Synthesis and Characterization of Amphiphilic Cationic Symmetrical ABCBA Pentablock Terpolymer Networks: Effect of Hydrophobic Content

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ABSTRACT: Group transfer polymerization was employed for the preparation of six amphiphilic terpolymer networks comprising the hydrophilic, pH-responsive 2-(dimethylamino)ethyl methacrylate (DMAEMA), the neutral hydrophilic methoxy hexa (ethylene glycol) methacrylate (HEGMA), and the hydrophobic *n*-butyl methacrylate (BuMA). 1,4-Bis(methoxytrimethylsiloxymethylene)cyclohexane was used as a bifunctional initiator, whereas ethylene glycol dimethacrylate served as the crosslinker to interconnect the linear terpolymer precursors to three-dimensional terpolymer network structures. Five of the terpolymer networks were model, with linear chains between crosslinks of precise length. Four of the five model networks were based on ABCBA pentablock terpolymers with theoretical structure DMAEMA_5-*b*-$\mathrm{BuMA}_{n/2}$-*b*-HEGMA_{10}-*b*-$\mathrm{BuMA}_{n/2}$-*b*-DMAEMA_5 with n values equal to 5, 10, 20, and 30. The model network based on the equimolar statistical terpolymer and the nonmodel randomly crosslinked terpolymer network were also prepared. The molecular weights and compositions of the linear pentablock terpolymer precursors to the networks were found to be close to the theoretically expected, while the network sol fractions were found to be relatively low. The degrees of swelling of the networks in water were found to decrease with increasing the hydrophobic content, whereas those in THF exhibited the opposite trend. Small-angle neutron scattering in deuterium oxide indicated structural organization in the most hydrophobic pentablock terpolymer networks. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 4420–4432, 2008

Keywords: ABCBA pentablock terpolymers; amphiphiles; amphiphilic model networks; block copolymers; composition; degree of swelling; gels; group transfer polymerization; hydrogels; hydrophobic content; networks; small-angle neutron scattering; structural organization

INTRODUCTION

Covalent amphiphilic polymer conetworks (APCNs)[1] represent an emerging class of biomaterials, whose preparation and study constitute the objectives of several research teams worldwide.[2] APCNs comprise hydrophilic and hydrophobic units chemically interconnected into a three-dimensional structure. The rich functional behavior of APCNs[3] renders them appropriate materials for several applications, including drug release,[4] tissue engineering,[5] enzyme immobilization,[6] synthesis of mesoporous silica,[7] growth of semiconducting nanocrystals,[8] soft

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contact lenses,[9] pervaporation membranes,[10] extractants of organic solvents from water,[11] temperature-activated actuators,[11] and biochemical sensors.[12]

Although structural perfection is rarely a prerequisite for the above applications, the preparation of model[13] APCNs represents a challenging synthetic target necessary for the derivation of accurate structure–property relationships. For the past 7 years our research group has been working for the development of synthetic methodologies for the preparation of quasi-model APCNs, characterized by high degrees of homogeneity in chain length and composition and a distribution in the number of arms at the crosslinking nodes.[14] In particular, we have been using group transfer polymerization (GTP),[15] a controlled polymerization method, for the development of methacrylate quasi-model APCNs of two different topologies: regular APCNs in which all chains are, in principle, end-linked,[16] and crosslinked star APCNs bearing an equal number of end-linked and singly attached (i.e., dangling) chains.[17]

Recently, we extended the compositional scope of our work on regular APCNs by preparing networks based on end-linked linear three-component polymer chains (terpolymers).[18] These chains were ABCBA pentablock terpolymers comprising a hydrophobic monomer, methyl methacrylate (MMA), and two different hydrophilic monomers: a nonionic one, methoxy hexa(ethylene glycol) methacrylate (HEGMA), and a weakly basic pH-responsive one, 2-(dimethylamino)ethyl methacrylate (DMAEMA). The three constituting monomers conveyed to the terpolymer networks their corresponding functions and a rich aqueous swelling behavior: the hydrophobic MMA restricted extensive aqueous swelling, DMAEMA introduced a pH-dependent swelling behavior, and HEGMA prevented the complete collapse of the networks at high pH where the DMAEMA units are uncharged. In that study, all six possible block sequence isomeric chains (and their corresponding networks) were prepared: ABCBA, BACAB, ACBCA, CABAC, BCACB, and CBABC.

In the present work, we continued our investigations on terpolymer networks, bearing three rather than just two functions, by focusing on the effect of terpolymer composition. Thus, the block sequence was fixed and the content in the hydrophobic component was systematically varied. Furthermore, *n*-butyl methacrylate (BuMA) rather than MMA was used as the hydrophobic monomer in this study to reduce the fragility and improve the mechanical properties of the networks. In addition to the characterization of the aqueous degrees of swelling (DSs) of the networks, their structural organization in D_2O was investigated using small-angle neutron scattering (SANS).

EXPERIMENTAL

Methods

The chemical structures and names of the three monomers, HEGMA (neutral-hydrophilic), DMAEMA (ionizable-hydrophilic) and BuMA (neutral-hydrophobic), the ethylene glycol dimethacrylate (EGDMA) crosslinker, and the bifunctional GTP initiator, 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane (MTSMC), are shown in Figure 1.

