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Multi-Functional Conetworks Based on Cross-Linked Star Polymers

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Summary: Three series of conetworks based on cross-linked star polymers of different architectures were prepared using group transfer polymerization. The first series of conetworks were amphiphilic, based on the hydrophobic monomer benzyl methacrylate and the ionizable hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA); the second series were double-hydrophobic, based on methyl methacrylate and *n*-butyl methacrylate; the third series were ampholytic, based on the negatively ionizable methacrylic acid (MAA) and the positively ionizable DMAEMA. The MAA units were introduced into the conetworks via the polymerization of tetrahydropyranyl methacrylate followed by its acid hydrolysis after network formation. All the precursors to the conetworks were characterized in terms of their molecular weights using gel permeation chromatography. The degrees of swelling (DSs) of all the conetworks were measured as a function of pH or in a mixture of solvents. Moreover, the effect of the architecture of the conetworks on the DS was investigated. The DS was found to be influenced more by the charge density of the conetwork than by the compatibility with the solvent, and more by the solvent compatibility than by the architecture of the conetwork.

Keywords: cross-linked star polymer networks; living polymerization; microphase separation; model gels; swelling

Introduction

Polymer networks are three-dimensional polymers in which the polymer chains are interconnected by chemical cross-links (Figure 1).[1] These materials are insoluble in all solvents, but depending on their compatibility with the solvent, they can absorb various amounts of solvent. This ability allows the polymer networks to be used in an increasing number of applications, such as superabsorbents, for drug and DNA delivery, and in tissue engineering).[2] In order to be able to predict and control network swelling for these applications, polymer networks of a controlled structure are required. These networks are called ‘‘model’’ networks and bear chains of well-defined molecular weight and composition.[3] To date, several model networks have been synthesized using different methodologies.[2] One interesting methodology is the cross-linking of star polymers[4] which produces polymer networks with many dangling chains (singly-attached polymer chains - see Figure 1b). An increased number of dangling chains causes increases in the swelling of the polymer networks since the dangling chains contribute to the osmotic pressure (mixing with the solvent) without contributing to the retractive force within the network.

In the present study, a systematic investigation of the swelling ability of cross-linked star copolymer networks was performed. In particular, three groups of conetworks were synthesized: 1) an amphiphilic one, based on

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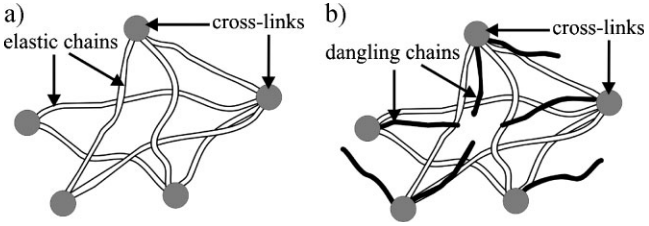

Figure 1.
Model polymer networks (a) without and (b) with dangling chains. The elastic chains, the dangling chains and the cross-links are colored in white, black and gray, respectively.

an ionizable hydrophilic monomer and a hydrophobic monomer, 2) a double-hydrophobic one, based on two hydrophobic monomers and 3) a polyampholytic one, based on a cationic hydrophilic monomer and an anionic hydrophilic monomer. The ability of the conetworks to swell in various solvents and pHs was studied, and the effect of the chemical structure, the charged density and the architecture of the networks on their swelling was investigated.

Experimental Part

All the reagents were purchased from Sigma-Aldrich, with the exception of the polymerization catalyst, tetrabutylammonium bibenzoate[5] and the tetrahydropyranyl methacrylate (THPMA)[6,7] monomer, which were both in-house synthesized. The chemical structures and the names of the main reagents used for the synthesis are shown in Figure 2. The cross-linked star copolymer conetworks were synthesized using sequential additions of monomers and cross-linker, ethylene glycol dimethacrylate (EGDMA), under group transfer polymerization (GTP) conditions.[4,5,8–13]

