Synthesis, Characterization, and Modeling of Double-Hydrophobic Model Networks Based on Cross-Linked Star Copolymers of *n*-Butyl Methacrylate and Methyl Methacrylate

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ABSTRACT: Seven model networks of a new structure, that of cross-linked "in−out" star polymers, were synthesized by the group transfer polymerization of the hydrophobic monomers methyl methacrylate (MMA) and *n*-butyl methacrylate (BuMA) and the cross-linker ethylene glycol dimethacrylate in a one-pot preparation. From the seven networks, two were the homopolymer networks of MMA and BuMA, while the remaining five were based on equimolar MMA−BuMA copolymer stars of different architectures: heteroarm (two), star block (two), and statistical. The synthesis of the networks involved at least four steps, starting from the synthesis of the linear polymers, proceeding to the preparation of the "arm-first" and "in−out" star polymers, and being completed with the cross-linking of the stars into a network. All the precursors to the networks were characterized in terms of their molecular weights using gel permeation chromatography. The sol fraction extracted from the networks was found to be equal to or lower than 20%. The degrees of swelling (DSs) in *n*-hexane/tetrahydrofuran (THF) mixtures of all networks increased with the solvent content in THF, a nonselective solvent, and this trend was confirmed by thermodynamic calculations. The DS in a 50−50 *n*-hexane−THF mixture of the statistical network was found to be the same as those of the segmented networks, suggesting absence of microphase separation in the latter type of networks, a trend confirmed by thermodynamic predictions.

Introduction

Polymer networks represent a technologically important class of polymeric materials with main uses as coatings and structural materials.[1] Although structure control in networks is not essential for the above-mentioned commodity uses, this is required in fundamental studies and also in the search for hi-tech applications of polymer networks,[2] such as drug release systems,[3] scaffolds for tissue engineering,[4] supports for enzymes,[5] templates for the synthesis of mesoporous silica,[6] hosts for the growth of CdS semiconducting nanocrystals,[7] soft contact lenses,[8] pervaporation membranes,[9] extractants of organic solvents from water,[10] and temperature-activated actuators.[10]

Polymer networks with perfect structure are called model polymer networks and consist of polymer chains between cross-links (elastic chains, those connecting two cores) of precise length and, strictly speaking, have a defined number of arms emanating from each cross-link.[11] The synthesis of model networks necessitates the use of "living" polymerization techniques[12] to ensure the size homogeneity of the elastic chains along with the use of cross-linkers of precise functionality to maintain the number of arms constant.

A new type of polymer model networks is that of cross-linked star[13] polymer model networks (CSPMNs)[14−17] developed recently by our research team, using group transfer polymerization (GTP).[18−22] The characteristic feature of CSPMNs is the presence of a large number of dangling chains in addition to the elastic chains. These networks are prepared by the sequential addition of monomer−cross-linker−monomer−cross-linker under GTP conditions. The dangling chains (primary arms) are formed upon the first addition of monomer, whereas the elastic chains (secondary arms) are formed upon the second addition of monomer. The two additions of cross-linker give rise to the formation of two different types of cores, the primary cores and the secondary cores, formed upon the first and second additions of cross-linker, respectively. Primary cores are only connected to secondary cores, and secondary cores are only connected to primary cores. The secondary cores bear only elastic chains, while the primary cores bear an equal number of dangling and elastic chains.

In our first publication on CSPMNs which were based on star homopolymers, we established that gelation can be achieved when the secondary arms are either longer or shorter than the primary arms.[14] Next, we managed to synthesize amphiphilic CSPMNs based on stars of different architectures whose degrees of swelling (DSs) in the ionized state depended on the star architecture because of their different segregation behavior.[15] In the following study, double-hydrophilic CSPMNs were prepared which presented DSs in the ionized and neutral state that depended on both composition and star architecture.[16] All the above networks were nonhydrolyzable due to the chemical stability of the cross-linker used. In our most recent investigation, we explored the reversibility of CSPMNs containing hydrolyzable cross-linkers in the primary or the secondary cores.[17]

The nonhydrolyzable CSPMNs studied previously contained one hydrophilic ionizable monomer, whose DS characterization was performed in water as a function of pH.[14−16] The ionic interactions among the charged polymer chains and the hydrogen bonding of the polymer network with water produce a complicated system. To have a simpler CSPMN system whose physicochemical behavior can be more easily interpreted, in this investigation we aimed at the synthesis of CSPMNs of various star architectures based on two different nonpolar monomers and the study of their swelling behavior in mixtures of two organic solvents. To the best of our knowledge, this is the first report on the characterization of double-hydrophobic model networks in mixtures of organic solvents and the first report on

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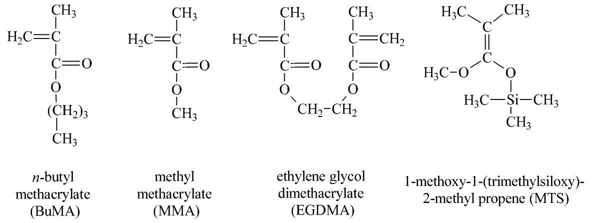

Figure 1. Chemical structures and names of the main reagents used for the network synthesis.

the synthesis and characterization of double-hydrophobic CSPMNs.

Experimental Section

Network Synthesis. *Materials.* The monomers, *n*-butyl methacrylate (BuMA, nonpolar hydrophobic) and methyl methacrylate (MMA, more polar hydrophobic), the cross-linker, ethylene glycol dimethacrylate (EGDMA), the initiator, 1-methoxy-1-(trimethylsiloxy)-2-methylpropene (MTS), tetrabutylammonium hydroxide, benzoic acid, calcium hydride (CaH_2), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, free radical inhibitor), basic alumina, and potassium metal were all purchased from Aldrich, Germany. Figure 1 shows the chemical structures and names of the monomers, the cross-linker, and the initiator. Sodium metal was purchased from Fluka, Germany. Tetrahydrofuran (THF) was purchased from Labscan, Ireland, and was used both as the polymerization solvent (reagent grade) and as the mobile phase in chromatography (HPLC grade).