DMAEMA, BuMA, and EGDMA were purchased from Aldrich, Germany, whereas HEGMA

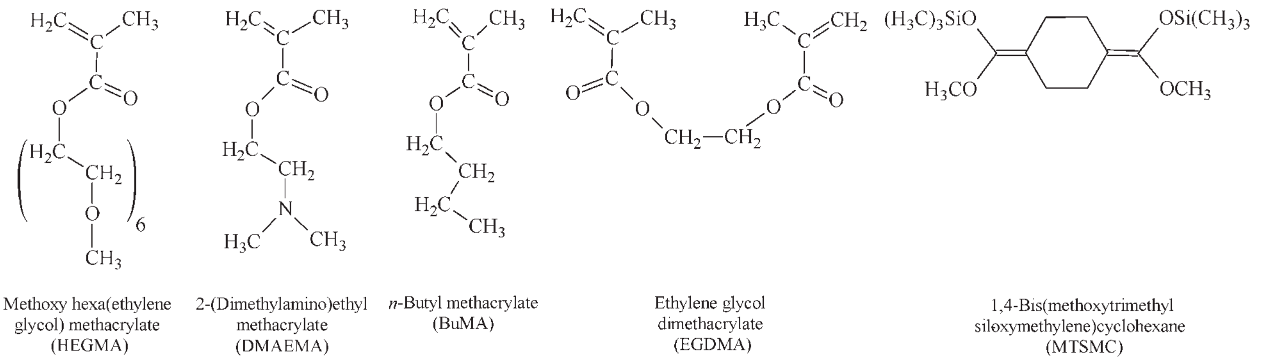


Figure 1. Chemical structures and names of the three monomers, the crosslinker and the initiator used for the preparation of the terpolymer networks.

was kindly donated by Cognis Performance Chemicals, UK. MTSMC was in-house synthesized by the silylation of dimethyl 1,4-cyclohexanedicarboxylate.[19] All monomers and the crosslinker were passed through basic alumina columns to remove the polymerization inhibitor and protic impurities. Because of the high viscosity of the neat monomer, a 50% v/v solution in freshly distilled tetrahydrofuran (THF) of the HEGMA monomer was used for the processing with basic alumina. The HEGMA monomer solution was passed twice through basic alumina columns, whereas BuMA, DMAEMA, and EGDMA were passed only once due to the higher initial purity of these materials. Subsequently, BuMA, DMAEMA and EGDMA were stirred over calcium hydride (to remove the last traces of moisture and protic impurities) overnight in the presence of a free radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), and were vacuum-distilled just prior to use. The HEGMA solution was stirred over calcium hydride (without DPPH) and was filtered through a 0.45 μm PTFE syringe filter directly into the polymerization flask. The MTSMC initiator was distilled one day before the polymerization. The polymerization solvent, THF, was refluxed over a potassium/sodium alloy for 3 days and was freshly distilled prior to use. The polymerization catalyst, tetrabutylammonium bibenzoate (TBABB) was prepared according to the literature[15(c)] and kept under vacuum until use.

Network Synthesis

All the networks reported in this study were prepared at room temperature using GTP and sequential monomer and crosslinker additions. Networks with different composition and different architecture were synthesized. The network composition was varied for networks with ABCBA pentablock terpolymer chain architecture by varying the degree of polymerization (DP) of the hydrophobic BuMA B-blocks. The network architecture was varied for networks equimolar in the three monomers by varying the order of addition of the monomers and the crosslinker. Three different network architectures were accessed: ABCBA pentablock terpolymer and statistical terpolymer model networks, and the randomly crosslinked network of the statistical terpolymer. The ABCBA pentablock terpolymer model network was prepared by four sequential additions: those of the three monomers and concluded by that of the crosslinker. The statistical terpolymer model network was prepared by two sequential additions: the first involving the simultaneous terpolymerization of the three monomers and the second involving the addition of the crosslinker. The randomly crosslinked network of the statistical terpolymer was prepared by adding the three monomers and the crosslinker together leading to their simultaneous quaterpolymerization. The synthetic sequences followed for the preparation of the various terpolymer networks are summarized in Figure 2.

A typical polymerization procedure for the preparation of one of the ABCBA pentablock terpolymer networks, and, in particular, that of the equimolar DMAEMA$_5$-*b*-BuMA$_5$-*b*-HEGMA$_{10}$-*b*-BuMA$_5$-*b*-DMAEMA$_5$-based network, is detailed below. Freshly distilled THF (32 mL) and 0.3 mL (0.36 g, 1.05 mmol) MTSMC initiator were syringed into a 100 mL round-bottom flask containing a small amount (10 mg) of TBABB, in this order. Subsequently, a 50% v/v solution of HEGMA in THF (7.0 mL of solution; 3.7 g or 10.5 mmol of neat HEGMA monomer) was added slowly under continuous stirring, which produced an exotherm (25.9–30.3 °C). The polymerization exotherm abated within 5 min, a sample for GPC analysis was extracted, and 1.7 mL (1.5 g, 10.5 mmol) of BuMA monomer was added (28.1–31.2 °C). After extraction of a sample for GPC analysis of the BuMA–HEGMA–BuMA triblock copolymer, 1.8 mL (1.7 g, 10.7 mmol) of DMAEMA was added to the solution, generating an exotherm, (29.6–33.2 °C), and a sample for GPC analysis of the DMAEMA–BuMA–HEGMA–BuMA–DMAEMA pentablock terpolymer was extracted. Finally, 1.6 mL (1.7 g, 8.5 mmol) of the EGDMA crosslinker was added (29.9–36.1 °C), which led to the gelation of the solution within seconds.

Characterization by GPC

Samples of linear homopolymers, ABA triblock copolymers and ABCBA pentablock terpolymers were withdrawn during the course of the polymerizations and before the crosslinking, and were characterized in terms of their molecular weights (MWs) and molecular weight distributions (MWDs) using GPC. GPC was performed on a Polymer Laboratories system equipped with a PL-LC1120 isocratic pump, an ERC-

