Characterization of Hydrophilic Networks Synthesized by Group Transfer Polymerization

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SUMMARY: Group transfer polymerization was used to synthesize several series of hydrophilic random and model networks. Cationic random networks were prepared both in bulk and in tetrahydrofuran (THF) using a monofunctional initiator and simultaneous polymerization of monomer and branch units, while a bifunctional initiator was employed in THF for the synthesis of model networks comprising basic or acidic chains. Upon polymerization of the monomer, the latter initiator gives linear polymer chains with two "living" ends, which are subsequently interconnected to a polymer network by the addition of a branch unit. Homopolymer network star polymers were also synthesized in THF by a one-pot procedure. The synthesis involved the use of a monofunctional initiator and the four-step addition of the following reagents: (i) monomer, to give linear homopolymers; (ii) branch unit, to form "arm-first" star polymers; (iii) monomer, to form secondary arms and give "in-out" star polymers; and, finally (iv) branch unit again, to interconnect the "in-out" stars to networks. Different networks were prepared for which the degree of polymerization (DP) of the linear chains between junction points was varied systematically. For all networks synthesized, the linear segments, the "arm-first" and the "in-out" stars were characterized in terms of their molecular weight (MW) and molecular weight distribution (MWD) using gel permeation chromatography (GPC). The degrees of swelling of both the random and model networks in water were measured and the effects of DP, pH, and monomer type were investigated.

Introduction

Hydrogels[1,2] are network hydrophilic polymers with a variety of modern applications, including actuators, valves, sensors, controlled-release systems for drugs, artificial muscles for robotics, chemical memories, optical shutters, and molecular separation systems.[3] Most hydrogels are randomly formed networks with an extremely broad distribution of the length of segments between junction points.[4] A control of the length distribution of the segments between junction points has been achieved by the use of "living" polymerization techniques, such as anionic polymerization, and the resulting networks are called the model networks.[5] The preparation and study of model hydrogels can provide a better understanding of their properties and can assist in the design of optimal hydrogels for a given application.

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Following our previous work in this area,[5] in the present study we report on the synthesis of hydrogels of various structures by using the group transfer polymerization (GTP).[6-8] Several series of randomly formed and model homopolymer networks were prepared, covering a range of polymer chain lengths between junction points. The networks were characterized in terms of their degree of swelling in aqueous media as a function of network structure, monomer type, elastic chain length, and solution pH. Finally, networks of a more complicated structure, namely cross-linked star polymers, of various lengths of the primary and secondary arms were synthesized using the same polymerization method. Characterization of the degree of swelling of these network star polymers is underway.

Experimental

Materials

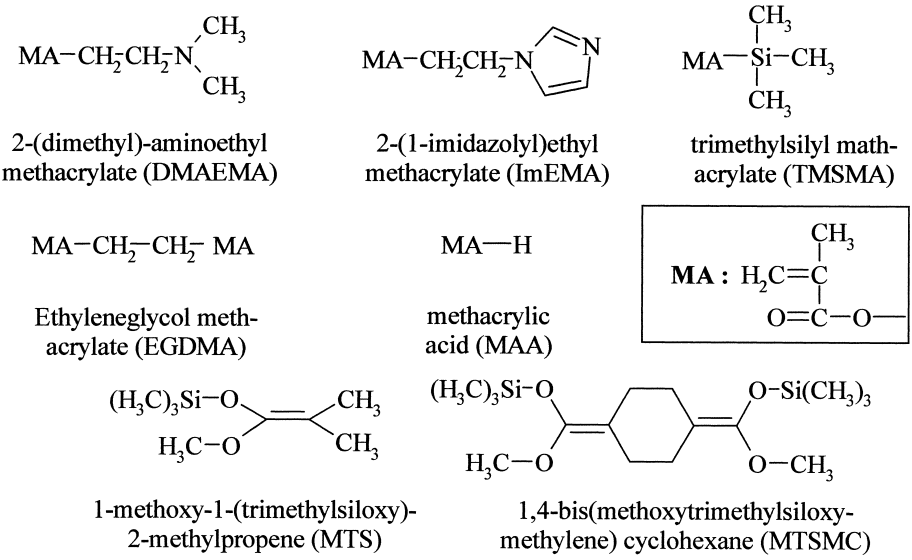

Fig. 1: Chemical formulas and names of the reagents (monomers, branch monomer, initiators) used for the network syntheses.