Methods. The methods used in this investigation were the same as those employed for typical GTP syntheses. The polymerization solvent, THF, was dried by refluxing it over a potassium/sodium alloy for 3 days prior to use. The monomers and the cross-linker were passed 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 stored in a refrigerator at 5 °C. All monomers and the cross-linker were freshly distilled under vacuum and kept under a dry nitrogen atmosphere until use. The initiator was distilled once prior to the polymerization. Dried powder of the tetrabutylammonium bibenzoate (TBABB) catalyst, which was in-house synthesized by the method of Dicker et al.,[20] was stored in a round-bottom flask under vacuum until use. All glassware was dried overnight at 120 °C and assembled hot under dynamic vacuum prior to use. The polymerizations were carried out in 100 mL round-bottom flasks, fitted with a rubber septum. Catalytic amounts (5−10 mg) of the TBABB catalyst were transferred to the reactor, which was immediately purged with dry nitrogen. Freshly distilled THF was subsequently transferred directly from the still into the reactor via a syringe, followed by the addition of the initiator, monomers, and cross-linker.

Polymerizations. The synthetic procedure followed was similar to that reported previously for the preparation of CSPMNs.[14−17] The reactions were carried out in 100 mL round-bottom flasks immersed in a water bath initially at 20 °C. The water bath would dissipate enough heat of polymerization to avert the boiling of THF, without lowering too much the rate of the polymerization (which happened when an ice bath was used initially). The polymerization exotherm was monitored by a digital thermometer in order to follow the progress of the reaction. The addition sequences employed for the synthesis of all cross-linked star structures are illustrated in Figure 2. Cross-linked heteroarm stars were prepared when only one type of monomer was added between cross-links, and the monomer added second was different from that used first (networks 3 and 4). If the monomer added second were the same as that added first, a homopolymer cross-linked star would be produced (networks 1 and 2). The simultaneous addition of the two different monomers before each addition of the EGDMA cross-linker resulted in the preparation of arms of statistical architecture, and it ultimately led to the formation of cross-linked statistical copolymer stars (network 6). The preparation of cross-linked block copolymer stars required the sequential addition of two different monomers before the EGDMA additions (networks 5 and 7).

The polymerization procedure for the synthesis of such a cross-linked block copolymer star with arms comprising linear diblock copolymers with 25 MMA units and 25 BuMA units is detailed below. Freshly distilled THF (50 mL) and 0.25 mL of MTS initiator (1.23 mmol) were syringed to a 100 mL round-bottom flask containing a small amount (∼10 mg) of TBABB. 3.3 mL of MMA (3.08 g, 30.8 mmol) was slowly added under stirring. The polymerization exotherm (20.8−26.1 °C) abated within 5 min, a sample for GPC was extracted, and 5.0 mL of BuMA (4.44 g, 30.8 mmol) was added slowly, giving an exotherm (21.5−23.9 °C). After sampling, 0.93 mL of EGDMA (0.98 g, 4.92 mmol) was added which produced an exotherm (22.3−24.9 °C). A sample was withdrawn again before 5.0 mL of BuMA (4.44 g, 30.8 mmol) was added, giving an exotherm from 22.2 to 25.1 °C. A sample was withdrawn once more, followed by the addition of 3.3 mL of MMA (3.08 g, 30.8 mmol) with an exotherm from 23.8 to 29.8 °C. In the final stage, 0.96 mL of EGDMA (0.98 g, 4.92 mmol) was added which promoted gelation within seconds.

Characterization of the Network Precursors. *Gel Permeation Chromatography.* Molecular weights (MWs) and molecular weight distributions (MWDs) of the linear, "arm-first" star, and "in−out" star precursors to the cross-linked star polymers were determined by gel permeation chromatography (GPC) using a single high MW range Polymer Laboratories PL-Mixed "D" column. The mobile phase was THF, delivered at a flow rate of 1 mL min^{-1} using a Polymer Laboratories PL-LC1120 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 seven narrow MW (630, 4250, 13 000, 28 900, 50 000, 128 000, and 260 000 g mol^{-1}) linear polyMMA standards which provided rough qualitative estimates for the MWs of the star polymers.

Static Light Scattering. Absolute weight-average MWs (M_ws) of the star polymers were measured using static light scattering (SLS) in a GPC configuration. Thus, the scattering intensity and the refractive index of the polymer samples were monitored simultaneously. A Brookhaven molecular weight analyzer, BI-MwA, equipped with a 30 mW red diode laser emitting at 673 nm and a multiangle detector determining the intensity of scattered light at seven different angles, 35°, 50°, 75°, 90°, 105°, 130°, and 145°, was used. A Polymer Laboratories PL-LC1120 isocratic pump was used to deliver the THF mobile phase at a flow rate of 1 mL min^{-1}. The refractive index signal was measured using a PL-RI 800 refractive index detector while a PL-Mixed "D" column was used, both supplied by Polymer Laboratories. The analysis for the calculation of the absolute M_ws was conducted using the PSS-WinGPC 7 SLS-flow software. Polymer samples were dissolved in HPLC-grade THF at 2% w/v polymer concentrations and were filtered through 0.45 μm pore size syringe filters. The refractive index increments (dn/dc) of the polymer solutions in THF were determined using an ABBE refractometer.

Characterization of the Networks. *Determination and Characterization of the Sol Fraction.* The prepared networks were taken out of the polymerization flasks and washed by placing them in 200 mL of THF for 1 week to extract the sol fraction. Next, the THF solution was recovered by filtration. The extraction procedure was repeated once more, and the solvent from the combined extracts was evaporated using a rotary evaporator. The recovered polymer was further dried under vacuum for 24 h at room temperature. The sol fraction was calculated as the ratio of the mass of the dried extracted polymer to the theoretical mass of the polymer in the network. The dried extractables were subsequently characterized in the terms of their MW and composition by GPC and proton nuclear magnetic resonance (^1H NMR) spectroscopy, respectively. A 300 MHz Avance Bruker NMR spectrometer equipped with an Ultrashield magnet was used for recording the spectra. The NMR solvent was $CDCl_3$ containing traces of tetramethylsilane (TMS), which was used as an internal reference.

