to THF, neutral water is a selective solvent for the hydrophilic DMAEMA units and a non-solvent for the hydrophobic BuMA (and EGDMA) units, leading to the collapse of the polyBuMA blocks in water and resulting in lower DSs in neutral water than in THF. It should be noted that the DMAEMA units

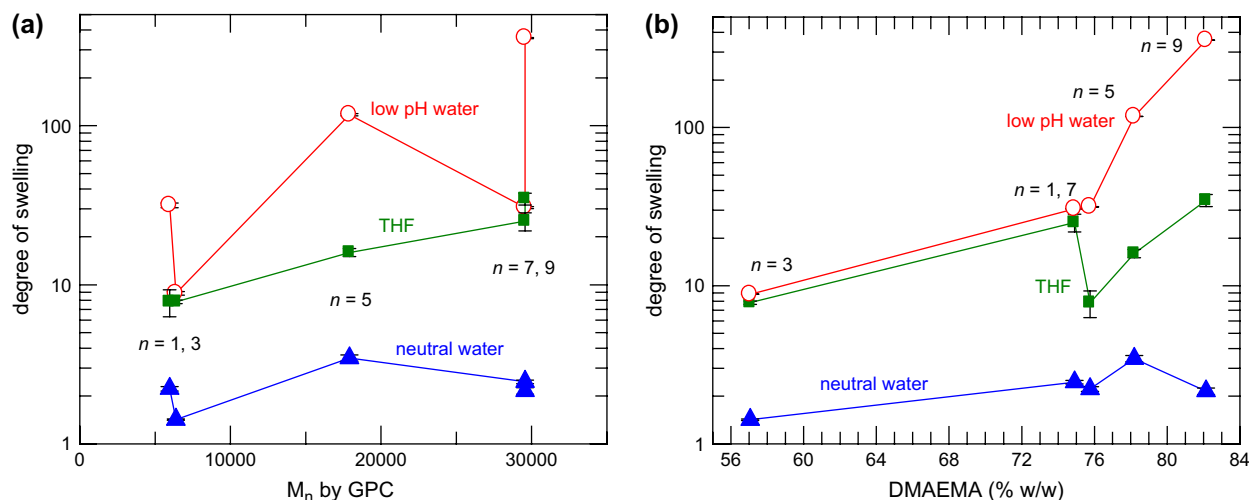


Fig. 5. Effect of (a) the molecular weight and (b) the DMAEMA overall content on the degrees of swelling of the (co)networks in different solvents.

were uncharged both in THF and in neutral water. The DSs in acidic water were highest compared to those in neutral water and in THF because of the full ionization of the DMAEMA units. Although the polyBuMA blocks were again collapsed in acidic water, the great extension in the polyDMAEMA blocks imparted by their electric charge largely counteracted the effect of hydrophobe collapse.

In Fig. 5(a), the DSs in the non-selective THF increased monotonically with the MWs (also with the number of blocks, n , with which the symbols are labeled in Fig. 5), as expected. In contrast, the DSs in water, both neutral and acidic, fluctuated with the MWs because water is a selective solvent and composition becomes more important than MW.

In Fig. 5(b), the DSs in the three solvents are plotted against the (co)network DMAEMA content, expressed as the DMAEMA weight fraction over the whole dry (co)network, taking also into account the presence of the hydrophobic EGDMA units. This DMAEMA weight fraction was calculated using the experimentally (by ^1H NMR) determined DMAEMA/BuMA molar ratio of the linear precursors (Table 1) and the theoretical DMAEMA/EGDMA molar ratio in the (co)networks. In this figure, the DSs in THF fluctuated with the DMAEMA content. However, the DSs in acidic water, and, to a smaller extent, in neutral water increased monotonically with the DMAEMA overall content, as expected. Plotting the DSs in water against the DMAEMA content without taking into account the presence of the EGDMA hydrophobic units did not produce a perfect monotonic trend. In particular, in that case, the DMAEMA homopolymer network deviated significantly from the monotonic

behavior of the other conetworks, as this network, based on the lowest MW precursor, has the highest EGDMA content.

3.6. Effective pKs of the networks

The pK values of the DMAEMA units in the (co)networks were read out from the degree of ionization vs. pH curves as the pH at 50% ionization and are presented in Table 3. All (co)networks were found to have similar pKs of the DMAEMA units, which, however, span a range of values from 4.9 to 5.4. These values were comparable to those measured for other DMAEMA-containing networks [20a].

4. Conclusions

GTP was employed for the preparation of five model (co)networks of DMAEMA and BuMA based on end-linked (co)polymers bearing up to nine blocks. The linear precursors to the model (co)networks were characterized in terms of their MWs and MWDs. The measured M_n s were close to the theoretically expected MWs and the MWDs were narrow confirming homogeneity of the lengths of the segments between cross-links. Furthermore, the precursor composition was determined and was also found to be in agreement with the theoretically expected values.

The extractables from all the (co)networks were isolated and characterized using the same methods as for the linear (co)network precursors. The percentage of the extractables (sol fraction) was found to be relatively low, indicating the well-defined structure of the (co)networks and sufficient incorporation of the linear chains into the (co)networks. Their MW was lower than that of the corresponding linear (co)polymer precursors, suggesting that termination occurs only at the first step. The composition of the extractables was similar to that of the linear (co)polymer precursors.

The swelling behavior of the (co)networks was studied in THF, in neutral (pure) water and in acidic water. The DSs were found to be affected by the solvent type and the number

Table 3
pKs of the DMAEMA monomer repeating units in the networks

No.	Polymer formula	pK
1	D ₂₅	5.4
2	Bu ₅ -b-D ₂₅ -b-Bu ₅	5.0
3	D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅	4.9
4	Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅	4.9
5	D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅ -b-Bu ₅ -b-D ₂₅	5.4

of blocks. Regarding the effect of the solvent, the lowest DSs were obtained in neutral water which was a selective solvent, intermediate DSs were observed in THF which was a non-selective solvent, and the highest DSs were measured in acidic water which was also a selective solvent but it induced the complete ionization of the DMAEMA units. Regarding the effect of the number of blocks, the DSs in THF increased with the number of blocks and the MW, while the DSs in acidic water fluctuated with the MW and the number of blocks reflecting the simultaneous variation of MW and composition with the number of blocks in this system. Future work will aim at decoupling the effects of MW and number of blocks on swelling by preparing model conetworks based on multiblock copolymers of constant MW and constant composition as the number of block varies.

Acknowledgments

The Cyprus Research Promotion Foundation is gratefully acknowledged for financial support for this work (grant ENISX/0505/19, project acronym POLYADRO). We also thank the A. G. Leventis Foundation for a generous donation that enabled the purchase of the NMR spectrometer of the University of Cyprus.

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