By altering the sequence of the additions of the monomers, polymer networks of different architectures were produced (Figure 3).[4,11–13] In particular, Network 1, the homopolymer cross-linked star network, was prepared by the sequential additions of monomer A/cross-linker/monomer A/cross-linker. The preparation of cross-linked star block copolymers, Networks 2 and 3, required the sequential addition of the two different monomers before the two EGDMA additions, while the synthesis of the cross-linked statistical copolymer star, Network 4, required the simultaneous addition of the two monomers before the cross-linker additions. The cross-linked heteroarm star, Network 5, was prepared by the sequential additions of monomer B/cross-linker/monomer A/cross-linker. The preparation of Network 6 required the sequential addition of the two monomers before the first EGDMA addition and afterwards the addition of

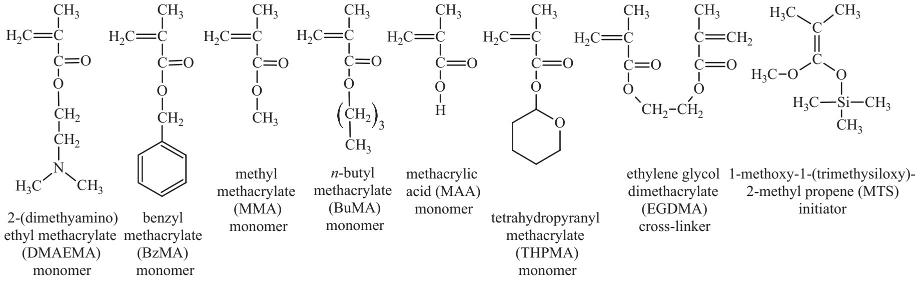

Figure 2.
Chemical structures and names of the main reagents used for the network synthesis.

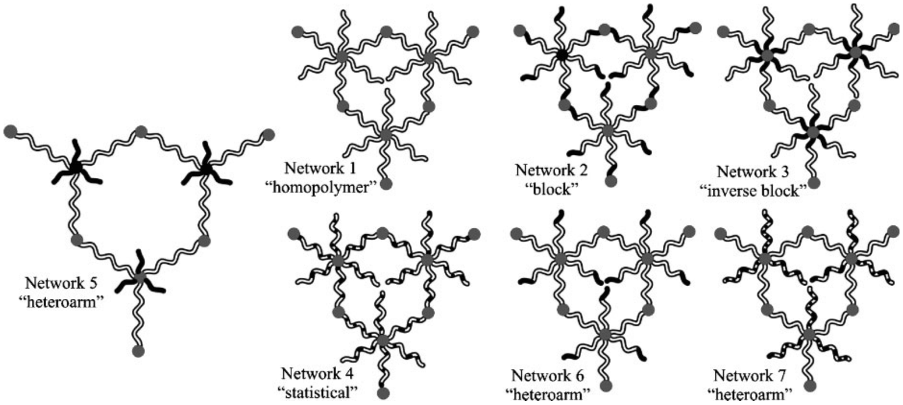

Figure 3.
Schematic representation of the architectures of the model networks. The units of monomer A and B are colored in white and black, respectively, while the cross-links are colored in gray.

monomer A, while Network 7 required the simultaneous addition of the two monomers before the first addition of the cross-linker and the last addition of the monomer A.

It should be noted that after the first addition of the cross-linker, ''arm-first'' star polymers were produced which bore the active sites of the polymerization in the core (in the cross-linker units). Upon further addition of monomer, ''in-out'' star polymers were produced which bore the active groups at the outer part of the star (at the end of the arm).

Three groups of conetworks based on cross-linked star polymers of different architectures were prepared: 1) an amphiphilic group based on the hydrophobic monomer benzyl methacrylate (BzMA) and the ionizable hydrophilic 2-(dimethylamino)ethyl methacrylate (DMAEMA), 2) a double-hydrophobic group based on methyl methacrylate (MMA) and *n*-butyl methacrylate (BuMA) and 3) an ampholyte group based on the negatively ionizable methacrylic acid (MAA) and the positively ionizable DMAEMA. The MAA units were introduced via the polymerization of THPMA followed by its acid hydrolysis after network formation.[14,15]

The linear precursors to the networks were characterized in terms of their molecular weights (MWs) and composition using gel permeation chromatography (GPC). The network degrees of swelling (DSs), defined as the network swollen mass divided by the network dry mass, were determined gravimetrically in water or/and tetrahydrofuran (THF) – hexane mixtures.