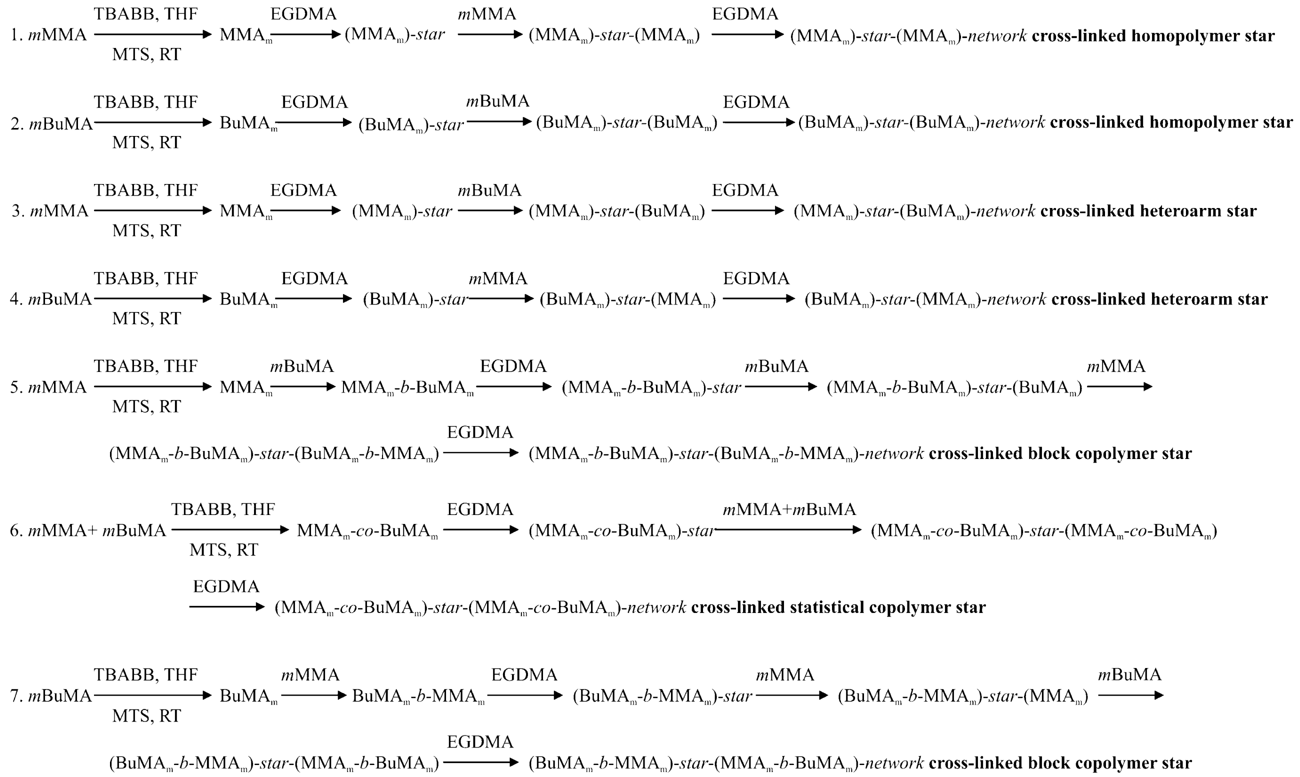

Figure 2. Synthetic addition sequences employed for the preparation of the various cross-linked star architectures of this study.

Characterization of the Degree of Swelling. The washed networks were cut into small cubes with edge dimensions 5−10 mm. The mass of the THF swollen cubes was measured gravimetrically before placing all samples in a vacuum oven for drying for 72 h at room temperature. The dry network mass was determined, followed by the transfer of the networks in an organic solvent (THF or *n*-hexane or mixture of the two) or in water. The samples were allowed to equilibrate for 1 week, and the wet network masses were measured. The DSs were calculated as the ratio of the wet network mass divided by the dry network mass. All DSs were determined in triplicate, and the averages of the measurements are presented along with their 95% confidence intervals.

Thermodynamic Modeling of Network Swelling Behavior

The DSs of the model networks were predicted theoretically using a molecular thermodynamic model developed by our group.[23,24] This model considered the two Gibbs free energy components in the system. These were the elastic free energy and the free energy of mixing. When microphase separation was considered, a third component was also included, namely the interfacial free energy. The mixing free energy was composed of the two enthalpic terms describing the interaction of each hydrophobic block with the solvent via the appropriate Flory−Huggins χ parameters, and the entropic term describing the translational entropy of the solvent molecules, but ignoring the translational entropy of the polymer network, following the approach of Flory.[25] The total Gibbs free energy was minimized with respect to the polymer volume fraction with the aid of a numerical code written in GWBASIC. The DS at equilibrium was calculated as the inverse of the polymer volume fraction at the free energy minimum.

The following constant inputs were required for the code: first, the polymer volume fraction upon cross-linking, which was taken equal to 0.25 in all cases, consistent with the network synthesis procedure; second, the number of arms per cross-link, which was determined for each network by characterizing its star precursors using SLS; and, finally, the number of backbone carbon atoms in each block, taken as twice the corresponding degree of polymerization.

Table 1. Solubility Parameters, δ, of the MMA and BuMA Units and the Solvents Water, THF, and *n*-Hexane[27]

polymer	solubililty parameter δ_p (cal/cm^3)$^{1/2}$	solvent	solubililty parameter δ_s (cal/cm^3)$^{1/2}$
MMA	9.5	H_2O	23.4
BuMA	8.8	THF	9.1
		n-hexane	7.3

The Flory−Huggins interaction parameters χ between the solvent and each of the blocks, χ_{MMA} and χ_{BuMA}, were also required and were calculated using the following equation:[26]

$$\chi = 0.34 + \frac{V_s}{RT}(\delta_p - \delta_s)^2 \qquad (1)$$

where V_s is the molar volume of the solvent, and δ_p and δ_s are the solubility parameters of the polymer and the solvent, respectively. The solubility parameters of THF, *n*-hexane, the MMA, and the BuMA monomer units are listed in Table 1.[27] To calculate the DSs of the networks in different solvent compositions, the value of δ_s was varied between those of *n*-hexane and THF, which resulted, through eq 1, in the calculation of the corresponding values of χ_{MMA} and χ_{BuMA}.

