Synthesis and Characterization of Novel Networks with Nano-Engineered Structures: Cross-Linked Star Homopolymers

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Group transfer polymerization was used for the one-pot preparation of a network structure comprising cross-linked star homopolymers. The structure contains many dangling chains (constituting the arms of the primary stars), whose number is approximately equal to the number of the elastic chains. 2-(Dimethylamino)ethyl methacrylate and ethylene glycol dimethacrylate were used as the monomer and cross-linker, respectively. The synthesis involved a four-step sequential addition of monomer/cross-linker/monomer/cross-linker, which produced linear polymer, “arm-first” star polymer, “in-out” star polymer, and cross-linked star polymer network, respectively. The products of the first three steps of the synthesis were characterized in terms of their relative molecular weights by gel permeation chromatography, and in terms of their absolute molecular weights by static light scattering, which indicated that the number of arms in the “arm-first” stars is about 50, whereas that in the “in-out” stars is about 100. Seven networks were prepared in total, covering a range of degrees of polymerization of the primary and the secondary arms. The degrees of swelling of all the networks were measured in water and were found to increase by lowering the pH, a result of the ionization of the tertiary amine group of the monomer repeat unit.

Introduction

Star polymers[1−7] and polymer networks[8] are two interesting polymer structures that can be obtained by available synthetic methods, and each has various useful applications. Applications of star polymers include such uses as toughening of plastics and coatings[9,10] with good processibility due to low solution and melt viscosity imparted by the inherent molecular compactness of these polymers.[11] Applications of traditional hydrophobic polymer networks include uses as coatings and structural materials.[8] Water-compatible networks (hydrogels)[12,13] have uses as superabsorbents,[14,15] drug release systems, and tissue-engineering scaffolds,[16] and are expected to be used in modern applications such as actuators, valves, sensors, and artificial muscles for robotics.[17]

Star polymers comprise several linear chains interconnected at one end, whereas both chain ends are interconnected in polymer networks. The combination of star polymers and polymer networks will yield a more complex architecture (cross-linked star polymers) with new features and potentially new applications. For example, the constitution of the network from multiarmed stars will render it a denser material than conventional networks. The synthesis and study of such a complex architecture was the aim of this investigation. Two other important features of the materials prepared in this study are, first, the precise control over the length of the arms of the stars, and the star size,

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(1) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978,** *51*, 406.

(2) Bywater, S. *Adv. Polym. Sci.* **1979,** *30*, 90.

(3) *Star and Hyperbranched Polymers*; Mishra, M. K., Kobayashi, S., Eds.; Marcel Dekker: New York, 1999.

(4) Hadjichristidis, N. *J. Polym. Sci.: Part A: Polym. Chem.* **1999,** *37*, 857−871.

(5) Pitsikalis, M.; Sioula, S.; Pispas, S.; Hadjichristidis, N.; Cook, D. C.; Li, J.; Mays, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1999,** *37*, 4337−4350.

(6) Bartelink, C. F.; De Pooter, M.; Grünbauer, H. J. M.; Beginn, U.; Möller, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000,** *38*, 2555−2565.

(7) Pasquale, A. J.; Long, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2001,** *39*, 216−223.

(8) *Cross-Linked Polymers: Chemistry, Properties and Applications*; Dickie, R. A., Labana, S. S., Bauer, R. S., Eds.; ACS Symposium Series 367; Amercian Chemical Society: Washington, DC, 1988.

(9) Simms, J. A.; Spinelli, H. J. *J. Coatings Technol.* **1987,** *59*, 125−131.

(10) Simms, J. A. *Rubber Chem. Technol.* **1991,** *64*, 139−151.

(11) Rempp, P. F.; Lutz, P. J. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, 1996; Vol. 10, pp 7880−7885.

(12) Tanaka, T. *Sci. Am.* **1981,** *244*(1), 124−138.

(13) Osada, Y.; Ross-Murphy, S. B. *Sci. Am.* **1993,** *268*(5), 42−47.

(14) Buchholz, F. L.; Peppas, N. A., Eds. *Superabsorbent Polymers*; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1995.

(15) *Modern Superabsorbent Polymer Technology*; Buchholz, F. L., Graham, A. T., Eds.; Wiley: New York, 1998.

(16) Jen, A. C.; Wake, M. C.; Mikos, A. G. *Biotechnol. Bioeng.* **1996,** *50*, 357.

(17) Dagani, R. *Chem. Eng. News* **1997,** *75*, 26−37.