Results and Discussion

Figure 4 displays the GPC traces of the five precursors to the block copolymer conetwork [($DMAEMA_{10}$-*b*-$THPMA_{10}$)-*star*-($THPMA_{10}$-*b*-$DMAEMA_{10}$)]-*network*. The molecular weight distributions (MWDs) of

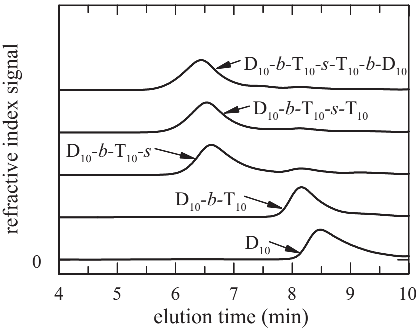

Figure 4.
Gel permeation chromatograms of the five precursors to ($DMAEMA_{10}$-*b*-$THPMA_{10}$)-*star*-($THPMA_{10}$-*b*-$DMAEMA_{10}$)-*network*. In the curve labeling, D, T and *s* are (further) abbreviations for DMAEMA, THPMA, and *star*, respectively.

the linear DMAEMA homopolymer and the DMAEMA-THPMA diblock copolymer were narrow and unimodal, as expected. The MWD of the main peak corresponding to the ‘‘arm-first’’ star, ($DMAEMA_{10}$-*b*-$THPMA_{10}$)-*star*, was also narrow but the distribution was bimodal, containing a small amount of unattached linear chains in addition to the stars. A fraction of these chains had originated from accidental deactivation during synthesis and thus it could not grow upon further addition of monomer, while a second part had not participated in the reaction with EGDMA due to steric hindrance and was still ‘‘living’’ and, therefore, it could grow upon further addition of monomer. The chromatograms of the ‘‘in-out’’ stars, ($DMAEMA_{10}$-*b*-$THPMA_{10}$)-*star*-($THPMA_{10}$-*b*-$DMAEMA_{10}$), were also bimodal for the same reasons as above, with a narrow MWD of the main peak corresponding to the star polymers. The MW of the main peak increased from the initial homopolymer to the final ‘‘in-out’’ star polymer, as expected, indicating the growth of the structure as a whole. Similar results were obtained for all the precursors to the (co)networks synthesized in this and previous studies.[4,11–13]

Table 1 shows the first (linear) and last (‘‘in-out’’ star) precursor to all the cross-linked star polymers prepared in this study and their GPC characterization data. These include the apparent number-average MWs, M_ns, the polydispersity indices (PDIs, M_w/M_ns) and the peak MWs, M_ps. The M_ns of all linear polymers were almost equal to or slightly higher than the theoretical MWs due to partial initiator deactivation, while their PDIs were low (≤ 1.18). For the ‘‘in-out’’ star polymers, the last precursor before the formation of the network, the PDIs shown were relatively low for star polymers (≤ 1.73).

Figure 5 shows how the DS of the network was affected by the pH of the solvent and the solvent composition. In particular, the pH-dependence (a and c) and solvent composition-dependence (b) of the DSs of (a) [($DMAEMA_{22.5}$-*co*-$BzMA_{7.5}$)-*star*-($BzMA_{7.5}$-*co*-$DMAEMA_{22.5}$)]-*network*, (b) [($BuMA_{25}$-*b*-MMA_{25})-*star*-(MMA_{25}-*b*-$BuMA_{25}$)]-*network* and (c) [(MAA_{10}-*b*-$DMAEMA_{10}$)-*star*-($DMAEMA_{10}$-*b*-MAA_{10})]-*network*.