Results and Discussion

Synthesis and Structure of Cross-Linked Star Polymers. This is the first time that double-hydrophobic model networks are synthesized with the CSPMN novel architecture, bearing a large number of dangling chains. Hild and Lamps have previously reported the synthesis of simple double-hydrophobic model networks based on glycidyl methacrylate (GlyMA) and MMA[28] and GlyMA and styrene.[29] Networks of less controlled structures, based on monodisperse polyisobutylene (PIB) macro-cross-linkers and a second component of a higher polydispersity,

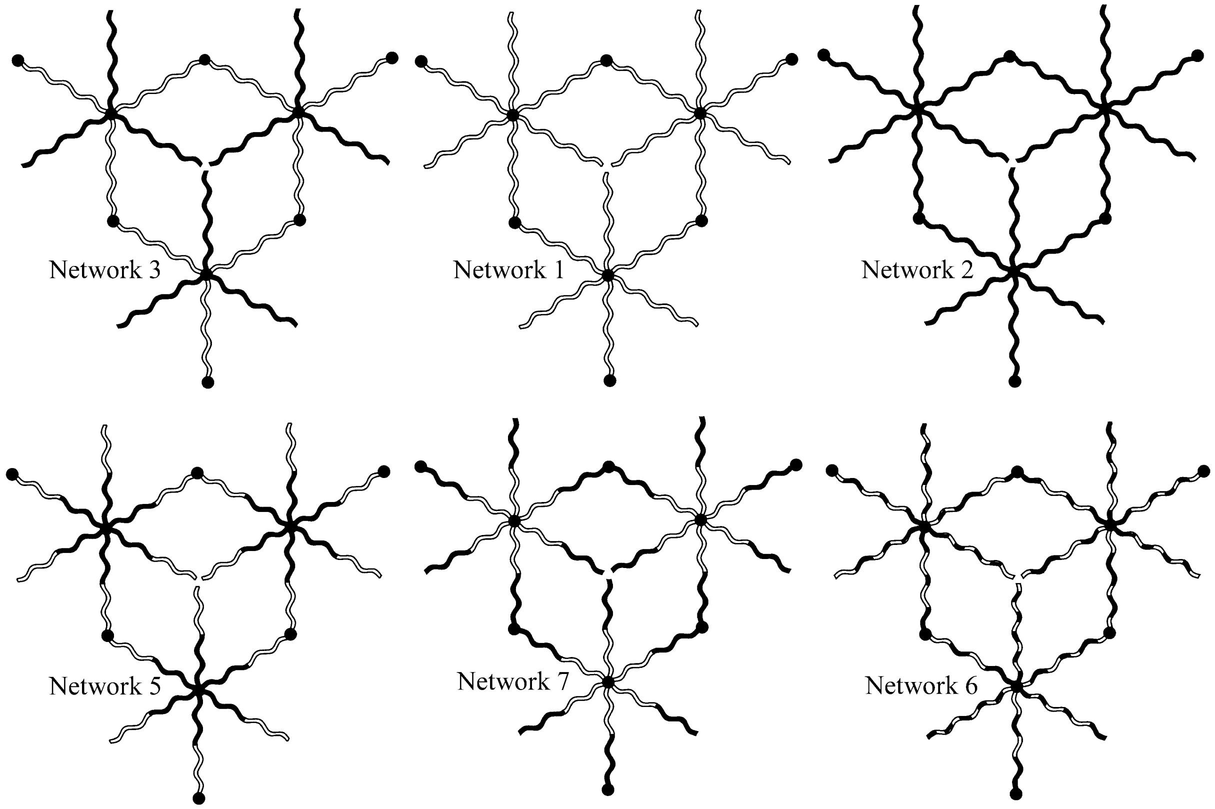

Figure 3. Schematic representation of the architectures of the model networks of this study. The MMA units are depicted in white, while the BuMA units are colored black.

poly(dimethylsiloxane) (PDMS),[30−32] polyMMA,[33,34] or poly(ethyl acrylate),[35] have also been reported. Similar networks based on a well-defined polybutadiene component and a higher polydispersity polystyrene component have been reported by Li and Ruckenstein.[36] Finally, Shiomi and co-workers[37,38] reported the synthesis of networks based on well-defined polyTHF or PDMS combined with higher polydispersity polyMMA or polystyrene.

The addition sequences for the preparation of the networks in this study are summarized in Figure 2. The GTP synthesis comprised a successful multistep (4- or 6-step) sequential addition in a one-pot preparation. The linear "living" (co)polymers that were produced upon the addition of methacrylate monomer(s) to a solution containing monofunctional initiator and catalyst were converted to "arm-first" star polymers with "living" cores upon the addition of a dimethacrylate cross-linker. These "arm-first" star polymers were further grown from the core outward upon the addition of more monomer(s) to yield "in−out" star polymers. Finally, the addition of the dimethacrylate cross-linker effected the interconnection of these stars to a network.

Figure 3 shows all network structures based on cross-linked stars synthesized in this study. These are isomeric structures with equimolar MMA−BuMA compositions and overall theoretical degrees of polymerization of the primary and secondary arms constant and equal to 50. The MMA units are illustrated in white and the BuMA units in black. The two network structures on the top right, network 1 and network 2, are the two homopolymer networks. Network 3 is a cross-linked heteroarm star copolymer whose primary and secondary arms are different types of homopolymers. Network 4 has the reverse structure, but it is not drawn in this figure. Network 5 and network 7 are cross-linked star-block copolymers whose arms are diblock copolymers. The last network structure, network 6, is based on cross-linked statistical copolymer stars.

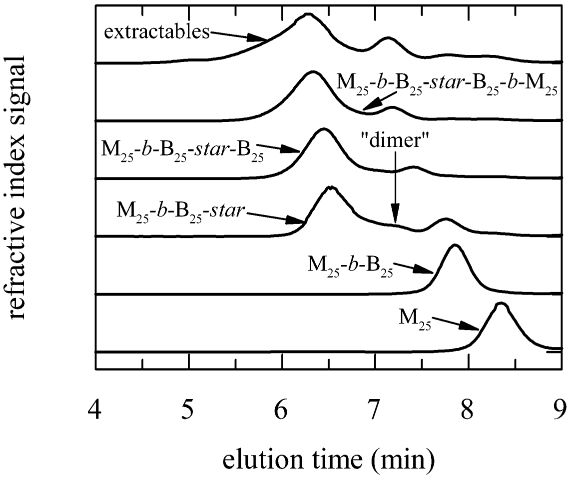

Figure 4. Gel permeation chromatograms of the five precursors to network 5, [(MMA_{25}-*b*-$BuMA_{25}$)-*star*-($BuMA_{25}$-*b*-MMA_{25})]-*network*. In the curve labeling, M and B are (further) abbreviations for the MMA and BuMA units, respectively, while the polymer nomenclature follows that introduced in Figure 2.

It is important to point out that the number of arms at the cross-links is not 3 or 6, as indicated in Figure 3, but it may range between 4 and 80, as it was concluded from the SLS experiments discussed below.