10.1021/cm010569e CCC: $20.00

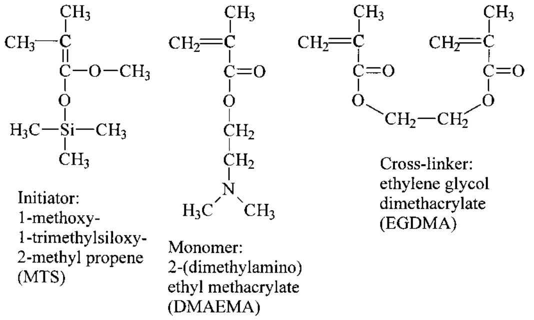

Figure 1. Chemical formulas of the initiator, monomer, and cross-linker used for the network synthesis.

resulting in model networks,[18] and, second, the hydrophilic, ionizable nature of the monomer repeat unit, leading to polyelectrolyte hydrogels.[19]

In particular, group transfer polymerization (GTP)[20−23] was used for the synthesis of the cross-linked star polymers, employing a four-step sequential addition of monomer/cross-linker/monomer/cross-linker. The synthetic strategy relies on the unabated activity of a GTP active end group on a polymer such that:

(i) A linear polymer is formed with one active GTP end.

(ii) A star polymer of uncontrolled functionality is obtained by reaction of the linear polymer with a divinyl reactant, such that the active GTP ends are situated in the core of the star polymer.

(iii) When additional monomer is added, new chains grow from the GTP active sites to create a new star polymer, with GTP active sites at the ends of the new branches, whereas the original branches have unreactive end groups.

(iv) Reaction of the GTP active sites with additional divinyl reactant produces a cross-linked network, with the original chains forming dangling chains in the network.

The network precursors were characterized in terms of their size by gel permeation chromatography (GPC) and static light scattering (SLS), whereas all networks were characterized in terms of their degrees of swelling (DSs) in water as a function of pH and tetrahydrofuran (THF).

Experimental Section

Materials. All chemicals used are commercially available and were purchased from Aldrich, Germany. They were used as received unless otherwise stated. The chemical formulas and names of the initiator, 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS), the monomer, 2-(dimethylamino)ethyl methacrylate (DMAEMA), and the cross-linker, ethylene glycol dimethacrylate (EGDMA), are shown in Figure 1. The polymerization catalyst was tetrabutylammonium bibenzoate (TBABB), and it was synthesized in-house by the method of Dicker et al.,[22] whereas THF served as the polymerization solvent.

Methods. All glassware was dried overnight at 120 °C and assembled hot under dynamic vacuum before use. THF was dried by refluxing over a potassium/sodium alloy for 3 days before use. The DMAEMA monomer and the EGDMA cross-linker were passed through basic alumina columns to remove inhibitors and protic impurities. They were subsequently stirred over calcium hydride in the presence of free-radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), and stored at 5 °C. They were freshly distilled under vacuum and kept under a dry nitrogen atmosphere until use. The initiator was distilled once before the polymerization. The dried catalyst powder was stored in a round-bottom flask under vacuum until use. The polymerizations were performed in 100-mL round-bottom flasks, fitted with a rubber septum. Catalytic amounts (5−10 mg) of 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 sequential addition of the initiator, monomer, cross-linker, again monomer, and again cross-linker. The amount of the EGDMA cross-linker used during each one of its two additions was four times the number of moles of the MTS initiator, as determined in our previous work[24,25] in which the synthesis of DMAEMA star homopolymers was optimized. The reactions were performed at ambient temperature (20 °C) without thermostating the polymerization reactor. The polymerization exotherm was monitored by a digital thermometer and was used to monitor the progress of the reaction.

Synthesis. An example is provided in this section describing the synthesis of the ($DMAEMA_{20}$-*star*-$DMAEMA_{50}$)-*network*, having primary arms comprising 20 DMAEMA units and secondary DMAEMA arms with degree of polymerization (DP) 50. To a 100-mL round-bottom flask kept under dry nitrogen atmosphere and containing a small amount (∼10 mg) of TBABB catalyst were syringed 40 mL of freshly distilled THF and 0.2 mL MTS initiator (0.98 mmol), in this order. DMAEMA (3.3 mL;19.6 mmol) was slowly added under stirring. The polymerization exotherm (26−33 °C) abated within 5 min, samples for GPC and SLS were extracted, and 0.74 mL EGDMA (3.94 mmol) were added, which produced an exotherm (33−36 °C). After sampling, 8.3 mL DMAEMA (49.2 mmol) were added (exotherm 34−47 °C) and samples were withdrawn again. In the final stage, 0.74 mL EGDMA (3.94 mmol) were added which promoted gelation within seconds.