All chemicals were purchased from Aldrich, Germany. Fig. 1 shows the chemical formulas and names of the reagents used for the network syntheses: the monomers, 2-(dimethylamino)ethyl methacrylate (DMAEMA), 2-(1-imidazolyl)ethyl methacrylate (ImEMA), trimethylsilyl methacrylate (TMSMA), methacrylic acid (MAA), the branch monomer, ethylene

glycol dimethacrylate (EGDMA), and the initiators, 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS) and 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane (MTSMC).

All the chemicals are commercially available except for the ImEMA monomer and the MTSMC initiator, which were synthesized in our laboratory. The ImEMA monomer synthesis[9-11] involved a two-step procedure: the reaction of imidazole with excess of ethylene carbonate in refluxing toluene at 110°C to give 2-imidazol-1-yl-ethanol at 50 % yield, followed by the reaction of 2-imidazol-1-yl-ethanol with methacryloyl chloride (10% excess) to give ImEMA monomer at yields above 90%. The MTSMC initiator was synthesized[12-14] by the reaction of dimethyl 1,4-cyclohexanedicarboxylate with diisopropylamine and butyllithium in absolute tetrahydrofuran at –78 °C, followed by the silylation with trimethylsilyl chloride under the same conditions.

The THF solvent was dried by refluxing it over potassium for three days. Due to the insolubility of poly(ImEMA) in THF which is the most common GTP solvent, propylene carbonate was used for the synthesis of the ImEMA homopolymer networks. This solvent was dried over calcium hydride and distilled prior to use. The polymerization catalyst, tetrabutylammonium bibenzoate (TBABB), was in-house synthesized by the method of Dicker et al.[8] TMSMA was used as a protected monomer for MAA. Thus, TMSMA was polymerized to obtain the corresponding model network, which then spontaneously hydrolyzed in water to yield the poly(MAA) model network.

Methods

All glassware was dried overnight at 120 °C and assembled hot under dynamic vacuum prior to use. The polymerizations were carried out in 15 mL cylindrical glass vials 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 (when required) was subsequently transferred directly from the still into the reactor via a syringe. The monomers and the branch monomer, EGDMA, 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. All monomers and the cross-linker were freshly distilled under vacuum and kept under dry nitrogen atmosphere prior to use. The initiators were

distilled once prior to polymerization. The dried catalyst powder was stored in a round-bottomed-flask under vacuum until used.

Characterization by GPC in THF

Molecular weights (MWs) and molecular weight distributions (MWDs) of the linear polymer precursors to the model networks were determined by gel permeation chromatography (GPC) using a single Polymer Laboratories PL-Mixed 'E' column. For the linear, "arm-first" star, and "in-out" star precursors to the network star polymers, a single high molecular weight Polymer Laboratories PL-Mixed 'D' column was used instead. The mobile phase was tetrahydrofuran (THF, flow rate 1 mL min^{-1}), delivered using a Polymer Laboratories PL-LC1120 isocratic pump. The refractive index signal was measured using a EGC-7515A refractive index detector supplied by Polymer Laboratories. For the linear polymer precursors to the model networks the calibration curve was based on six narrow MW (1400, 2400, 4250, 7600 and 22650) linear poly(methyl methacrylate) standards and provided accurate MW calculations. For the linear, "arm-first" star, and "in-out" star precursors to the cross-linked star polymers, a different calibration curve was used based on seven narrow MW (630, 4250, 13000, 28900, 50000, 128000 and 260000) linear poly(methyl methacrylate) standards. The calibration provided good estimates for MWs of linear polymers but only qualitative estimates for star polymers.