The first graph on the left (Figure 5a) reveals that the pH was a factor that profoundly affected the DSs of all the networks. In particular, as the pH was lowered, the DSs of all networks of the first group increased. This was due to the fact that all the networks of this group contained DMAEMA ionizable units. DMAEMA is a weakly basic tertiary amine, which is uncharged at high pH but becomes positively charged at low pH. The electrostatic repulsion created by the network charges and the osmotic pressure due to the chloride counterions at low pH both promoted network swelling.

The graph in the middle (Figure 5b) shows the DSs of a BuMA-MMA conetwork in THF/*n*-hexane mixtures as a function of the THF volume fraction of the solvent mixture. As the THF fraction increased, the DSs of all the BuMA-MAA networks increased. This is because both monomer repeat units, MMA and BuMA, are more compatible with THF than with *n*-hexane. THF is a good solvent for both MMA and BuMA units, while *n*-hexane is a non-solvent for these two units.

The graph on the right (Figure 5c) shows how the pH affected the DSs of all the polyampholyte conetworks. In particular, the DSs of all the polyampholyte conetworks presented a characteristic minimum in their DSs at intermediate pH values, while they increased again at acidic and basic pHs. This behavior is typical of polyampholytes, due to the existence of the isoelectric point, p*I*, the pH of zero net charge. At and near the p*I*, the van der Waals and the hydrophobic attractive forces contribute significantly to the polyampholyte collapse, while the electrostatic repulsions of the charged DMAEMA and MAA units at low and high pH, respectively, promote the network swelling.

It is noteworthy that the DSs were higher in water of low pH or high pH,

Table 1.
MW characteristics of the cross-linked star network precursors.

Net.	Theoretical structure[1]	Theoretical MW	GPC results		
No			M_n	M_p	M_w/M_n
1	D_{30}	4800	4800	5300	1.06
	D_{30}-*s*-D_{30}	*	26800	35500	1.33
2	$Bz_{7.5}$	1400	2100	2200	1.08
	$Bz_{7.5}$-*b*-$D_{22.5}$-s-$D_{22.5}$-*b*-$Bz_{7.5}$	*	44100	76800	1.41
3	$D_{22.5}$	3600	3500	3900	1.06
	$D_{22.5}$-*b*-$Bz_{7.5}$-s-$Bz_{7.5}$-*b*-$D_{22.5}$	*	47300	61400	1.20
4	$D_{22.5}$-*co*-$Bz_{7.5}$	5000	4900	5300	1.07
	$D_{22.5}$-*co*-$Bz_{7.5}$-s-$Bz_{7.5}$-*co*-$D_{22.5}$	*	33000	45300	1.27
5	Bz_{15}	2800	3000	3500	1.09
	Bz_{15}-*s*-D_{45}	*	92600	140100	1.56
6	Bz_{15}	2800	2800	3300	1.10
	Bz_{15}-*b*-D_{15}-*s*-D_{30}	*	88500	109700	1.29
7	Bz_{15}-*co*-D_{15}	5102	5500	6000	1.07
	Bz_{15}-*co*-D_{15}-*s*-D_{30}	*	34000	69100	1.37
8	M_{50}	5110	7220	7840	1.11
	M_{50}-*star*-M_{50}		238000	228000	1.28
9	B_{50}	7310	9370	9810	1.12
	B_{50}-*star*-B_{50}	*	89200	181000	1.86
10	M_{50}	5110	8000	8600	1.11
	M_{50}-*star*-B_{50}	*	171000	181000	1.18
11	B_{50}	7310	9500	9810	1.11
	B_{50}-*star*-M_{50}	*	97900	164000	1.67
12	M_{25}	2600	3210	3440	1.13
	M_{25}-*b*-B_{25}-*star*-B_{25}-*b*-M_{25}	*	110000	181000	1.73
13	M_{25}-*co*-B_{25}	6210	8620	9190	1.13
	M_{25}-*co*-B_{25}-*star*-M_{25}-*co*-B_{25}	*	95100	149000	1.64
14	B_{25}	3600	3390	3550	1.12
	B_{25}-*b*-M_{25}-*star*-M_{25}-*b*-B_{25}	*	189000	194000	1.17
15	D_{20}	3240	4460	5381	1.12
	D_{20}-*star*-D_{20}	*	68100	73700	1.20
16	T_{20}	3500	4620	5520	1.13
	T_{20}-*star*-T_{20}	*	88900	90900	1.28
17	D_{10}	1670	2480	3360	1.18
	D_{10}-*b*-T_{10}-*star*-T_{10}-*b*-D_{10}	*	75700	81900	1.22
18	T_{10}	1800	2180	3020	1.22
	T_{10}-*b*-D_{10}-*star*-D_{10}-*b*-T_{10}	*	70500	77700	1.18
19	D_{10}-*co*-T_{10}	3370	3910	4850	1.15
	D_{10}-*co*-T_{10}-*star*-D_{10}-*co*-T_{10}	*	63600	71820	1.19
20	D_{20}	3240	3940	4980	1.15
	D_{20}-*star*-T_{20}	*	59000	68200	1.17
21	T_{20}	3500	4960	5970	1.14
	T_{20}-*star*-D_{20}	*	95200	95800	1.29