Characterization by GPC. 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 GPC by using a single high-molecular-weight range Polymer Laboratories PL-Mixed 'D' column. The mobile phase was THF at a flow rate of 1 mL min^{-1}, delivered with a Polymer Laboratories PL-LC1120 isocratic pump. The refractive index signal was measured with an ERC-7515A refractive index detector 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 poly(methyl methacrylate) (PMMA), standards which provided only qualitative estimates for the MWs of the star polymers.

Characterization by SLS. The absolute weight-average molecular weight (M_w) of the two ("arm-first" and "in-out") star precursors to the ($DMAEMA_{20}$-*star*-$DMAEMA_{50}$)-*network* was measured by SLS with a Wyatt Technology DAWN spectrometer equipped with 18 detectors and a 5-mW He−Ne linearly polarized laser operating at 632.8 nm. The polymer samples for the SLS were dissolved in HPLC grade THF and filtered through 0.45-μm-pore-size filters. The refractive index incre-

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(18) Hild, G. *Prog. Polym. Sci.* **1998,** *23*, 1019−1149.

(19) Dušek, K., Tanaka, T., Eds. *Responsive Gels: Volume Transitions*; Advances in Polymer Science, Vols. 109 and 110; Dušek, K., Tanaka, T., Eds.; Springer-Verlag: Berlin, 1993.

(20) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983,** *105*, 5706−5708.

(21) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987,** *20*, 1473−1488.

(22) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990,** *23*, 4034−4041.

(23) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000,** *38*, 2855−2860.

(24) Simmons, M. R.; Yamasaki, E. N.; Patrickios, C. S. *Polymer* **2000,** *41*(25), 8523−8529.

(25) Simmons, M. R.; Yamasaki, E. N.; Patrickios, C. S. *Macromolecules* **2000,** *33*, 3716−3719.

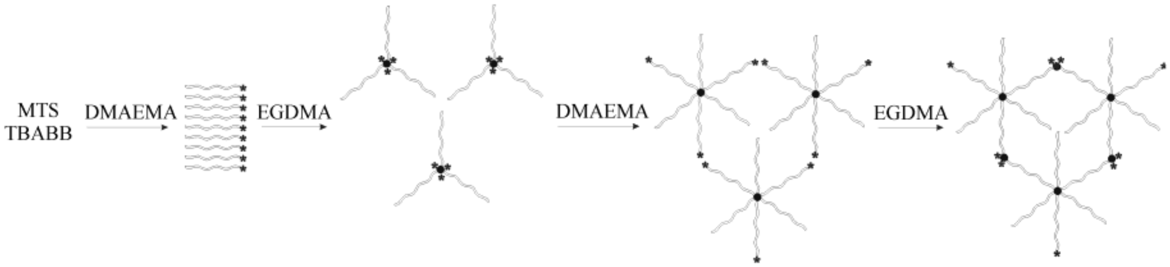

Figure 2. Schematic representation of the synthetic procedure used for the preparation of the cross-linked star polymers. The number of arms is not 3 or 6, as indicated in the figure, but much higher, 50 or 100. The filled dots indicate the EGDMA cores, and "*" symbols indicate the "living" sites of the polymerization.

ments (d*n*/d*c*) were determined using a Wyatt Technology Optilab DSP differential refractometer at a wavelength of 633 nm.

Characterization of the Degree of Swelling. The gels were taken out of the reactor where polymerization and cross-linking took place, washed in THF to remove the sol fraction, and cut into small cubes of 5−10 mm. The mass of the THF swollen cubes was measured gravimetrically before placing all samples in a vacuum oven for drying for 48 h at 40 °C. The dry gel mass was determined, followed by the transfer of the gels in water. The pH of the gel samples in water was varied by the addition of the appropriate volume (typically several drops) of solutions of 0.5 M HCl or 0.5 M NaOH. The samples were allowed to equilibrate for 3 weeks, and the solution pH and wet gel mass were measured. All degrees of swelling were determined in triplicate and the average of the measurements is presented. The degrees of swelling in THF and in the aqueous phase were calculated as the ratio of the wet network mass in THF or water, respectively, divided by the dry gel mass.