Swelling Degree

The gels were removed from the glass polymerization vials, cut into small cubes of size 5–10 mm and thoroughly washed free of THF by placing them in bottles containing distilled water for four weeks and changing water every 2–3 days. The water-swollen cubes were then weighed. The degree of swelling was determined by vacuum drying gel samples overnight and determining the dry gel masses. Subsequent swelling experiments at different pHs involved re-equilibration of the gels in water after introducing appropriate volumes (typically several drops) of 0.5 M HCl or 0.5 M NaOH. The solution pH and gel mass were determined three weeks later. All degrees of swelling were determined in triplicate and the averages of the measurements are presented. The size of error bars is slightly greater than the size of symbols used in the plots.

Results and Discussion

Random DMAEMA Networks Prepared in the Bulk[15)]

For the synthesis of random DMAEMA networks in the bulk the reagents used were TBABB catalyst, DMAEMA monomer, EGDMA branch monomer and MTS monofunctional initiator, added in this order. A typical polymerization procedure yielding a network with a monomer to initiator ratio of 100 (nominal DP 100) is detailed as follows. To a 15 mL glass vial containing ≈ 5 mg TBABB catalyst (10 μmol) and a stirring bar, 8.4 mL DMAEMA (50 mmol) were added via a glass syringe, followed by the addition of 0.75 mL (4 mmol) EGDMA. To this was rapidly added under stirring 0.1 mL MTS (0.5 mmol). The mixture gelled within seconds, as manifested by the immobilization of the stirring bar. This synthetic strategy for the preparation of random networks is similar to that employed for the synthesis of randomly formed hydrogels[1)] using free radical polymerization, in which the monomer and branch monomer are polymerized simultaneously. This procedure gives networks in which the chain length distribution between junction points is broad as opposed to the narrow distribution of precise chain lengths obtained from the synthesis of model networks (see later). Compared to the homopolymer random networks prepared in THF (see later) the present synthesis is expected to give a network structure with more defects (e.g. chain entanglements), due to the close proximity of growing polymer segments from different parts of the network during synthesis in bulk.

A series of homopolymer random networks were prepared in bulk with monomer to initiator molar ratios of 5, 10, 20, 50, 100 and 200. The present approach requires only a monofunctional initiator which is commercially available as opposed to the bifunctional initiator (not commercially available), which was used for the synthesis of model homopolymer networks (see later). This is a clear advantage of the method in cases when control over the network structure is not essential.

The number of moles of branch units used was eight times the number of the MTS initiator. Since EGDMA is a divinyl compound, it acts as a tetrafunctional branch point, with two of the four arms belonging to the same chain. This implies that the presence of "half" a EGDMA molecule in a network chain reduces its nominal DP (calculated from the molar ratio of

monomer to initiator) by a factor of 2. One "whole" (= two "halves") EGDMA molecule would reduce the nominal DP by a factor of 3. With 8 EGDMA molecules per initiator molecule, the total reduction factor would be 1/(2×8+1) =1/17. Thus, the nominal DPs of the chains must be divided by 17 to estimate the average number of DMAEMA units (DPs) between junction points. In a more precise approach, one should also take into account possible dangling (semi-attached) chains and unattached chains. The distribution of junction points within the network will create a greater number of elastic segments in the sample compared to the case of model networks (see later), in which four branch units are placed consecutively per "living" polymer end. Thus, based on the distribution of lengths between junction points, the randomly formed networks of this study are expected to swell less than the corresponding model networks (see later). Also, based on the very high initial polymer volume fraction for the networks prepared in the bulk they are expected to swell less than their analogues prepared in THF.