* D: DMAEMA, Bz:BzMA, M:MMA, B:BuMA; T:THPMA(MAA)

where the polymers were charged (Figure 5c), than in a non-selective organic solvent (THF, Figure 5b), despite the greater degree of polymerization of the chains in the latter case.

Figure 6 shows the dependence of the DSs on the architecture of the star polymers in different solvents for the three groups of polymers: (a) the DMAEMA-BzMA, (b) the BuMA-MAA and (c) the DMAEMA-MAA based networks. Three main observations can be made:

1) In the collapsed state, i.e. for DSs lower than 5, where the networks were in a non-solvent, the polymer architecture did not affect the swelling since all the conetworks of a series presented similar DSs.
2) Similarly, in a compatible organic solvent, THF or a THF-hexane mixture,

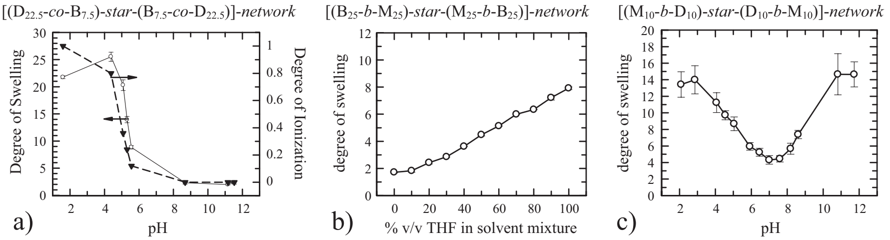

Figure 5.
pH-dependence (a and c) and solvent composition-dependence (b) of the degrees of swelling of (a) [(DMAEMA$_{22.5}$-*co*-BzMA$_{7.5}$)-*star*-(BzMA$_{7.5}$-*co*-DMAEMA$_{22.5}$)]-*network*, (b) [(BuMA$_{25}$-*b*-MMA$_{25}$)-*star*-(MMA$_{25}$-*b*-BuMA$_{25}$)]-*network* and (c) [(MAA$_{10}$-*b*-DMAEMA$_{10}$)-*star*-(DMAEMA$_{10}$-*b*-MAA$_{10}$)]-*network*.

the conetworks presented similar DSs. Thus, the architecture of the networks did not influence the swelling in organic solvents.

3) On the other hand, when the networks were in water at a pH where one of the two monomers was charged (and the DS was high), the effect of the polymer architecture was clear. In particular, by comparing two DMAEMA homopolymers (from Figure 6a and c), the effect of the degree of polymerization on the DS can be seen. By increasing the degree of polymerization of the arm the DS increases. The same effect was observed for the DMAEMA-BzMA based networks, where the network with the highest degree of polymerization of the chains between the cross-links (equal to 45) presented the highest DS from all the conetworks.