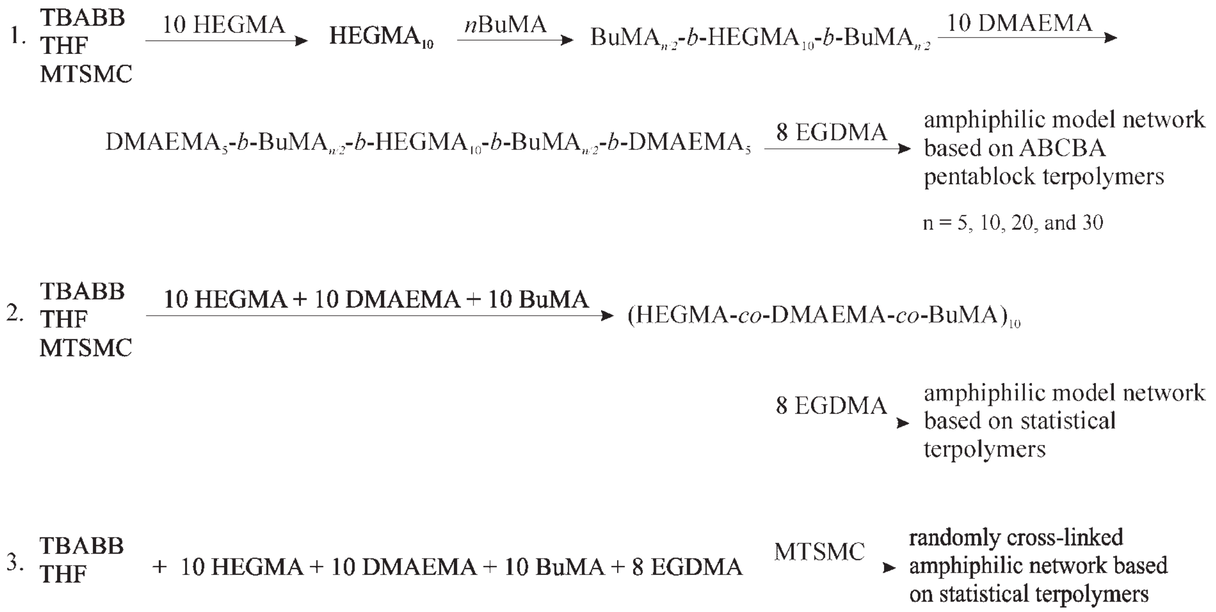


Figure 2. Synthetic sequences followed for the preparation of the six terpolymer networks with four different compositions and three different architectures.

7515A refractive index detector and a PL Mixed "E" column. The eluent was THF, pumped at 1 mL min^{-1}. The MW calibration was based on six narrow MW (630, 1400, 4250, 7600, 13,000, and 28,900 g mol^{-1}) PMMA standards also supplied by Polymer Laboratories.

Characterization by ^{1}H NMR

The compositions of the linear terpolymer (pentablock and statistical) precursors to the networks were determined by ^{1}H NMR using a 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet. The solvent was $CDCl_3$, containing traces of tetramethylsilane, which was used as an internal reference.

Recovery and Characterization of Extractables

First, the networks were removed from the polymerization flasks and were placed in excess THF for one month to extract the polymer not incorporated in the network. The THF solution of the extracted material was dried in a rotary evaporator and the mass of that polymer was determined. Samples of the extractables were characterized by GPC in THF and by ^{1}H NMR in $CDCl_3$ using the equipment described above.

Measurement of the DS and the p*K*

The DSs of the networks were measured in THF, in water and in aqueous solutions covering the pH range of 2–12. After the equilibration in excess THF and the removal of the extractables (as described in the preceding paragraph), 10 pieces were cut from each network. Each piece was weighed and subsequently dried in a vacuum oven at room temperature for fourteen 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 terpolymer network. To measure the DSs in aqueous media at different pH values, 5 mL of deionized water was added to each sample of the dried networks, followed by the addition of the appropriate volume of a 0.5 M HCl solution to adjust the pH within the range 2–8, corresponding to degrees of ionization between 100 and 0% (eight samples used). 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. Small volumes of a 0.5 M NaOH solution were added to the two remaining samples of each network to cover the pH range from 8 to 12. The DSs were measured four times and the average values are presented, along with the 95% confidence intervals. The effective p*K*s of the

DMAEMA repeating units in the networks were estimated as the pH at 50% ionization.

SANS

All the terpolymer networks (in the uncharged state) were characterized using SANS in deuterium oxide (D_2O). For sample preparation, the networks were first dried from THF and subsequently equilibrated in D_2O for 10 days. The SANS experiments were performed on the 30 m NG3 instrument at the Center for Neutron Research of the National Institute of Standards and Technology in the USA with incident neutron beam wavelength (= 6 Å. Each one of the samples was loaded in 1 mm gap thickness quartz cells. Three sample-to-detector distances, 1.35, 4.5, and 13.1 m, were employed, covering a q-range [$q = 4\pi/\lambda \sin(\theta/2)$] from 0.004 $Å^{-1}$ to q 0.44 $Å^{-1}$. The data were averaged and corrected for empty cell and background, whereas the measured counts were azimuthally averaged.

RESULTS AND DISCUSSION

Three-Component Networks

Although the literature abounds of reports on one-component (homopolymer) networks and two-component (copolymer) conetworks, reports on three-component (terpolymer) networks are rare, particularly those in which each of the three types of units is arranged in long segments (segmented networks). From the small number of such reports, the work from the Hatton and coworkers[20] and Kurian and Kennedy[21] is worth mentioning. Hatton and coworkers prepared terpolymer networks of poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and acrylic acid (AA) by subjecting commercially available PEO-*b*-PPO-*b*-PEO triblock copolymers (known as Pluronics) to simultaneous grafting with AA and crosslinking using EGDMA.[20] On the other hand, the terpolymer networks of Kurian and Kennedy[21] comprised PEO, polyisobutylene and poly(dimethylsiloxane) segments. However, the structural control in these terpolymer networks was limited as the MW of the segments was not precisely controlled in the former case[20] and the arrangement of the segments was not regular in the latter.[21] Terpolymer networks with well-defined structure were first developed and presented in our recent publication where all three components were incorporated by sequential "living" GTP[15] and precisely arranged in five blocks.[18] The focus in that first report was on block position, as all six possible block sequence isomeric terpolymer networks were prepared and characterized. The interest in the present investigation is in terpolymer composition, and, in particular, in the hydrophobic content which is to be varied systematically at a fixed block sequence.