Molecular Weights. Figure 4 shows the GPC chromatograms of the five precursors to network 5, the block copolymer star network [(MMA_{25}-*b*-$BuMA_{25}$)-*star*-($BuMA_{25}$-*b*-MMA_{25})]-*network*. The MWDs of the linear MMA homopolymer (M_{25}) and the linear MMA−BuMA diblock copolymer (M_{25}-*b*-B_{25}) were narrow and unimodal, as expected. The MWD of the main peak of the "arm-first" star (M_{25}-*b*-B_{25}-*star*) was also narrow, but the whole distribution was trimodal, containing two other small peaks: one that corresponded to unattached arms (same elution

Table 2. GPC Characterization of All the Precursors and SLS Characterization of the “Arm-First” and the “In−Out” Star Polymer Precursors to the Cross-Linked Star Polymer Networks

			GPC results			SLS results	
network no.	theoretical structure[a]	theor MW	M_n	M_w/M_n	M_p	M_w	no. of arms
1	M_{50}	5110	7220	1.11	7840	−	−
	M_{50}-*star*		120000	1.17	140000	174000	21.7
	M_{50}-*star*-M_{50}		238000	1.28	228000	633000	79.0
2	B_{50}	7310	9370	1.12	9810	−	−
	B_{50}-*star*	*	35600	2.45	126000	37800	3.6
	B_{50}-*star*-B_{50}	*	89200	1.86	181000	91800	8.7
3	M_{50}	5110	8000	1.11	8600	−	−
	M_{50}-*star*	*	83600	1.28	111000	152000	17.1
	M_{50}-*star*-B_{50}	*	171000	1.18	181000	268000	25.1
4	B_{50}	7310	9500	1.11	9810	−	−
	B_{50}-*star*	*	41800	2.64	140000	81700	7.7
	B_{50}-*star*-M_{50}	*	97900	1.67	164000	304000	34.2
5	M_{25}	2600	3210	1.13	3440	−	−
	M_{25}-*b*-B_{25}	6210	8430	1.13	9190	−	−
	M_{25}-*b*-B_{25}-*star*	*	89000	1.31	126000	88000	9.2
	M_{25}-*b*-B_{25}-*star*-B_{25}	*	75700	1.83	144000	−	−
	M_{25}-*b*-B_{25}-*star*-B_{25}-*b*-M_{25}	*	110000	1.73	181000	339000	35.6
6	M_{25}-*co*-B_{25}	6210	8620	1.13	9190	−	−
	M_{25}-*co*-B_{25}-*star*	*	103000	1.25	131000	118000	12.1
	M_{25}-*co*-B_{25}-*star*-M_{25}-*co*-B_{25}	*	95100	1.64	149000	294000	30.2
7	B_{25}	3600	3390	1.12	3550	−	−
	B_{25}-*b*-M_{25}	6210	8850	1.12	9190	−	−
	B_{25}-*b*-M_{25}-*star*	*	88800	1.23	107000	153000	15.4
	B_{25}-*b*-M_{25}-*star*-M_{25}	*	146000	1.17	159000	−	−
	B_{25}-*b*-M_{25}-*star*-M_{25}-*b*-B_{25}	*	189000	1.17	194000	384000	38.7

[a] M and B are (further) abbreviations for MMA and BuMA, respectively.

time as M_{25}-*b*-B_{25}) and a smaller shoulder that appeared at earlier elution times than that of the unattached arms, probably formed by the coupling reaction between two “living” linear chains (arms) with one EGDMA molecule and is indicated as “dimer” in Figure 4. The unattached arms were probably composed of “living” and “nonliving” chains. The “nonliving” unattached chains originated from accidental deactivation during synthesis (due to termination and chain transfer reactions), and they could not grow upon further addition of monomer. The “living” unattached chains did not react with EGDMA (due to steric hindrances and high solution viscosity) but could grow upon addition of more monomer. The chromatograms of the “in−out” stars (M_{25}-*b*-B_{25}-*star*-B_{25} and M_{25}-*b*-B_{25}-*star*-B_{25}-*b*-M_{25}) were also multimodal for the same reasons as above but with a narrow MWD of the main peaks of the star polymers. The MWs of the main peaks of the five chromatograms increased from the initial M_{25} homopolymer to the final “in−out” star polymer, M_{25}-*b*-B_{25}-*star*-B_{25}-*b*-M_{25}, as expected, indicating the growth of the structure as a whole. Similar results were obtained for the precursors to all the networks synthesized in this study.

Table 2 shows all the precursors to all cross-linked star polymers prepared in this study and their GPC and SLS characterization data. These include the apparent number-average MWs (M_ns), the polydispersity indices (M_w/M_n), the peak MWs (M_ps) obtained from GPC, and the absolute M_ws and number of arms for the star precursors determined using SLS. The nomenclature used in Table 2 is that introduced in Figure 2. The M_w/M_ns of all linear polymers were low (≤ 1.13), but their M_ns were slightly higher than the theoretical due to partial initiator deactivation. For the “arm-first” star polymers the M_w/M_ns shown were also relatively low (≤ 1.31) with two exceptions: networks 2 and 4, where there was extensive overlap between the peaks of the star and the “dimer” for network 2 and the star, the “dimer”, and the unattached arms for network 4, and the calculated M_w/M_ns included both (network 2) or all three (network 4) peaks. Broad and bimodal MWDs were obtained for the “in−out” star polymers of four (networks 2, 4, 5, and 6) out of the seven networks due to peak overlaps, while the “in−out” star polymers of the remaining three networks exhibited relatively low (≤ 1.28) M_w/M_ns. The M_ns of the “in−out” star polymers were higher than those of the respective “arm-first” stars, as expected, with two exceptions: the star polymers of networks 5 and 6, where there was extensive peak overlap. The corresponding M_ps are also provided for all cases. After each reagent addition, the M_ps grew without exception because they were not affected by peak overlap.

Because the M_ns determined by GPC for the star polymers were only apparent values, their absolute M_ws were measured using SLS and are also shown in Table 2. The SLS M_ws were higher than the GPC MWs due to the compact nature of the star structure compared to the linear polyMMA MW calibration standards.[39,40] The number of arms of the star polymers was calculated by dividing the SLS absolute M_w of the star polymers by the GPC M_w of their arms and is listed in Table 2.