Results and Discussion

Synthesis and Structure of Cross-Linked Star Polymers. Figure 2 is a schematic representation of the synthetic procedure used for the preparation of the networks. This comprises a four-step sequential monomer addition in a one-pot preparation, starting with the synthesis of the DMAEMA homopolymer linear segments that are to form the primary arms of the stars and the dangling chains of the final network, followed by the addition of the EGDMA cross-linker to yield the "arm-first" star polymers, succeeded by the addition of DMAEMA monomer for a second time to lead to the formation of the secondary arms of the "in-out" star polymers, and concluded by the addition of EGDMA to induce the interconnection of the "in-out" star polymers. The active polymerization sites are indicated by the star symbols, whereas the filled dots indicate the EGDMA cores. Note that, in addition to the primary EGDMA core in the initial star polymer, a secondary EGDMA core is created on the interlinking of the stars containing the active sites. The resulting network structure has many dangling chains, whose number must be approximately equal to the number of elastic chains because of the conservation of the total number of the active sites in a "living" polymerization such as GTP. The actual numbers of arms in the "arm-first" and "in-out" stars are not 3 or 6, as indicated in Figure 2, but much higher, about 50 and 100, as suggested by the SLS measurements discussed below, because of the ability of EGDMA to be added repeatedly at the core bringing together a large number of chains.[10,26] However, the length of primary and secondary arms is precisely controlled because of the "living" character of GTP. This also implies that the diameter of the stars and the inter-star spacing, both of nanoscopic dimensions, are precisely controlled too.

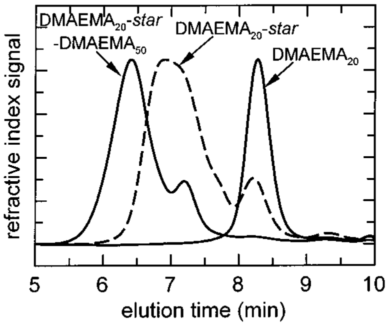

Figure 3. Gel permeation chromatograms of the three precursors to the (DMAEMA$_{20}$-*star*-DMAEMA$_{50}$)-*network*.

The present approach provides one of the first examples of a network architecture possessing a large, but controlled, number of dangling chains. Peppas et al.[27] and Lutz[28] have prepared similar networks based on poly(ethylene oxide) star polymers, in which the final cross-linking step was performed by free radical polymerization. The cross-linking of "core-first"[29,30] and "arm-first"[31] star polymers, and of dendrimers,[32] has also been reported, but the resulting network architectures do not contain any intentional dangling chains.

MWs and MWDs of Network Precursors. Figure 3 shows typical GPC chromatograms of the network precursors which are similar to chromatograms obtained for other "arm-first" and "in-out" heteroarm star polymers.[26,33] The particular chromatograms are those of the precursors to the (DMAEMA$_{20}$-*star*-DMAEMA$_{50}$)-*network*. The MWD of the linear DMAEMA homopolymer is narrow and unimodal. The MWD of the "arm-first" star is broad and bimodal, containing an amount of unattached linear chains in addition to the stars. The

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(26) Kanaoka, S.; Omura, T.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992,** *25*, 6407−6413.

(27) Keys, K. B.; Andreopoulos, F. M.; Peppas, N. A. *Macromolecules* **1998,** *31*, 8149−8156.

(28) Lutz, P. J. *Macromol. Symp.* **2001,** *164*, 277−292.

(29) Mendes, E.; Lutz, P.; Bastide, J.; Boué, F. *Macromolecules* **1995,** *28*, 174−179.

(30) Plentz Meneghetti, S.; Lutz, P. J.; Rein, D. Star-Shaped Polymers via Anionic Polymerization Methods. In *Star and Hyperbranched Polymers*; Polymer Frontiers; Mishra, M. K., Kobayashi, S., Eds.; Marcel Dekker: New York, 1999; pp. 27−57.

(31) Lopina, S. T.; Wu, G.; Merrill, E. W.; Griffith-Cima, L. *Biomaterials* **1996,** *17*, 559−569.

(32) Viers, B. D.; Bauer, B. J.; Akpalu, Y.; Gröhn, F.; Liu, D.; Kim, G. *Polym. Prepr.(Am. Chem. Soc. Div. Polym. Chem.)* **2000,** *41*(1), 728−729.

(33) Tsitsilianis, C.; Papanagopoulos, D.; Lutz, P. *Polymer* **1995,** *36*(19), 3745−3752.