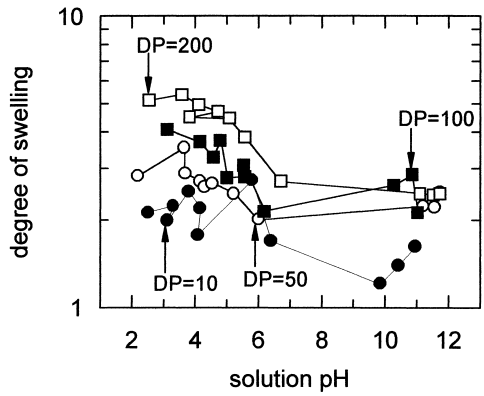

Fig. 2: pH-dependence of the aqueous degree of swelling of the DMAEMA homopolymer randomly cross-linked networks prepared in the bulk.

Fig. 2 shows the aqueous degrees of swelling of the networks synthesized in the bulk with nominal DPs 10, 50, 100 and 200 as a function of solution pH, without added salt. All gels are shrunk in pure water (pH ≈ 6) and alkaline conditions (pH > 7), but swell under acidic conditions (pH < 5). This increase in the degree of swelling at lower pH values is attributed to the ionization of the DMAEMA monomer units, which is a weak base. This ionization results in the repulsion between the charged polymer segments and also causes an increase in the osmotic pressure within the gel due to the counterions to the protonated tertiary amine repeat units, leading to the swelling of the gel. To examine how ionization affects the degree of swelling, we performed hydrogen ion titration on the networks and determined their effective pK, which is the pH at 50% ionization. The pKs were found to be around 4.5, consistent with the onset of swelling below pH 5 observed in Fig. 2. The low pK values measured for the gels as compared to the pK value of 8.6 for the DMAEMA monomer and the effective pK of 7.1 determined for linear

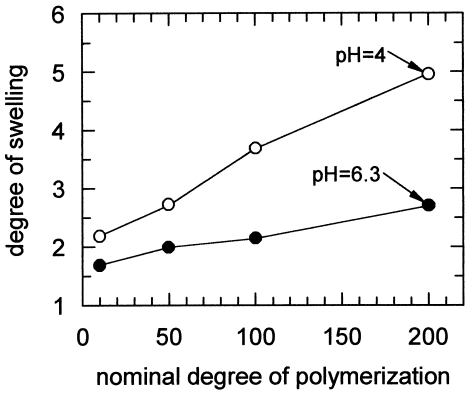

Fig. 3: Dependence of the aqueous degree of swelling of the DMAEMA homopolymer randomly cross-linked networks prepared in the bulk on the monomer to initiator molar ratio.

DMAEMA homopolymers can be attributed to the stronger electric field on the polymer than on the monomer, and to counterions partitioning into the gel phase.[16)]

Fig. 3 shows the degrees of swelling of the random networks in the absence of added salt as a function of the nominal DP and at two different pH values, 4 and 6.3. At both pHs the degree of swelling increases with the nominal DP. This is attributed to the reduction of the junction point density with the increase in the DP of the chains between junction points. In addition, the degrees of swelling at pH 4 are higher than those at pH 6.3 due to the DMAEMA ionization at the former pH value, as discussed earlier.

It should be noted that the degrees of swelling of the networks prepared in the bulk are remarkably low, with 5 being the highest value. These values are much lower than those for both the random and the model DMAEMA networks prepared in THF (see later) due to the high polymer volume fraction (equal to 1) during synthesis in bulk, which prevents chain extension, and also introduces chains entanglements, which further restrict swelling.

Random DMAEMA Networks Prepared in THF[17)]

The synthesis of these networks followed a similar procedure to that used to synthesize the random DMAEMA networks prepared in bulk with the difference that THF solvent was charged to the reaction flask before the addition of the DMAEMA monomer, the EGDMA branch monomer and the MTS initiator. Again, the number of moles of EGDMA used was eight times the number of moles of the initiator. The simultaneous polymerization of monomer and branch monomer results in a broad distribution of chain lengths between junction points. This distribution is similar to that for the random networks prepared in bulk (see earlier) and differs from the narrow chain length distribution obtained from the synthesis of model networks (see later). The networks prepared by the present approach are also expected to have fewer defects than bulk networks as well as higher degrees of swelling due to the lower initial polymer volume fraction in THF. A series of DMAEMA homopolymer

random networks were prepared in THF with monomer to initiator molar ratios of 5, 10, 20, 50, 100 and 200.