The GPC M_w and the calculated number of arms were absolute only for networks 1 and 3, bearing polyMMA (same type of polymer as the GPC MW calibration standards) primary arms. The number of arms depended on star composition and ranged between 4−22 and 9−79 for the “arm-first” and “in-out” star polymers, respectively. In general, higher number of arms were obtained when MMA was polymerized (both before or after EGDMA) compared to BuMA, possibly reflecting weaker steric hindrances in the case of MMA than the bulkier BuMA. Thus, the cross-link points of the various networks did not bear the same number of arms. Although the number of arms of the “in−out” star polymer precursor to network 2 was approximately twice as high as that of the corresponding “arm-first” star precursor, as expected, this was not true for the rest of the networks. In particular, with the exception of network 3, in all other networks, and most notably in networks 1, 4, and 5, the “in−out” star polymer bore up to 4 times the number of arms of its corresponding “arm-first” star, possibly indicating star−star coupling during star growth.

Mass Percentage, MW, and Composition of the Sol Fraction of the Networks. Table 3 shows the mass percentage,

Table 3. Mass Percentage, Molecular Weights, and Compositions of the Extractables from the Cross-Linked Star Networks As Measured by Gravimetry, GPC, and ^{1}H NMR

			GPC results			^{1}H NMR
network no.	theoretical chemical stucture[a]	w/w % extractables	M_n	M_w/M_n	M_p	% mol MMA
1	(M_{50}-*star*-M_{50})-*network*	11.0	357000	2.10	252000	100
2	(B_{50}-*star*-B_{50})-*network*	3.5	41200	1.05	41500	0
3	(M_{50}-*star*-B_{50})-*network*	5.8	6100	1.19	7550	76
4	(B_{50}-*star*-M_{50})-*network*	15.2	237000	1.34	221000	49
5	[(M_{25}-*b*-B_{25})-*star*-(B_{25}-*b*-M_{25})]-*network*	20.4	220000	1.37	207000	54
6	[(M_{25}-*co*-B_{25})-*star*-(M_{25}-*co*-B_{25})]-*network*	5.1	8930	1.12	10500	54
7	[(B_{25}-*b*-M_{25})-*star*-(M_{25}-*b*-B_{25})]-*network*	5.3	7960	1.45	9500	44

[a] M and B are (further) abbreviations for MMA and BuMA, respectively.

the M_n, the M_w/M_n, and the M_p of the largest peak and the composition of the extractables from each network as measured by gravimetry, GPC, and ^{1}H NMR. With the exceptions of ($BuMA_{50}$-*star*-MMA_{50})-*network* and [(MMA_{25}-*b*-$BuMA_{25}$)-*star*-($BuMA_{25}$-*b*-MMA_{25})]-*network* which had 15.2% and 20.4% w/w extractables, respectively, all the other networks exhibited relatively low sol fractions ($\leq$11%). The low values of these sol fractions support previous findings[14−16] where a 4-fold molar excess of EGDMA cross-linker with respect to the initiator has been determined as the optimal ratio for sufficiently high conversion to star polymer during "arm-first" star polymer synthesis. Similar results were also obtained from studies on "arm-first" star polymer synthesis using "living" anionic[41] and "living"cationic[40] polymerization, in which high star polymer yields (>85%) were obtained. These low amounts of extractables also indicate satisfactory control over the network structure during synthesis.

In addition to their mass percentage, the relative M_ps of the highest peak in the GPC chromatogram and the composition of the extractables are also shown in this table. From these results, the synthetic step where the highest deactivation occurred could be identified. For networks 1, 4, and 5, the highest deactivation occurred after the formation of the "in−out" star polymer because the M_ps of the extractables were high and corresponded to an "in−out" star polymer (comparison with Table 2). For networks 3, 6, and 7, linear chains seemed to be the main contents of the extractables because the M_ps were low and corresponded to those of the linear precursors. For network 2, the extractables consisted mainly of the dimer and the "in−out" star. It is noteworthy that networks 1, 4, and 5, whose extractables were of the highest MWs, also contained the highest percentage of extractables. The common feature of these three networks is that the final cross-linking step was performed by the addition of EGDMA off PMMA "living" chain ends. A possible explanation why this would reduce the cross-linking efficiency (as evidenced by high sol fractions and high sol MWs) might be a higher cross-reactivity of EGDMA from MMA than from BuMA, leading to a faster gelation process from MMA which would not allow for all the polymer chains to properly react and interconnect in the network. In the case of adding EGDMA to BuMA units, the cross-linking reaction would be slower, allowing more polymer chains to be incorporated in the network and resulting in a lower sol fraction.

Degrees of Swelling of the Networks. Figure 5 shows the DSs of the cross-linked stars in THF/*n*-hexane mixtures as a function of the THF content in the solvent mixture. As the THF content increased, the DSs of all the networks increased. This is because both monomer repeat units, MMA and BuMA, are more compatible with THF than with *n*-hexane, as evidenced by the solubility parameters listed in Table 1. THF is a good solvent for both MMA and BuMA units, having a solubility parameter intermediate between and close to those of these units. On the other hand, *n*-hexane is a nonsolvent for these two units, with a solubility parameter much lower than those of the MMA and BuMA units. The DSs of the cross-linked star homopolymer networks depended on solvent composition in a nonlinear fashion. The DSs of the (MMA_{50}-*star*-MMA_{50})-*network* started to increase only when the solvent was composed of more that 50% THF. This was in marked contrast to the behavior of the ($BuMA_{50}$-*star*-$BuMA_{50}$)-*network* whose DSs increased substantially even when the solvent content in THF was increased from 0 to 10%. The DS vs THF solvent content curve of the cross-linked statistical copolymer star was also nonlinear and sigmoidal, while the curves of the other four cross-linked segmented (heteroarm or block) star copolymers were almost linear, indicating that the segmented structure smoothes out the swelling behavior.