Table 1. Molecular Weight Characterization by GPC of the DMAEMA Gel Precursors

sample[a]	theoretical structure of the sample	theor. MW	apparent M_n	M_w/M_n	apparent M_p
1A	DMAEMA$_{20}$	3244	2900	1.14	3400
1B	DMAEMA$_{20}$-*star*		11900	2.20	34700
1C	DMAEMA$_{20}$-*star*-DMAEMA$_{20}$		17300	2.00	50500
2A	DMAEMA$_{50}$	7961	8300	1.12	9000
2B	DMAEMA$_{50}$-*star*		18800	1.81	48000
2C	DMAEMA$_{50}$-*star*-DMAEMA$_{50}$		29500	1.72	63400
3A	DMAEMA$_{100}$[b]	15822	–	–	–
3B	DMAEMA$_{100}$-*star*[b]		–	–	–
3C	DMAEMA$_{100}$-*star*-DMAEMA$_{100}$[b]		–	–	–
4A	DMAEMA$_{20}$	3244	4000	1.11	4100
4B	DMAEMA$_{20}$-*star*		18200	2.39	50200
4C	DMAEMA$_{20}$-*star*-DMAEMA$_{10}$		24800	2.14	57700
5A	DMAEMA$_{50}$	7961	10800	1.09	10900
5B	DMAEMA$_{50}$-*star*		33800	1.86	69500
5C	DMAEMA$_{50}$-*star*-DMAEMA$_{10}$		45700	1.68	76300
6A	DMAEMA$_{20}$	3244	3800	1.08	4000
6B	DMAEMA$_{20}$-*star*		15600	2.07	42100
6C	DMAEMA$_{20}$-*star*-DMAEMA$_{50}$		71600	1.75	96900
7A	DMAEMA$_{50}$	7961	12700	1.09	12000
7B	DMAEMA$_{50}$-*star*		36800	1.80	72300
7C	DMAEMA$_{50}$-*star*-DMAEMA$_{20}$		51000	1.64	87000
8A	DMAEMA$_{50}$	7961	12000	1.10	11300
8B	DMAEMA$_{50}$-*star*		41100	1.06	83400
8C	DMAEMA$_{50}$-*star*-DMAEMA$_{1}$		45400	1.77	83400
8D	(DMAEMA$_{50}$-*star*-DMAEMA$_{1}$)-*network*		65900	3.04	152000

[a] Samples A, linear polymers; samples B, "arm-first" stars (primary stars); samples C, "in-out" stars. [b] No polymerization was observed.

shoulder on the low MW tail of the chromatogram of the "arm-first" star corresponds to the dimer of the linear precursor and has been observed in star polymers prepared by anionic polymerization.[34] The MWD of the "in-out" star polymer is also broad and bimodal, with the main peak having a higher MW than that of the "arm-first" star, as expected.

Table 1 shows the theoretical structural formulas and the results of the GPC characterization of the network precursors. The polymerizations in samples 3 were not successful because of the high MW attempted and the MW limitations in GTP.[21] The polymerizations in all other samples were successful and gelation took place in all cases except for sample 8. The average DP of the secondary arms in sample 8 was only 1, much smaller than the DP of the corresponding primary arms of 50. Thus, the steric hindrances present did not allow for efficient interconnection of the star polymers to lead to network formation. In this case, instead of a network, bigger stars were produced, as GPC analysis indicated (compare MWs of samples 8C and 8D). It is remarkable that network formation did take place in samples 4, 5, and 7, in which the secondary arms were also shorter than the primary arms. Apparently, the steric hindrances present in these cases were not strong enough to inhibit gelation. Gelation was also successful when the secondary arms were equal in length (samples 1 and 2) or longer than the primary arms (sample 6).

The M_n and M_w/M_n values of all samples calculated from GPC are also listed in Table 1. All linear polymers exhibit low PDIs (<1.15) and M_ns which are reasonably close to the theoretical MWs. For the star polymers, the PDIs are relatively high (~2), because the calculation included both the main star peak and its precursor peak because of their overlap. Comparing the "arm-first" with the "in-out" stars, the latter always have higher M_ns than the former, as expected. The corresponding peak MWs, M_ps, which are also provided, exhibit the same trend, but are always higher than the corresponding M_ns. It must be pointed out that the M_ns determined by GPC of all star polymers are lower than their actual ones because of the compactness of the star structure compared with the linear MW calibration standards.[10,26] This is further explored in the next paragraph.

Absolute Molecular Weights. SLS measurements for the two star precursors to the (DMAEMA$_{20}$-*star*-DMAEMA$_{50}$)-*network* allowed the determination of their absolute weight-average MWs, M_ws, and thus the number of primary (dangling chains of the network) and secondary (elastic chains of the network) arms of the star. The first linear precursor could not be measured by this technique because of the very low MW of the polymer (~4000 g mol^{-1}) which was below the detection limit of the instrument (~10 000 g mol^{-1}). The MW used for this sample was that measured by GPC, as satisfactory accuracy for linear poly(DMAEMA) is expected based on the calibration curve of linear PMMAs. The relatively small molecular size of the star polymers precluded the evaluation of the radii of gyration. The absolute M_ws for the "arm-first" and the "in-out" stars were 194 900 g mol^{-1} and 604 200 g mol^{-1}, respectively. Dividing the former value by the M_n of the linear polymer (3800 g mol^{-1} by GPC) gives an "arm-first" star that comprises 51 arms which are to form the dangling chains of the final network structure. Similarly, by subtracting the molecular weight of the "arm-first" star from that measured for the "in-out" star and assuming a DP of 50 (MW = 7861 g mol^{-1}) for the secondary arms, a value of 52 secondary arms, which are to form the elastic chains of the polymer network, is calculated. From the above, the total number of arms for the "in-out" star can be calculated to be 51 + 52 = 103 arms. By setting the DP of the secondary arms equal to 50, the calculation assumes a constant number of active sites, which is a well-established (by GPC) trait of GTP,