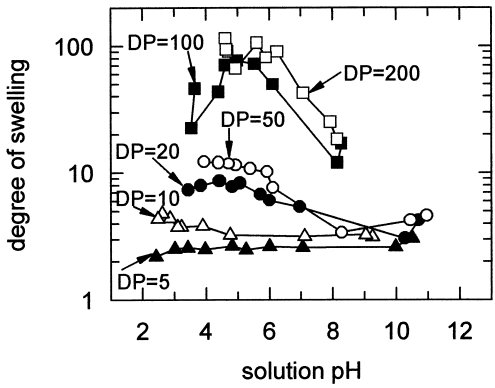

Fig. 4: pH-dependence of the degree of swelling of DMAEMA randomly cross-linked networks prepared in THF.

Fig. 4 shows the degrees of swelling of the random networks prepared in THF with nominal DPs 5, 10, 20, 50, 100 and 200 as a function of the solution pH. Similar to the random networks synthesized in bulk, these gels are shrunk at and above pH 7, but exhibit a gradual increase of swelling degree when pH is lowered. This is again attributed to the ionization of the DMAEMA units at acidic pH, which creates repulsion between the chains and also leads to an increase in the osmotic pressure within the network. The titration curves of the networks give an effective pK of around 5.5, consistent with the onset of swelling of the gels below pH 7.

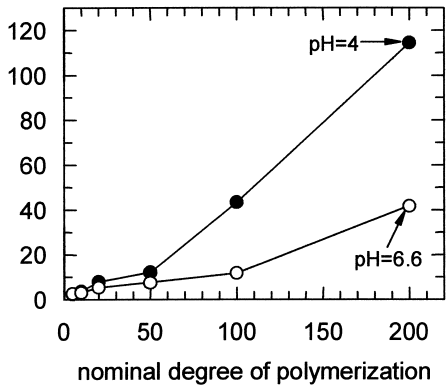

Fig. 5: Dependence of swelling degree of DMAEMA randomly cross-linked networks prepared in THF on the monomer to initiator molar ratio.

Fig. 5 illustrates the degree of swelling of the networks as a function of the nominal DP and for two different pH values, 4 and 6.6. Similar to the random networks prepared in the bulk, an increase in the degree of swelling with the nominal DP is observed, attributed to the decrease of junction point density with the nominal DP of network chains. The higher degrees of swelling at pH values lower than 4 compared to those at pH 6.6 are consistent with the ionization of the DMAEMA repeat units at acidic pH.

All random networks prepared in THF exhibit much higher degrees of swelling than those of their analogues prepared in bulk. As

expected, the very high polymer volume fraction during synthesis in bulk, prevents the subsequent extensive increase in the degree of swelling. However, compared to the homopolymer model networks prepared in THF, the present random networks exhibit similar degrees of swelling, suggesting that the network structure has little effect on this property.

Homopolymer[11,14] Model Networks Prepared in THF

The synthetic procedure for the preparation of model networks employed the use of the MTSMC bifunctional initiator to sequentially polymerize the monomer(s) and the branching monomer, and to produce near-model networks, in which the chains between junction points were of uniform length, but the number of arms at the junctions followed a Poisson distribution. The syntheses involved the use of an 8-fold molar excess of EGDMA with respect to the initiator, equivalent to a 4-fold molar excess with respect to the initiator's active sites, as determined in our previous work,[14] in which the synthesis of DMAEMA star homopolymers was optimized. A typical polymerization procedure is described below. It yields a DMAEMA model network with 100 monomer repeat units of DMAEMA.

Table 1: MW characteristics of the precursors to the model networks.