Constructed from the data in Figure 5, Figure 6 shows the DSs of all the networks in THF/*n*-hexane mixtures with 100%, 50%, and 0% THF content as well as the DSs in water. The DSs of all networks in water were very low, with values between 1.5 and 2.2, because both monomers are hydrophobic and water-incompatible. The fact that these DSs in water were not even lower, i.e., equal to 1.0,[23,24] can be attributed to a combination of the porous and rather glassy nature of these materials, which tend to retain some water. The DSs in water of other hydrophobic polymethacrylate networks have also been found to range between 1.5 and 2.0.[15,42,43]

The DSs in 100% THF ranged from 6.4 to 9.7 while the DSs in 100% *n*-hexane ranged from 1.3 to 2.0. As mentioned before, all networks were compatible with THF but not with *n*-hexane, and therefore, all networks swelled more in THF than in *n*-hexane. Moreover, the DS of each network in the 50−50 *n*-hexane−THF mixture was intermediate between those in the two pure solvents. It is noteworthy that the all the copolymer networks and the polyBuMA network swelled in this solvent mixture, whereas the polyMMA network collapsed. Furthermore, in the solvent mixture, the polyBuMA network presented the highest swelling, while all the copolymer networks had the same DS, independent of their architecture, and intermediate between those of the two homopolymers.

All the above experimental observations can be explained by the Flory−Huggins interaction parameters of polyBuMA, polyMMA, and the 50−50 copolymer of BuMA−MMA in the four different solvents, *n*-hexane, THF, 50−50 *n*-hexane−THF, and water, shown in Table 4. These interaction parameters were calculated using the solubility parameters of Table 1[27] along with the equation[26] given in the Experimental Section. In particular, Table 4 shows that the χ values for the three polymers in water and *n*-hexane are all above 0.5, the value for a θ-solvent, confirming that these two liquids are nonsolvents for these polymers. In contrast, the χ values for the three polymers in THF are all below 0.5, suggesting that THF is a good solvent. Finally, the χ values in the 50−50 *n*-hexane−THF mixture

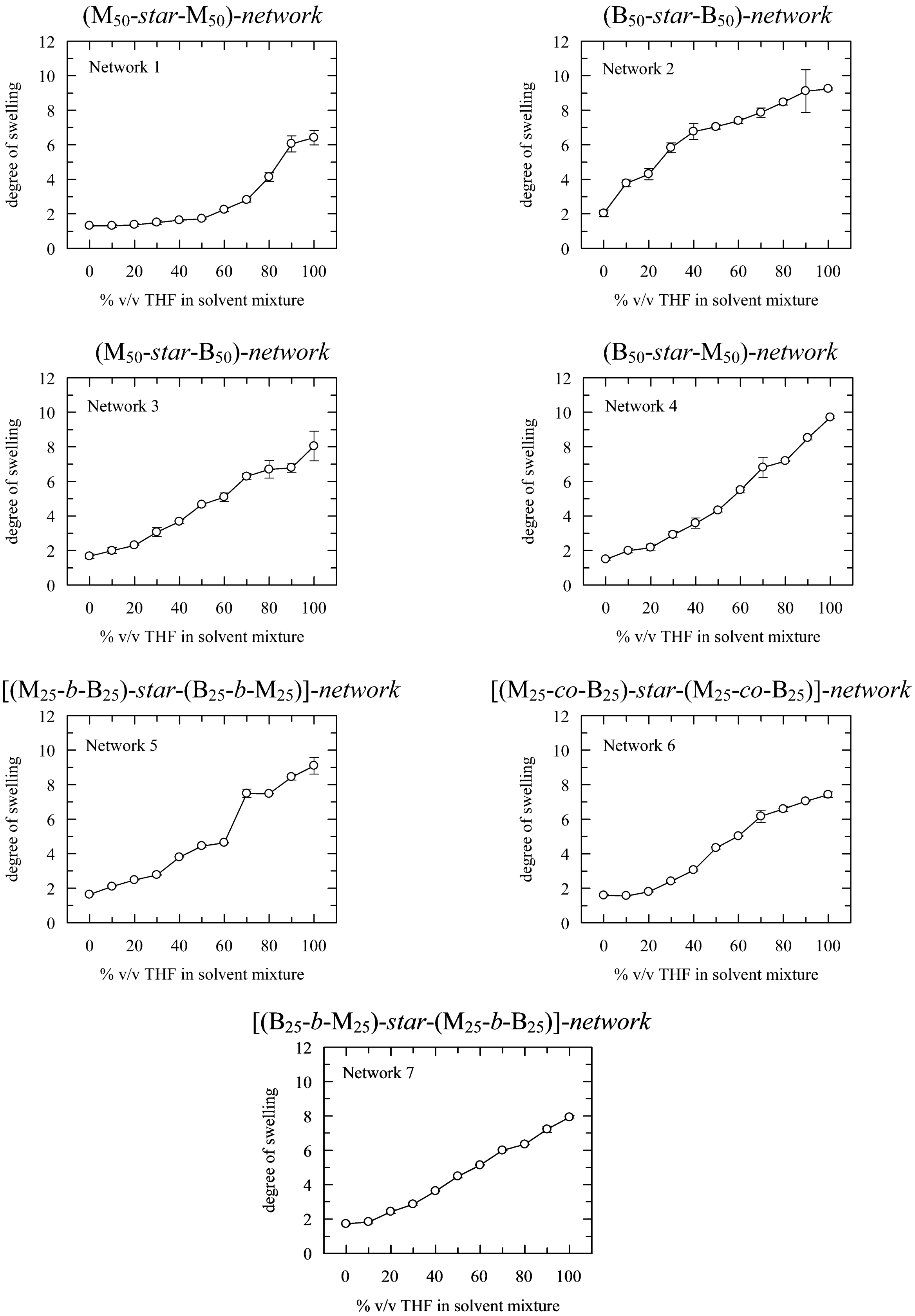

Figure 5. Degrees of swelling of the cross-linked star networks as a function of the THF content in the solvent mixture.

imply a good solvency for polyBuMA, a poor solvency for polyMMA, and a near-θ-solvency for the copolymer.

Because the 50−50 *n*-hexane−THF mixture is a good solvent for the one and a poor solvent for the other unit, there was a possibility for microphase separation in the segmented networks. This was theoretically investigated in the next section where a thermodynamic model was used for predicting the swelling behavior of the networks.