Polymerization Methodology

Thus, all ABCBA pentablock terpolymer networks in this study had the same block sequence but different contents in the hydrophobic monomer. The hydrophobic content was systematically varied by varying the DPs of the BuMA blocks which were the intermediate B-blocks (located between the A- and C-blocks). The HEGMA units constituted the central C-block with a DP of 10, while the DMAEMA units constituted the two A- end-blocks with DPs of 5 each. Figure 3 illustrates schematically the synthesis of the model network based on the

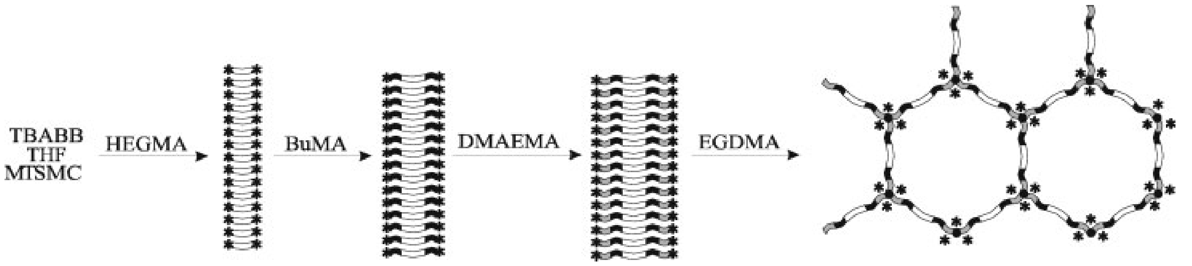


Figure 3. Schematic representation of the synthetic procedure followed for the preparation of the model network based on the symmetrical pentablock terpolymer $DMAEMA_5$-*b*-$BuMA_5$-*b*-$HEGMA_{10}$-*b*-$BuMA_5$-*b*-$DMAEMA_5$. The DMAEMA units are shown in gray, the HEGMA units in white, and the BuMA units in black. The "*" symbols indicate the "living" sites of the polymerization.

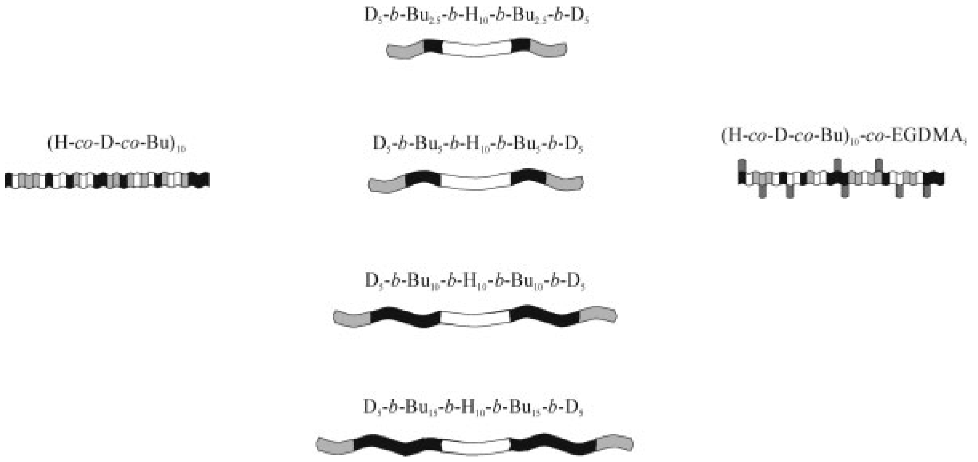


Figure 4. Schematic representations of the chains between the crosslinks of the terpolymer networks prepared and characterized in this study. The HEGMA (H) units are illustrated in white, the DMAEMA (D) units in gray and the BuMA (Bu) units in black.

equimolar $DMAEMA_5$-*b*-$BuMA_5$-*b*-$HEGMA_{10}$-*b*-$BuMA_5$-*b*-$DMAEMA_5$ pentablock terpolymer, by sequential addition of the three monomers and the crosslinker. The first step leads to the formation of a linear HEGMA homopolymer, active at both ends, which will constitute the central C-block of the pentablock. In the second step, BuMA is added, resulting in the placement of the units of this monomer symmetrically at either end of the central HEGMA-block to give the B-blocks. Addition of the third monomer, DMAEMA, results in the formation of the A-end-blocks and yields the pentablock terpolymer chains having both of their ends active. The crosslinker is added last, effecting the interconnection of the linear chains at both of their ends, forming the three-dimensional network. The number of moles of the added crosslinker was eight times the number of moles of the MTSMC initiator to optimize interchain connection and network formation, according to a previous study.[22]

The other model networks based on ABCBA pentablock terpolymers were prepared in the same way but by using different amounts of BuMA. For the preparation of the model network based on the statistical terpolymer, the three monomers were added simultaneously and the crosslinker was added last. The synthesis of the randomly crosslinked network of the statistical terpolymer involved simultaneous quaterpolymerization of the three monomers and the crosslinker.

Schematic representations of the linear terpolymer chains between the crosslinks for all the networks along with their theoretical formulas are displayed in Figure 4. The color-coding is: white for the HEGMA (H) units, gray for the DMAEMA (D) units and black for the hydrophobic BuMA (Bu) units. The four terpolymers displayed vertically in Figure 4 have constant DPs of the HEGMA and the DMAEMA blocks and varying DPs of the BuMA blocks: moving from the top to the bottom of the figure, the DPs of the BuMA blocks (and hence network hydrophobicity) increase. In contrast, the three terpolymers drawn in the same row have the same composition (equimolar) and overall chain lengths but different architectures: from left to right, schematic representations of the statistical terpolymer, the ABCBA pentablock terpolymer and the randomly crosslinked statistical terpolymer network are illustrated.