Sample	Theory		Observed by GPC[c]	
	Formula[a]	MW[b]	M_n	M_w/M_n
MS188	$DMAEMA_{10}$	1766	1977	1.35
MS189	$DMAEMA_{20}$	3336	4643	1.15
MS190	$DMAEMA_{50}$	8046	6866	1.12
MS191	$DMAEMA_{100}$	15896	13450	1.10
MS192	$ImEMA_{10}$	1996		
MS193	$ImEMA_{20}$	3796		
MS194	$ImEMA_{50}$	9196		
MS195	$ImEMA_{100}$	18196		
MS178	$TMSMA_{20}$	3356		
MS177	$TMSMA_{35}$	5726		
MS180	$TMSMA_{50}$	8096		
MS179	$TMSMA_{100}$	15996		

[a]Number of monomer units.
[b]Weight from initiator fragment (196 g mol^{-1}) included.
[c]In THF using PMMA MW standards.

MTSMC (0.05 mL, 0.12 mmol) was added via a glass syringe to the polymerization vial, which contained 8 mL THF and 5 mg TBABB (10 μmol). Subsequently, 2.0 mL of freshly distilled DMAEMA (12 mmol) was slowly syringed into the vial. The reactor temperature

quickly rose from 22.0 to 37.6 °C. After 5 minutes the exotherm abated and a 0.1 mL aliquot of the reaction solution was extracted for GPC analysis. Next, 0.19 mL EGDMA (0.96 mmol, 8-fold molar excess with respect to the initiator) was added and the temperature increased from 30.8 to 32.1°C, with the concomitant gelation of the solution.

Table 1 shows the model networks prepared using this method and the results of the GPC characterization of the linear polymer segments before network formation. Three different homopolymer families have been prepared. The monomer type (basic, nucleophilic and acidic) and the degree of polymerization of linear chains between junction points were varied systematically. The GPC data confirm the homogeneity in lengths of the network chains as narrow molecular weight distributions were obtained for all DMAEMA model networks (M_w/M_n < 1.2), and the average molecular weights were close to the theoretical ones. GPC analysis of the chains between junction points for the ImEMA networks was not possible due to the insolubility of poly(ImEMA) in the eluent THF. TMSMA network precursors were also not analyzed by GPC due to the spontaneous hydrolysis of the TMS groups to yield poly(MAA) which also has a low solubility in THF.

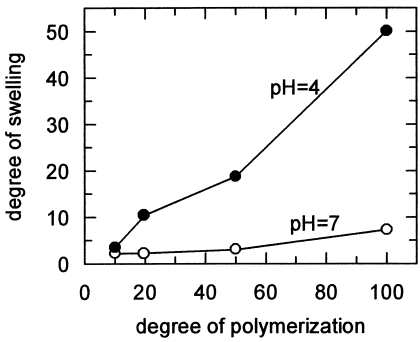

Fig. 6a: Dependence of swelling degree of DMAEMA homopolymer model networks on the DP between junction points.

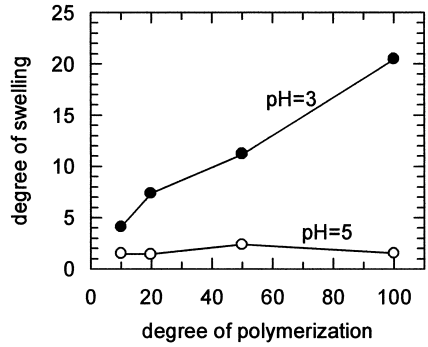

Fig. 6b: Dependence of swelling degree of ImEMA homopolymer model networks on the DP between junction points.