By comparing three networks from the same group of polymers, a more interesting observation can be made: that the monomer distribution in the chain also affected the swelling. In particular, three networks: [(BzMA$_{7.5}$-*b*-DMAEMA$_{22.5}$)-*star*-(DMAEMA$_{22.5}$-*b*-BzMA$_{7.5}$)]-*network*,

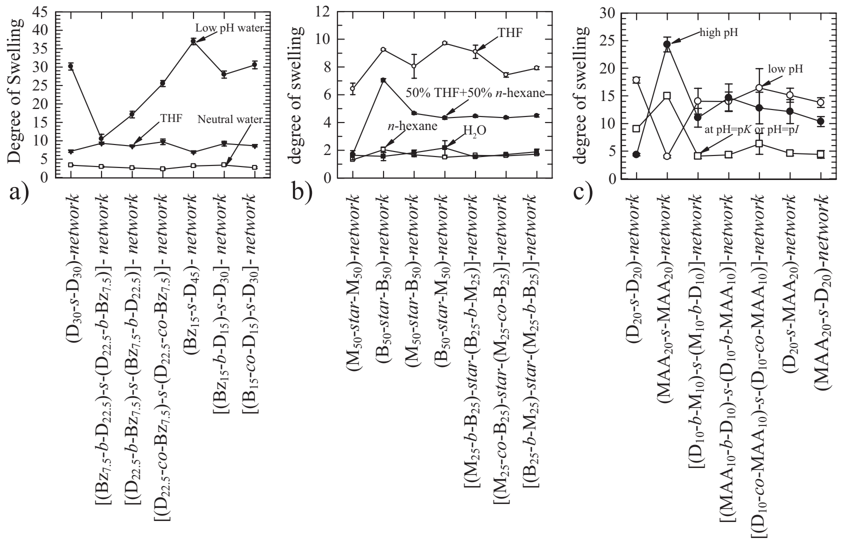

Figure 6.
Degrees of swelling of the cross-linked star networks (a) in low pH water, in neutral pH water and in THF and (b) in water, hexane, THF and 50% - 50% THF-hexane and (c) in high and low pH water and at pH = p*K* (homopolymer networks) or pH = p*I* (polyampholyte conetworks) D, Bz, B, M and *s* are (further) abbreviations for DMAEMA, BzMA, BuMA, MAA and *star*, respectively.

[($DMAEMA_{22.5}$-*b*-$BzMA_{7.5}$)-*star*-($BzMA_{7.5}$-*b*-$DMAEMA_{22.5}$)]-*network* and [($DMAEMA_{22.5}$-*co*-$BzMA_{7.5}$)-*star*-($DMAEMA_{22.5}$-*co*-$BzMA_{7.5}$)]-*network* (Networks 2, 3 and 4, respectively) had amphiphilic polymer chains of the same degree of polymerization. From the three, Network 4 presented the highest DS. This can be attributed to the random distribution of the two monomers in its elastic chains. The random distribution of the BzMA units in the network allowed the unhindered expansion of the elastic and dangling chains of the network. The star block based-conetworks [($BzMA_{7.5}$-*b*-$DMAEMA_{22.5}$)-*star*-($DMAEMA_{22.5}$-*b*-$BzMA_{7.5}$)]-*network* and [($DMAEMA_{22.5}$-*b*-$BzMA_{7.5}$)-*star*-($BzMA_{7.5}$-*b*-$DMAEMA_{22.5}$)]-*network* presented the lowest DSs because of microphase separation, since the hydrophobic blocks could aggregate to form hydrophobic microdomains.

Conclusion

The successful GTP synthesis of functional conetworks based on cross-linked "in-out" star copolymers of various architectures (heteroarm, block and statistical stars) was accomplished using a monofunctional initiator in a four-, five- or six-step preparation. It is noteworthy that GTP was active even after 6 monomer additions, allowing the synthesis of networks with such complicated structures. The DSs in of all the networks synthesized was measured in different solvents. The DSs depended more by the charge density of the network than by the solvent compatibility, and more by the solvent compatibility than by the network architecture.

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