Characterization of the Linear Precursors

Molecular Weights

The MWs and MWDs of the homopolymer, the ABA triblock copolymer and the pentablock terpolymer precursors to the networks were determined by GPC in THF and are given in Table 1. The polymer formula of each terpolymer is listed in the second column of the Table, with the subscripts indicating the nominal DPs.

Table 1. Molecular Weights and Compositions of the Linear Precursors to the Networks and the p*K*s of the DMAEMA Units in the Networks

No.	Polymer Formula[a]	Theor. MW[b]	GPC Results		Composition % mol (H-Bu-D)		p*K*
			M_n	M_w/M_n	Theor.	^{1}H NMR	
1	H_{10}	3,700	5,440	1.08			
	$Bu_{2.5}$-*b*-H_{10}-*b*-$Bu_{2.5}$	4,420	6,100	1.09			
	D_5-*b*-$Bu_{2.5}$-*b*-H_{10}-*b*-$Bu_{2.5}$-*b*-D_5	5,990	7,370	1.12	40-40-20	38-37-25	4.8
2	H_{10}	3,700	5,910	1.08			
	Bu_5-*b*-H_{10}-*b*-Bu_5	5,140	7,410	1.11			
	D_5-*b*-Bu_5-*b*-H_{10}-*b*-Bu_5-*b*-D_5	6,710	8,770	1.15	33-33-33	32-35-33	4.2
3	(D-*co*-Bu-*co*-H)$_{10}$	6,710	9,660	1.13	33-33-33	37-32-31	4.6
4	(D-*co*-Bu-*co*-H)$_{10}$-*co*-E_8	–	N/A[c]	N/A[c]	33-33-33	N/A[c]	4.1
5	H_{10}	3,700	5,730	1.09			
	Bu_{10}-*b*-H_{10}-*b*-Bu_5	6,580	9,750	1.16			
	D_5-*b*-Bu_{10}-*b*-H_{10}-*b*-Bu_{10}-*b*-D_5	8,150	11,750	1.21	25-50-25	27-47-26	4.3
6	H_{10}	3,700	6,030	1.08			
	Bu_{15}-*b*-H_{10}-*b*-Bu_{15}	5,860	14,100	1.25			
	D_5-*b*-Bu_{15}-*b*-H_{10}-*b*-Bu_{15}-*b*-D_5	7,430	17,750	1.28	20-60-20	23-59-18	4.2

[a] H, HEGMA; Bu, BuMA; D, DMAEMA; E, EGDMA.

[b] The initiator fragment of 196 g mol^{-1} was also included in the MW calculation.

[c] N/A: the data were not available as the system formed a network almost immediately after the addition of initiator to the THF solution of the three monomers, the crosslinker and the catalyst.

According to the data listed in this Table, the MWs were almost twice the theoretically expected, attributed to partial initiator deactivation and to differences in the hydrodynamic volumes of the present samples with the PMMA MW calibration standards. The MWDs were narrow with the M_w/M_n values being always lower than 1.3 (and lower than 1.2 for most of the samples), indicating the size homogeneity of the chains. Also, it is noteworthy that the GPC traces (not shown) after each addition were monomodal indicating uniform and complete incorporation of the monomer added each time to the polymer chain.

Composition

The compositions of the linear terpolymer network precursors were determined by ^{1}H NMR in $CDCl_3$. This was accomplished by calculating the areas of the most characteristic peak from each monomer repeating unit in the ^{1}H NMR spectra. The characteristic peaks were those corresponding to the three methoxy protons in HEGMA at 3.3 ppm, the two azamethylene protons in DMAEMA at 2.55 ppm, and the two oxymethylene protons in BuMA at 3.9 ppm. The theoretically calculated compositions based on the amount of the three monomers fed during the synthesis and the experimentally determined compositions are listed in the sixth and seventh columns of Table 1, respectively, and were close to each other.

Characterization of the Extractables

Further to the characterization of linear precursors, the extractables of the networks were collected and characterized in terms of their mass fraction, MWs, M_w/M_n values and compositions. These results are presented in Table 2. The theoretical formulas of the terpolymer chains between crosslinks are listed in the second column of the table, where the subscripts denote the nominal DPs.

In the third column of the Table, the percentage of the extractables (sol fraction) is listed. The sol fraction was found to be relatively low, ranging from 9 to 19% and indicating a satisfactory incorporation of the linear chains into the networks. Thus, the molar ratio of 8:1 of crosslinker to initiator[22] employed during synthesis was sufficiently high.

By comparing the MWs of the extractables and the precursors listed in Tables 2 and 1, respectively, it is apparent that the extractables from the networks had lower MWs than the precursors to the networks in all cases. This can be

Table 2. Mass Fractions, Molecular Weights, and Compositions of the Extractables from the Terpolymer Networks

No.	Polymer Formula[a]	Extractables (% w/w)	GPC Results M_n	GPC Results M_w/M_n	% mol H-Bu-D
1	D_5-*b*-$Bu_{2.5}$-*b*-H_{10}-*b*-$Bu_{2.5}$-*b*-D_5	17.0	6,370	1.13	60-22-20
2	D_5-*b*-Bu_5-*b*-H_{10}-*b*-Bu_5-*b*-D_5	12.7	7,440	1.18	52-32-16
3	(D-*co*-Bu-*co*-H)$_{10}$	9.3	8,190	1.24	39-30-31
4	(D-*co*-Bu-*co*-H)$_{10}$-*co*-E_8	19.4	16,790	2.62	32-35-33
5	D_5-*b*-Bu_{10}-*b*-H_{10}-*b*-Bu_{10}-*b*-D_5	15.1	8,770	1.25	32-55-13
6	D_5-*b*-Bu_{15}-*b*-H_{10}-*b*-Bu_{15}-*b*-D_5	17.9	10,313	1.38	31-48-21

[a] H, HEGMA; Bu, BuMA; D, DMAEMA; E, EGDMA.

explained by recalling that the extractables were early-terminated homopolymer, ABA triblock copolymer or ABCBA pentablock terpolymer chains not incorporated in the network. Comparing the compositions of the extractables listed in the last column of Table 2 with the compositions of the linear precursors given in Table 1 it can be concluded that the extractables from the networks were richer in the monomer of the first addition. This was also reported for the extractables of the networks discussed in earlier work[18] and was attributed to the fact that the content of the first (middle) block was subjected to chain inactivation longer than the other two components.