In Figures 6a, b and c, the aqueous degrees of swelling of the three homopolymer series, DMAEMA, ImEMA and MAA, respectively, are plotted as functions of polymerization degree (DP) of the linear chains between junction points for two different pH values. When the networks are ionized, there is an increase in the degree of swelling with DP, consistent with the decrease of junction point density. The higher degrees of swelling at lower pH values

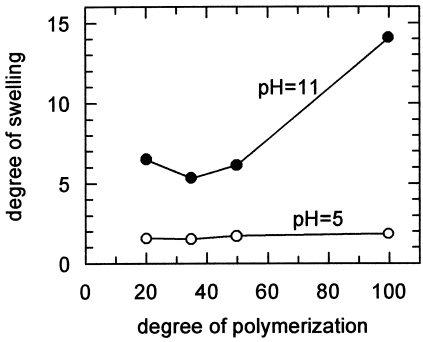

Fig. 6c: Dependence of swelling degree of MAA homopolymer model networks on the DP between junction points.

for the basic monomers, DMAEMA and ImEMA, are due to the ionization of the units under acidic conditions. ImEMA, being a weaker base than DMAEMA, is ionized only at a pH as low as 3. At pH 5, the ImEMA networks are collapsed, exhibiting a low degree of swelling. This behavior is consistent with the deprotonation of ImEMA units, which become hydrophobic when unionized, as manifested by the precipitation of linear poly(ImEMA) in water at pH above 5.8. Similar results are obtained for MAA networks. In this case, MAA, being an acidic monomer, is ionized at high pH values and becomes unionized when the pH is lowered.

At pH 4, the DMAEMA homopolymer model networks (Fig. 6a) swell only slightly more than their random counterparts (of the same nominal DP) prepared in THF (Fig. 5) despite the broad distribution of chain lengths between junction points of the latter. This result suggests that the network structure has only a small effect on the maximum degree of swelling, which is determined by the average (nominal) DP and polymer volume fraction during synthesis.

Network Star Polymers Prepared in THF[18)]

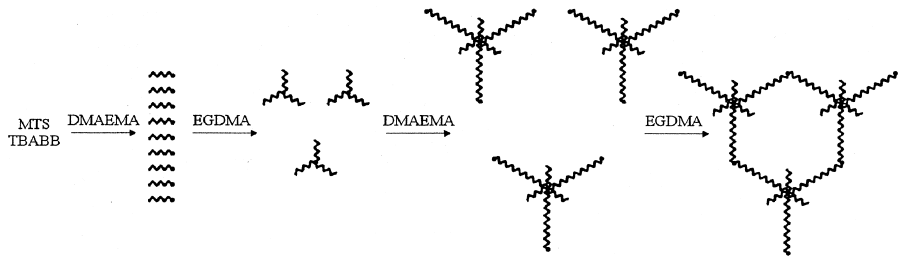

Fig. 7: Synthetic procedure for preparation of network star homopolymers, and possible structures of the network star copolymers.

Table 2: GPC characterization of the precursors to network DMAEMA stars.

Sample	Theoretical number of DMAEMA units	Theoretical MW	M_n by GPC	M_w/M_n by GPC	Peak MWs (M_ps)
1a	20	3319	2900	1.14	3390
1b	arm-first 20		11900	2.20	34650
1c	arm-first 20-in-out 20		17300	2.00	50450
2a	50	8035	8300	1.12	9020
2b	arm-first 50		18800	1.81	47960
2c	arm-first 50-in-out 50		29500	1.72	63360
3a	20	3319	4000	1.11	4100
3b	arm-first 20		18200	2.39	50230
3c	arm-first 20-in-out 10		24800	2.14	57740
4a	50	8035	10800	1.09	10860
4b	arm-first 50		33700	1.86	69520
4c	arm-first 50-in-out 10		45700	1.68	76280
5a	20	3319	3800	1.09	3730
5b	arm-first 20		14600	2.06	35950
5c	arm-first 20-in-out 50		55000	1.56	76530
6a	50	8035	12700	1.09	12000
6b	arm-first 50		36800	1.80	72290
6c	arm-first 50-in-out 20		51000	1.64	87010
7a	50	8035	12000	1.10	11330
7b	arm-first 50		41100	1.06	83360
7c	arm-first 50-in-out 1		45400	1.77	83360
7d	network(arm-first 50-in-out 1)		65900	3.04	151700