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(34) Tsitsilianis, C.; Chaumont, P.; Rempp, P. *Makromol. Chem.* **1990,** *191*, 2319–2328.

Table 2. Sol Fraction, Degrees of Swelling, and p*K* Values of Homopolymer Cross-Linked Stars

network	% extractables	effective p*K*	degree of swelling low pH	high pH	THF
(DMAEMA$_{20}$-*star*-DMAEMA$_{20}$)-*network*	2.8	5.2	12.5	2.4	4.2
(DMAEMA$_{50}$-*star*-DMAEMA$_{50}$)-*network*	2.3	5.6	53.2	3.3	9.1
(DMAEMA$_{20}$-*star*-DMAEMA$_{10}$)-*network*	4.3	5.2	9.9	1.9	3.9
(DMAEMA$_{50}$-*star*-DMAEMA$_{10}$)-*network*	5.5	5.5	22.4	3.0	7.1
(DMAEMA$_{20}$-*star*-DMAEMA$_{50}$)-*network*	3.5	5.6	36.0	2.6	7.1
(DMAEMA$_{50}$-*star*-DMAEMA$_{20}$)-*network*	15.5	5.7	23.1	2.3	6.2

at least for linear chains. However, this is difficult to confirm experimentally for star polymers, and definitely beyond the scope of this work. The 51 arms determined for the "arm-first" star polymer compare favorably with the number of arms of other "arm-first" star polymers synthesized by GTP, anionic, and "living" cationic polymerization which were found (by SLS) to be 15−40,[10] 5−20,[33−35] and 5−20,[26,36−38] respectively.

Swelling Behavior of Hydrogels in Water. After synthesis all networks were washed in THF to remove the sol fraction, which is shown in Table 2, and in most cases is less than 6%. Subsequently, the degrees of swelling (DSs) of the networks, defined as the wet divided by the dry network mass, were determined in water as a function of pH and in THF. Figure 4 shows the aqueous DSs and the degrees of ionization (calculated as the number of HCl equivalents added divided by the number of DMAEMA equivalents in the sample) of the cross-linked star polymers as a function of the solution pH. All networks exhibit a large increase in the DS at pH values below 8. This increase is attributed to the ionization of DMAEMA residues below this pH, because of the increase in the osmotic pressure created within the gel by the counterions to the charged monomer repeat units and the electrostatic repulsion between the positively charged chains.[24,25,39−42] The DS curve does not follow closely that of the degree of ionization, but the former curve rises more sharply than the latter by decreasing the pH. This is due to the very large increase in DS on first ionizing the gel (degree of ionization ~10%). At this point there is a change in the balance of the dominant forces affecting the network equilibrium. In particular, the mixing and electrostatic energies determine the swelling properties of slightly ionized gels (ionization <10%), whereas the balance between the electrostatic and elastic components governs the behavior of more extensively ionized gels. This phenomenon has been observed both theoretically[43,44] and experimentally[45,46] and is responsible for the discontinuous swelling of gels.[12] All ionized (>10%) homopolymer gels break into small pieces of size ~1 mm below pH 8, in agreement with previous observations.[24,47] This has been attributed to the strong electrostatic repulsion, which causes the rupture of the backbone carbon−carbon bonds. This breakage of the gels can lead to an overestimation of the actual DSs because of water entrapment between the gel pieces. The decrease in the DS of the networks below pH 2 is due to the high ionic strength of the solution at this pH conferred by the relatively high hydrochloric acid concentration, which results in charge screening in the gel.[48] At high pH values (pH > 8) where DMAEMA is not ionized, low DSs are obtained, as expected.