Characterization of the Networks

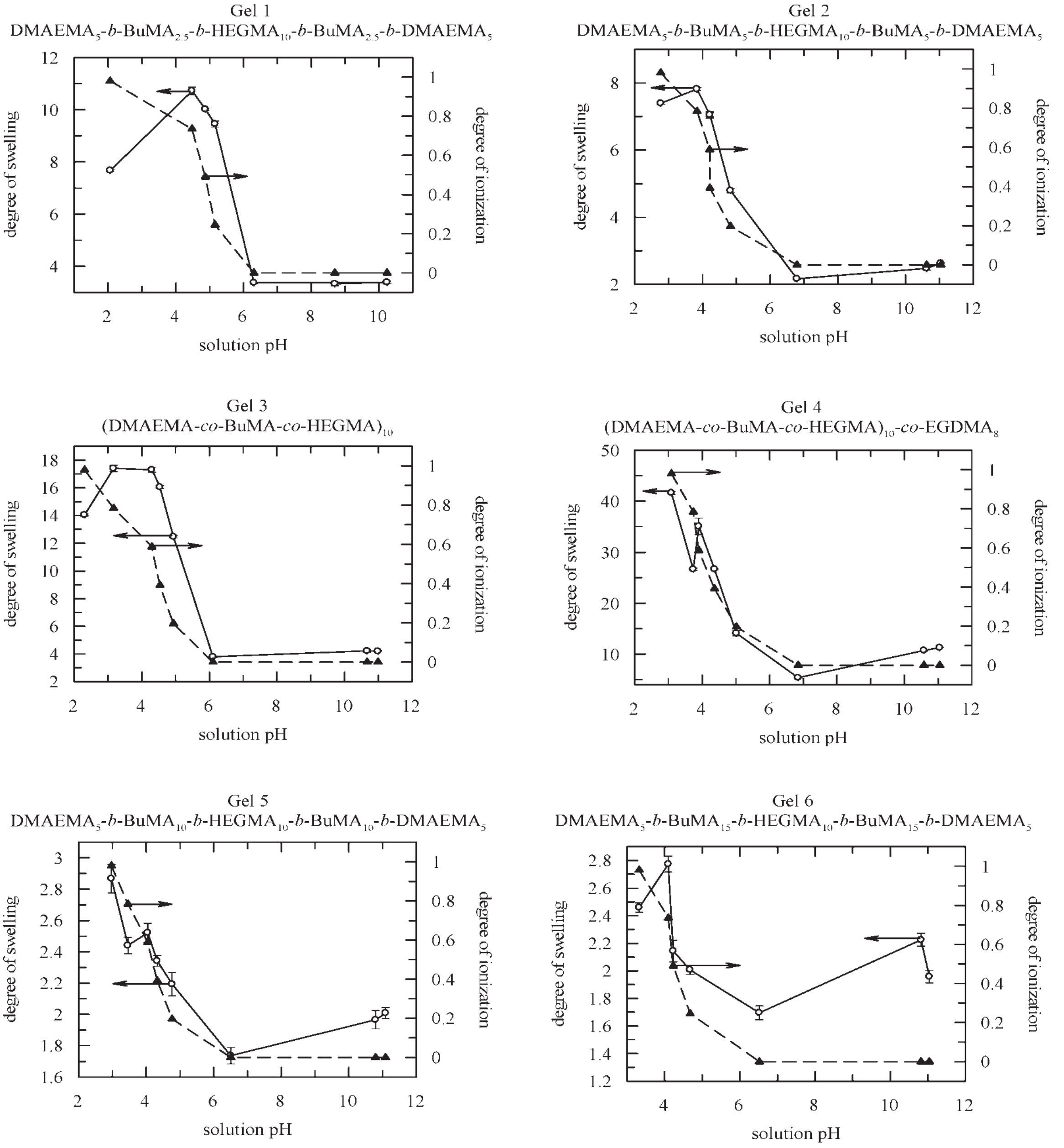
Aqueous DSs and Degrees of Ionization

The experimentally determined DSs and degrees of ionization of all the networks are plotted against the pH of the supernatant solution in Figure 5. The theoretical chemical formula of the chains between the crosslinks for each network is shown above each plot. In all cases, the DS curves followed the degree of ionization curves, underlining the importance of ionization for the swelling of these networks.

The main observation from the plots in Figure 5 is that all the terpolymer networks exhibited the same aqueous swelling behavior with respect to the solution pH, that is, low swelling at high pH values and increased swelling up to a maximum value upon decreasing the pH. The same behavior was reported for model networks based on linear DMAEMA–MMA[16(b)] and HEGMA–DMAEMA[23] triblock copolymers. The increase in the DSs observed upon a decrease in the solution pH was due to the ionization of the DMAEMA units. DMAEMA is a tertiary amine which becomes positively charged below pH 7. This ionization induced electrostatic repulsions between the terpolymer chains which promoted network swelling. Network swelling was further enhanced by the build-up of an osmotic pressure, created by the presence of the counterions to the charges in the network.[24] At very low pH values (~ 2–3), a decrease in the DSs was observed, attributed to charge screening due to the high ionic strength imparted by the relatively high HCl concentration under the particular conditions.