Networks comprising star polymers were also prepared. These materials are also model networks because the length of chains between junction points and the length of arms of the stars are both controlled. Unlike common model networks, whose preparation requires a bifunctional initiator, a monofunctional initiator was used for preparation of network star polymers. The synthetic procedure comprised a four-step sequential addition in one pot and is illustrated in Fig. 7. In the first step, the linear homopolymer chains, that are to form the primary arms of the stars and the dangling chains of the final network, are prepared upon addition of the first monomer. Next, EGDMA branch monomer is added to yield the "arm-first" star polymers, succeeded by the addition of monomer for a second time to lead to the formation of secondary arms of the "in-out" star polymers. The synthesis is concluded by the addition of EGDMA to induce the inter-connection of the "in-out" star polymers. The amount of the EGDMA used was 4 times the number of moles of the MTS initiator. The number of arms at the junctions is not 3 or 6, as indicated in Fig. 7, but much higher, probably between

20 and 50, due to the ability of EGDMA to be added repeatedly at the core bringing together a large number of chains.

As an example, we describe the synthesis of a "20-50" network having primary arms comprising of 20 DMAEMA units and secondary arms with 50 DMAEMA units. To a 100 mL round bottom flask containing a small amount (≈ 10 mg) of TBABB, 40 mL of freshly distilled THF and 0.2 mL MTS initiator (0.98 mmol) were syringed, in that order. Then, 3.3 mL DMAEMA (19.6 mmol) were slowly added under stirring. The polymerization exotherm (26–33 °C) abated within 5 minutes, samples for GPC, NMR and SAXS were extracted, and 0.74 mL EGDMA (3.94 mmol) were added which produced a new 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.

Table 2 shows the precursors to the network star polymers prepared and their GPC data. The relative lengths of the primary and secondary arms were varied systematically. Network formation was successful not only when the secondary arms were longer than the primary arms, but also when the secondary arms were equal in length or even shorter than the primary arms, suggesting that steric hindrances were weaker than expected. Gelation was prevented only when the secondary arm was one unit long (sample 7 in Table 2). Yet some interconnection of the stars occurred as manifested by the increase in the star molecular weight and PDI (sample 7d). The experimental measurement and theoretical calculation of the swelling degree of the network stars (Table 2) is underway and interesting results are expected.

The MWDs of all the linear polymers are low (M_w/M_n < 1.15) and their values of M_n are reasonably close to the theoretical MWs. For the "arm-first" star polymers the MWDs are broad and bimodal, containing amounts of unattached linear chains (≈15%) in addition to the stars that are also included in calculation of PDI for the main star peaks. These bimodal distributions together with the randomness of the network-forming process, which results in a broad distribution of the number of arms per star polymer, give the high PDI for the "arm-first" star polymers. Similarly broad and bimodal MWDs are also obtained for the "in-out" star polymers, but, as expected, they always have higher values of M_n than the "arm-first" stars. The corresponding peak MWs, M_p, also provided, exhibit the same trend, suggesting

that the whole distribution grows. It must me noted that the values of M_n determined by GPC for the star polymers are lower than the actual ones due to the compactness of the star structure compared to the linear MW calibration standards.[19)]

Conclusions

We have shown the facile GTP synthesis of different structures of homopolymer polyelectrolytic networks: randomly formed networks (both in bulk and in THF), model networks and model network stars. The degrees of swelling of the networks in water were measured and found to be affected by the pH, monomer type, MW between junction points, and polymer volume fraction during synthesis. An increase of the degree of swelling is observed upon ionization of the monomer repeat units, attributed to the electrostatic repulsions and the increase in the osmotic pressure within the gel due to the presence of counterions. The increase in the degree of swelling with nominal DP of network chains is due to the decrease of junction point density. Finally, a high polymer volume fraction during synthesis (i.e. in the bulk) prevents the subsequent extensive increase of the degree of swelling and such networks are more shrunk than their counterparts prepared at higher dilutions.

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