Predicted Degrees of Swelling and Microphase Behavior. Figure 7a shows the theoretically predicted DSs as a function

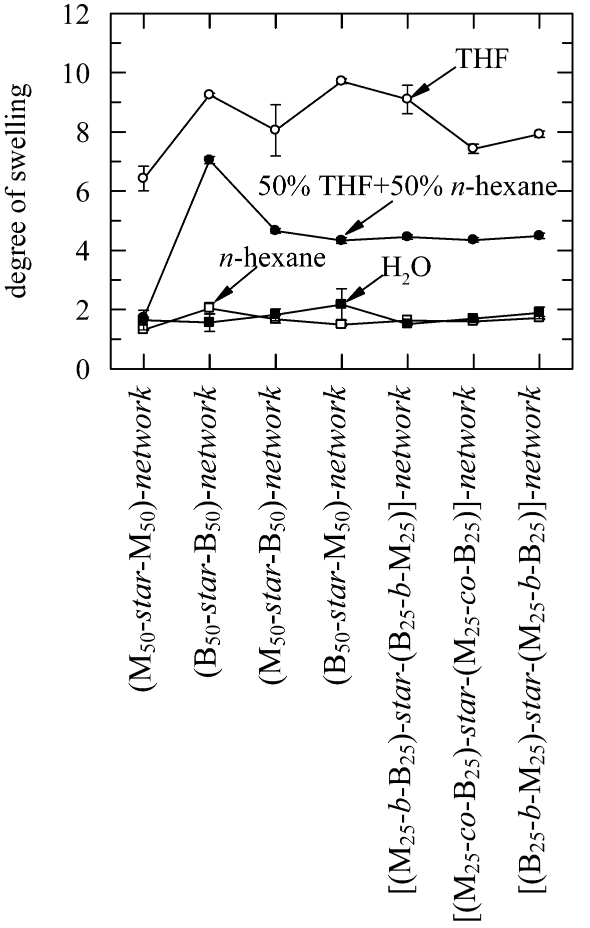

Figure 6. Degrees of swelling of the cross-linked star networks in various solvents as a function of the network type.

Table 4. Flory−Huggins Interaction Parameters for the 12 Combinations of the Four Solvents with the Three Polymers

	Flory−Huggins interaction parameter χ polymer		
solvent	BuMA	MMA	50−50 BuMA−MMA
n-hexane	0.752	1.227	0.989
THF	0.356	0.369	0.362
50−50 *n*-hexane−THF	0.406	0.650	0.528
H_2O	39.391	35.736	37.563

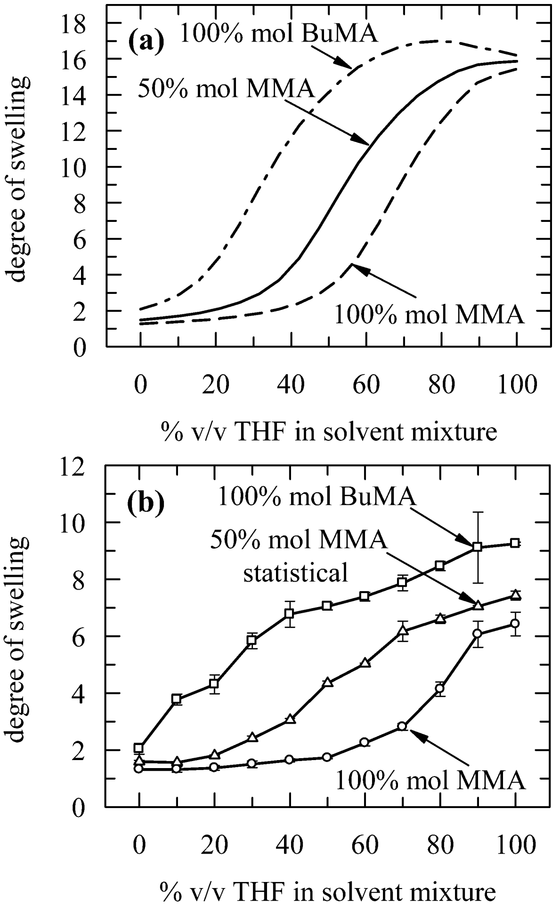

Figure 7. Dependence of the degrees of swelling of the two homopolymer networks and their 50−50 copolymer network on the THF content in the solvent mixture. (a) Theoretically predicted degrees of swelling. (b) Experimentally measured degrees of swelling.

of the solvent content in THF for the two homopolymer networks and their copolymer. The experimentally determined number of arms of 9, 79, and 30 were used in the calculations for the BuMA homopolymer, the MMA homopolymer, and the BuMA−MMA statistical copolymer networks, respectively. However, preliminary calculations indicated that the number of arms does not appreciably affect the network DS. As the THF content increased, the DSs of all three networks increased, with the polyBuMA and polyMMA networks exhibiting the highest and lowest DSs, respectively, and their copolymer network always displaying intermediate DSs. This predicted behavior was qualitatively very similar to the experimental measurements of Figure 5, which are summarized in Figure 7b. In this figure, the experimental DSs are ~50% lower than the theoretically predicted, possibly due to entanglements in the experimental system.

The present theoretical model examined for microphase separation in the segmented star copolymer networks, considering spherical, cylindrical, and lamellar morphologies.[24] The calculations showed that the Gibbs free energy of the disordered state was lower than those of the microphase-separated ones, indicating that the system was unstructured. This is consistent with the χ value of 0.65 between the MMA units and the 50−50 *n*-hexane−THF mixture of Table 4, which suggested only a small incompatibility, insufficient to drive the network to a microphase-separated state. The absence of microphase separation was also implied by the lack of differentiation among the DSs of the copolymer networks in the 50−50 *n*-hexane−THF mixture (Figure 7). Indeed, in our previous work on ionized amphiphilic CSPMNs, the microphase-separating segmented networks swelled significantly less than the disordered statistical network.[15]

Conclusions

The successful GTP synthesis of networks based on cross-linked “in−out” star copolymers of various architectures (heteroarm, block, and statistical stars) composed of two different hydrophobic monomers, MMA and BuMA, was accomplished using a monofunctional initiator in a four- or six-step procedure. The MMA and BuMA homopolymer cross-linked star networks were also synthesized. GTP remained “living” even after 6 monomer additions, allowing the synthesis of networks with such complicated structures. All copolymer and homopolymer networks swelled in THF, a good solvent for both monomer units, and collapsed in *n*-hexane, a poor solvent for both monomer units. In the 50−50 *n*-hexane−THF mixture, the BuMA and MMA homopolymer networks presented the highest and lowest swelling, respectively, whereas all copolymer networks presented almost the same degrees of swelling, intermediate between those of the homopolymer networks, displaying no architecture effect. The absence of differentiation in the swelling in the solvent mixture between the statistical network and the heteroarm and block networks suggests lack of microphase separation in the segmented networks, in agreement with the predictions of a thermodynamic model.

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