Table 2 also shows the measured effective p*K* values of the homopolymer cross-linked stars and their minimum and maximum DSs at high and low pH values, respectively. The DS in THF is also listed for each network. The effective p*K*s were taken as the pH values at 50% ionization with an uncertainty in their determination of ±0.2, slightly greater than the accuracy of the pH meter of 0.1. p*K* values of about 5.5 were measured which do not vary significantly with the chain lengths, similar to our previous work on DMAEMA homopolymer model networks which exhibited p*K*s of about 5.2.[24] The gel p*K*s are lower than that obtained for linear (not cross-linked) poly(DMAEMA) because of counterion partitioning in the gel phase.[49]

Table 2 shows that the aqueous DSs at high pH values, where DMAEMA is not ionized, are much lower than the corresponding ones at low pH values where DMAEMA is fully charged. Moreover, alkaline and acidic aqueous DSs increase with both the elastic and dangling chain length. This is illustrated in Figure 5 for the acidic DSs, which are plotted as a function of the DP of the elastic chain, with the DP of the dangling chain as a parameter. The trends in the figure are similar to those observed in DMAEMA model networks without dangling chains of similar DP of the elastic chains,[24] although the DSs of the latter type of gels were lower because of the absence of the dangling chains. To assess the relative importance of dangling and elastic chain lengths, we compare the DSs at low pH of two isomeric gels, (DMAEMA$_{20}$-*star*-DMAEMA$_{50}$)-*network* and (DMAEMA$_{50}$-*star*-DMAEMA$_{20}$)-*network* (Table 2). The network with the longer elastic chain swells more, because, although both the dangling and elastic chains

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(35) Grayer, V.; Dormidontova, E. E.; Hadziioannou, G.; Tsitsilianis, C. *Macromolecules* **2000,** *33*, 6330−6339.

(36) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992,** *25*, 6414−6418.

(37) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993,** *26*, 254−259.

(38) Kanaoka, S.; Sawamoto, M.; Higashimura, T.; Won, J.; Pan, C.; Lodge, T. P.; Fujiwara, M.; Hedstrand, D. M.; Tomalia, D. A. *J. Polym. Sci., Part B: Polym. Phys.* **1995,** *33*, 527−535.

(39) Siegel, R. A.; Firestone, B. A. *Macromolecules* **1988,** *21*, 3254−3259.

(40) Costa, C. N.; Patrickios, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **1999,** *37*, 1597−1607.

(41) Hadjiyannakou, S. C.; Yamasaki, E. N.; Patrickios, C. S. *Polymer* **2001,** *42*(22), 9205−9209.

(42) Vamvakaki, M.; Yamasaki, E. N.; Hadjiyannakou, S. C.; Patrickios, C. S. *Macromol. Symp.* **2001,** *171*, 209−224.

(43) Dušek, K.; Patterson, D. *J. Polym. Sci.* **1968,** *6A-2*, 1209.

(44) Vamvakaki, M.; Patrickios, C. S. *J. Phys. Chem. B* **2001,** *105*(21), 4979−4986.

(45) Tanaka, T. *Phys. Rev. Lett.* **1978,** *40*, 820−823.

(46) Tanaka, T.; Fillmore, D.; Sun, S.-T.; Nishio, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980,** *45*, 1636−1639.

(47) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp. 584−589.

(48) Ricka, J.; Tanaka, T. *Macromolecules* **1984,** *17*, 2916−2921.

(49) Philippova, O. E.; Hourdet, D.; Audebert, R.; Khokhlov, A. R. *Macromolecules* **1997,** *30*, 8278−8285.