Effect of Solvency and Network Composition on the DSs

The DSs in pure water (uncharged networks) and in acidified water (fully charged networks) for all the networks were extracted from Figure 5 and were plotted in Figure 6 against the composition of the networks in the hydrophobic monomer. In the same Figure, the DSs in THF were also plotted. According to the curves presented in Figure 6, the DSs in pure water and in acidified water decreased as the content in the hydrophobic monomer in the terpolymer chains between crosslinks increased. In particular, the DSs at low pH decreased from about 11 to 3 upon increasing the BuMA content from 20 to 60% mol. For the same change in the BuMA content, the DSs in pure water decreased from 3.4 to 1.7. Unlike the decreases observed in the values of the DSs in pure and in acidified water with increasing the BuMA content, the DSs in THF (nonselective solvent) were found to increase with increasing the hydrophobic content. This could be attributed to the increasing lengths of the chains between the crosslinks


Gel 1 $DMAEMA_5$-*b*-$BuMA_{25}$-*b*-$HEGMA_{10}$-*b*-$BuMA_{25}$-*b*-$DMAEMA_5$

Gel 2 $DMAEMA_5$-*b*-$BuMA_5$-*b*-$HEGMA_{10}$-*b*-$BuMA_5$-*b*-$DMAEMA_5$

Gel 3 (DMAEMA-*co*-BuMA-*co*-HEGMA)$_{10}$

Gel 4 (DMAEMA-*co*-BuMA-*co*-HEGMA)$_{10}$-*co*-$EGDMA_8$

Gel 5 $DMAEMA_5$-*b*-$BuMA_{10}$-*b*-$HEGMA_{10}$-*b*-$BuMA_{10}$-*b*-$DMAEMA_5$

Gel 6 $DMAEMA_5$-*b*-$BuMA_{15}$-*b*-$HEGMA_{10}$-*b*-$BuMA_{15}$-*b*-$DMAEMA_5$

Figure 5. DSs and degrees of ionization as a function of pH for all the terpolymer networks.

with the length of the hydrophobic BuMA blocks.

Focusing now on the effect of solvency on the swelling of the networks containing 20 and 33% BuMA, it is observed that their DSs increased in the order pure water < THF < acidified water as was also the case with the results for the model networks based on DMAEMA–MMA triblock copolymers.[16(b)] However, for BuMA contents 50% mol or higher, the order in the DSs changed, with the highest DS obtained in THF, intermediate in acidified water and the lowest in pure water. Thus, for the present terpolymer composition range, the hydrophobic interactions became dominant, as compared with the previous BuMA-poor composition regime where the repulsive electrostatic interactions dominated.

Effect of Network Architecture on the DSs

Figure 7 illustrates the effect of network architecture on the DSs in three different solvents.

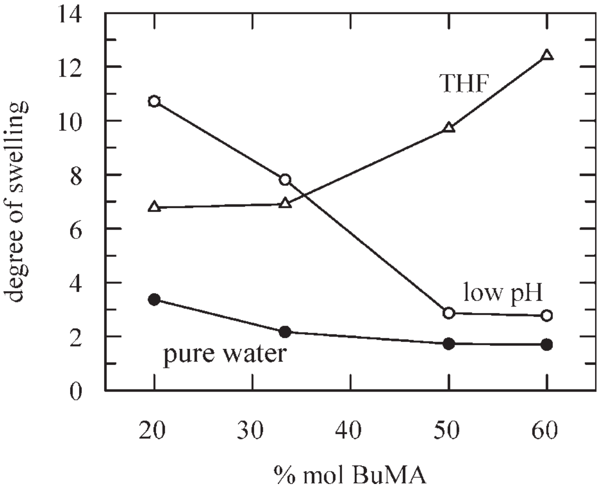


Figure 6. Effect of solvency and terpolymer ($DMAEMA_5$-*b*-$BuMA_{n/2}$-*b*-$HEGMA_{10}$-*b*-$BuMA_{n/2}$-*b*-$DMAEMA_5$) composition on the DSs of the networks.

In particular, the Figure depicts the DSs exhibited by the equimolar model networks based on the ABCBA pentablock terpolymer and the statistical terpolymer, as well as the randomly crosslinked statistical terpolymer network in acidified water, in pure water, and in THF. The Figure suggests that the DSs of all three networks increased from pure water to THF and to acidified water. These observations can be explained by the same arguments given in the preceding paragraph for the "BuMA-poor" terpolymer networks. The Figure also shows that the randomly crosslinked network of the statistical terpolymer presented the highest DS in all the solvents, probably due to the broad MWD of the chains between the crosslinks.

The model network based on the statistical terpolymer exhibited intermediate DSs, whereas the network based on the ABCBA pentablock terpolymer exhibited the lowest DSs. The higher acidic DS of the statistical terpolymer model network than that of its pentablock counterpart can be attributed to the dispersion of the hydrophobic BuMA units over the whole lengths of the terpolymer chains between crosslinks in the former network, which minimizes the driving force for structural organization.

It is noteworthy that the present BuMA-based equimolar pentablock terpolymer network exhibited a lower DS in water (~ 2) compared with its MMA-based counterpart (~ 4) reported earlier by our Group,[18] probably reflecting the higher hydrophobicity of the BuMA units compared with the MMA units.

Effective pKs of the DMAEMA units in the Networks

The p*K*s of the DMAEMA units in the networks were determined from the degree of ionization curves as the pH at 50% ionization and are also listed in Table 1. The p*K*s of the networks ranged from 4.1 to 4.8. These values were lower than those obtained for the MMA networks. As discussed earlier, this could be due to the increased hydrophobicity of the present networks, effecting a decrease in the dielectric constant within the networks, leading to stronger Coulombic interactions, making the ionization of the DMAEMA repeating units more difficult,[25] and requiring lower pH values to obtain the desired degrees of ionization.

Network Structuring in Water

All the terpolymer networks of this study were probed for structure-formation in D_2O using SANS. All networks were in their uncharged state as no acid was present in the system. The scattering profiles are displayed in Figure 8. Figure 8(a) illustrates the results for the networks with different compositions, while Figure 8(b) presents the curves for the networks with different architectures.