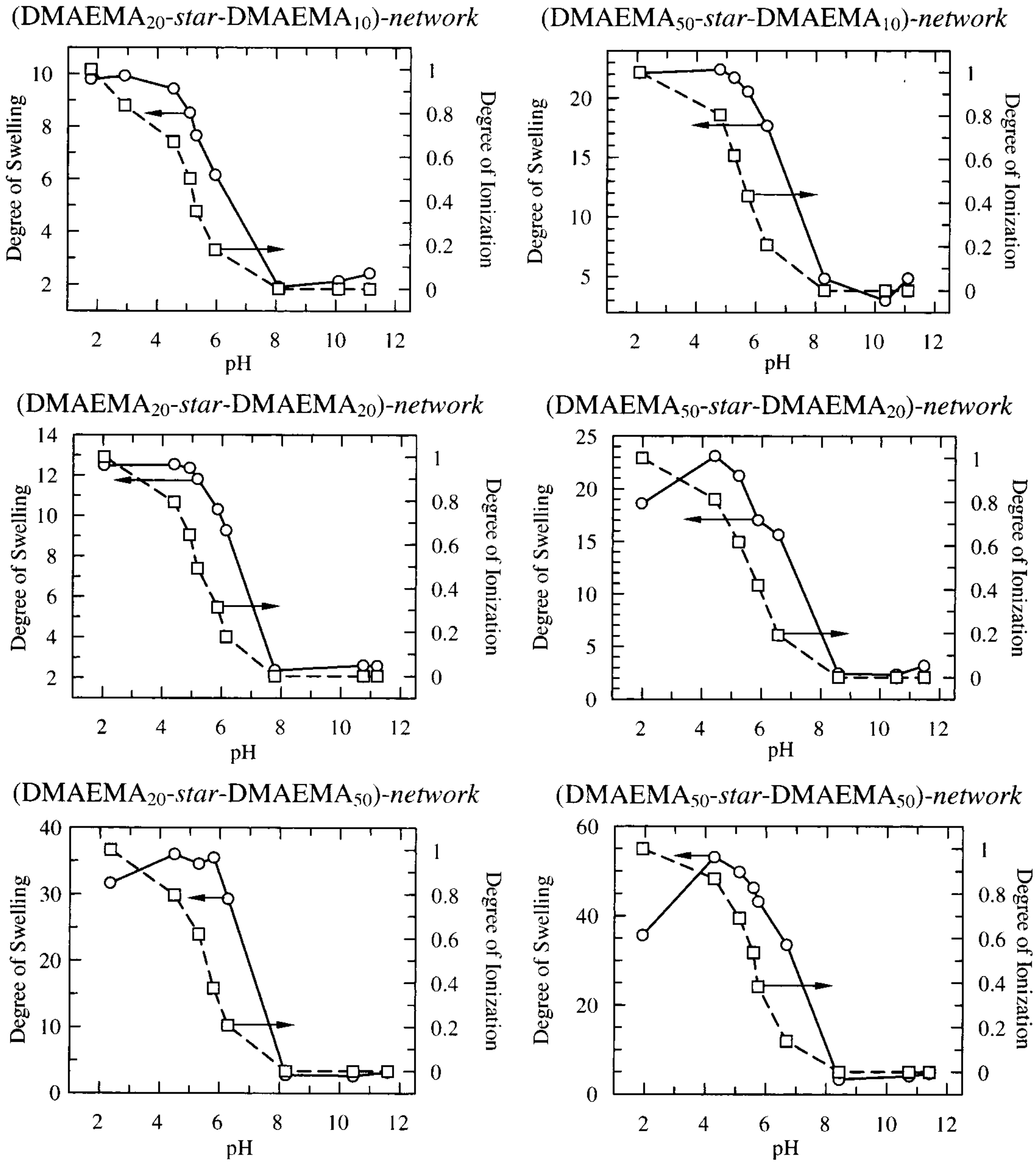

Figure 4. Aqueous degrees of swelling and degrees of ionization of all the homopolymer cross-linked stars as a function of the solution pH.

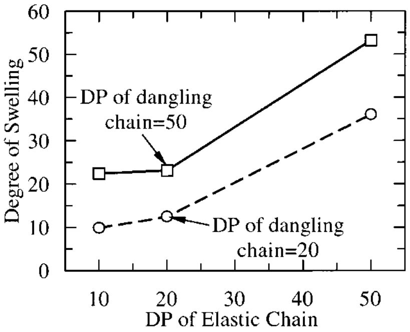

Figure 5. Dependence of the maximum degrees of swelling of the homopolymer cross-linked stars on the elastic chain lengths, with the DP of the dangling chains as a parameter.

contribute counterions and repulsion to the system, it is the elastic chain length that prevents the gel from swelling indefinitely and determines the limiting DS.

The DSs in THF are also shown in Table 2. These values are intermediate between those in acidic and alkaline water. In particular, the DSs in THF (unionized gels) are lower than those of the ionized gels in water at low pH, but they are higher than the ones in water at high pH (nonionized) because THF is a better solvent for DMAEMA than alkaline water. The latter result is not surprising considering that linear DMAEMA homopolymer is marginally soluble in water at high pH, having a lower critical solution temperature of 40 °C.[50]

Conclusions

We have used GTP to prepare a complex network structure, that of cross-linked star homopolymers with an approximately equal number of dangling and elastic chains. The DP of the dangling chains (primary arms) can be lower than, equal to, or even greater than that

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(50) Baines, F. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1996,** *29,* 3416–3420.

of the secondary arms. The aqueous degree of swelling of all the networks synthesized was measured and found to be affected by the solution pH, the length of the elastic and dangling chains, and the solvency (THF vs water). Thus, network structure design is shown to be critical for the swelling properties of the gel.

Future work will involve the preparation of cross-linked star copolymers, in which the precursors can be either heteroarm star polymers or star-block copolymers. In both cases, combination of a hydrophilic with a hydrophobic monomer will lead to novel amphiphilic network structures.

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