In Figure 8(a), the scattering curves for the two more hydrophobic networks, based on the pentablock chains D_5-*b*-Bu_{10}-*b*-H_{10}-*b*-Bu_{10}-*b*-D_5 and D_5-*b*-Bu_{15}-*b*-H_{10}-*b*-Bu_{15}-*b*-D_5, stand out as they present clear correlation peaks. This indi-

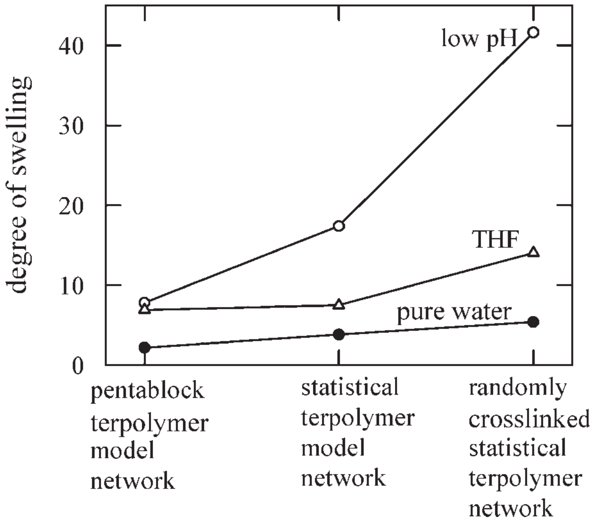


Figure 7. Effect of polymer architecture on the DSs of the terpolymer networks in three different solvents.

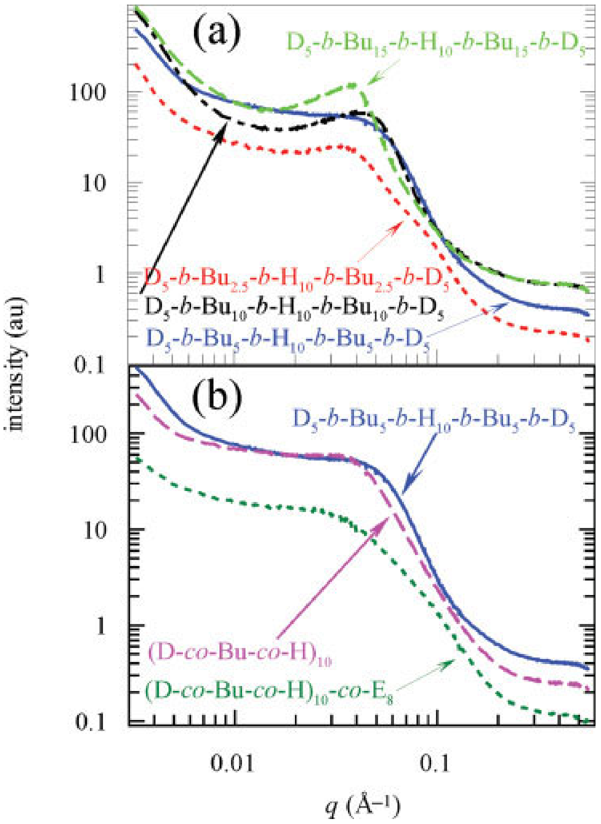


Figure 8. SANS profiles of all uncharged terpolymer networks equilibrated in deuterium oxide. (a) Networks with different composition. (b) Networks with different architecture.

cates the presence of relatively large scattering centers resulting from the intra- and interchain organization of the BuMA hydrophobic blocks. From the two networks, the more hydrophobic one displayed a more pronounced peak, probably due to the formation of larger organized domains. The position of the peak in the scattering profile of the more hydrophobic network was shifted to lower q-values, relative to that of the other network, corresponding to a greater distance between the correlated scattering centers due to the longer chains between crosslinks in the former case. These SANS curves presented no higher order peaks. This is consistent with neutron-scattering studies on amphiphilic two-[16(d)] and three-[18] component networks in D_2O recently reported by our Group. This absence of higher harmonics suggests polydisperse scattering centers of short-range liquid-like order.[26]

On the other hand, the other two, less hydrophobic networks, presented qualitatively different scattering profiles, exhibiting no clear peaks. In particular, the pentablock terpolymer network comprising D_5-*b*-$Bu_{2.5}$-*b*-H_{10}-*b*-$Bu_{2.5}$-*b*-D_5 chains displayed a slight peak, whereas the D_5-*b*-Bu_5-*b*-H_{10}-*b*-Bu_5-*b*-D_5-based one had only a shoulder, probably arising from scattering by the EGDMA crosslinker nodes. The lack of clear peaks in the SANS curves of these samples could be attributed to the small lengths of the hydrophobic blocks and their placement alternatingly between the DMAEMA and HEGMA hydrophilic blocks. Both of these factors made it more difficult for the hydrophobic units to organize into large enough microphases and resulted in the absence of clear correlation peaks.

Figure 8(b) displays the scattering profiles from the three equimolar terpolymer networks of different architecture: the ABCBA pentablock model network, the statistical model network and the randomly crosslinked network of the statistical terpolymer. Due to their relatively low hydrophobic content, these networks did not present any clear correlation peak. The pentablock and the statistical model networks presented almost identical scattering curves. The curve of the randomly crosslinked network was shifted to lower intensities relative to the other two due to the higher aqueous DSs presented by this sample.

CONCLUSIONS

Model networks based on amphiphilic ABCBA pentablock terpolymers with various lengths of the hydrophobic BuMA B-blocks were prepared using GTP and sequential monomer and crosslinker additions. The aqueous DSs of these terpolymer networks decreased with the BuMA hydrophobic content, with the DSs of ionized networks (low pH) being higher than those of uncharged networks. In contrast, the DSs in THF (uncharged networks) increased with the BuMA content as the MWs of the chains between the crosslinks were higher for the BuMA-rich networks. SANS indicated a pronounced structural organization of the BuMA-rich terpolymer networks in deuterium oxide suggesting microphase separation of these materials in the selective aqueous medium.

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