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Cationic homopolymer model networks and star polymers: synthesis by group transfer polymerization and characterization of the aqueous degree of swelling

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Abstract

A series of hydrophilic model networks based on homopolymers of a weak base were prepared using group transfer polymerization (GTP) and characterized in terms of their aqueous degree of swelling as a function of pH. This constitutes the first reported example of cationic hydrogels in which the length of segments between cross-links is kept constant. The synthesis involved the GTP of 2-(dimethylamino)ethyl methacrylate (DMAEMA, weak base monomer) in tetrahydrofuran (THF, solvent) using the bifunctional initiator, 1,4-bis(methoxytrimethylsiloxymethylene)-cyclohexane (MTSMC) and the subsequent in situ cross-linking with the addition of 8-fold mole excess with respect to the initiator of the difunctional monomer ethyleneglycol dimethacrylate (EGDMA). Four different model networks with degrees of polymerization (DP) of the linear segments between cross-links of 10, 20, 50 and 100 were prepared. The molecular weight (MW) and molecular weight distribution (MWD) of the linear segments were measured using gel permeation chromatography (GPC) in THF. The degree of swelling of all model networks was measured in water as a function of the solution pH. The conditions of gel synthesis were optimized with respect to cross-linker loading and monomer concentration using the results of a parallel study on the synthesis of star polymers of DMAEMA. The star polymers were also prepared by GTP of DMAEMA and linking (to stars) with EGDMA, but a monofunctional initiator, 1-methoxy-1-trimethylsiloxy-1-methyl-propene (MTS), was used rather than MTSMC. The star polymers were analyzed by GPC which revealed the percentage of free homopolymer relative to star polymer. The optimal conditions were identified as those under which the percentage of unlinked (free) homopolymer is minimized — the same conditions were adopted for the synthesis of the networks.

Keywords: Model networks; Gels; Hydrogels

1. Introduction

Cross-linked synthetic polymers are important materials which can be used in coatings and as structural materials [1]. When swellable in water, these materials are called hydrogels and related applications include uses as superabsorbents, artificial muscles (robotics), switches, actuators and drug delivery systems [2]. A growing number of studies on the synthesis of cross-linked polymers focuses on materials whose segments between cross-links are of precise size, called model networks [3]. Although these materials are more difficult and expensive to prepare than common cross-linked polymers, model networks are very important because they offer themselves for studies for the accurate determination of structure-property relationships.

There is only a small number of cross-linked polymers which are both model networks and hydrogels [3]. This is due to two factors: first, the interest of traditional polymer industry in water-incompatible materials and, second, the fact that the synthesis of water-compatible segments of precise MW is more difficult than that of water-incompatible segments. A special case of hydrogels is that based on polyelectrolytic segments, for which there are only two literature examples of model networks: one based on a weak acid, presented by Shefer and co-workers [4], and the other based on a weak base, presented by us [5].

This study is an extension of our previous work and describes the preparation and characterization of model hydrogels based on homopolymers of a weak base. The synthesis of the linear segments between cross-links was

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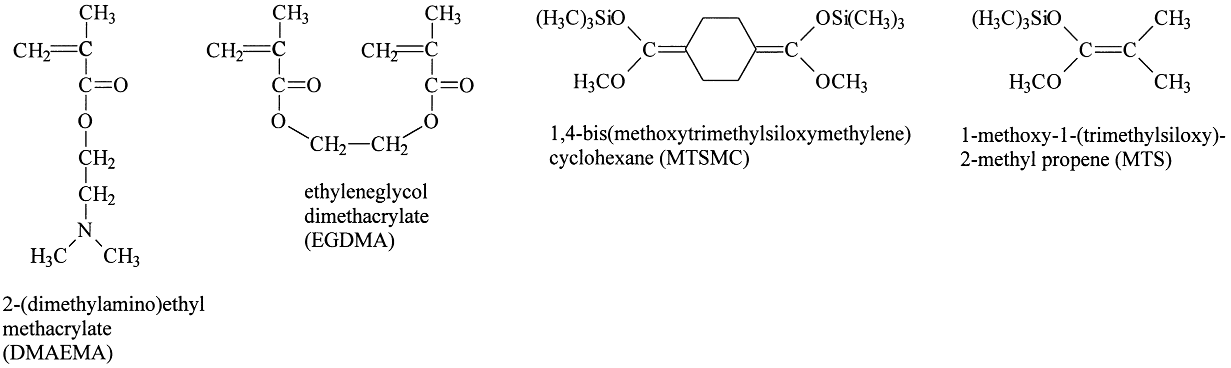

Fig. 1. Chemical formulas of the monofunctional methacrylate monomer, DMAEMA, the difunctional methacrylate monomer (cross-linker), EGDMA, and the two GTP initiators: the bifunctional MTSMC and the monofunctional MTS.

accomplished by the group transfer polymerization (GTP) [6–8] of 2-(dimethylamino)ethyl methacrylate (DMAEMA). A bifunctional initiator, 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane (MTSMC), was used for the network preparation, while the monofunctional initiator, 1-methoxy-1-(trimethylsiloxy)-2-methyl-propene (MTS), was used in preliminary experiments to prepare star polymers. Finally, the difunctional monomer, ethyleneglycol dimethacrylate (EGDMA), was the cross-linker used both for the network and star polymer formation. Fig. 1 shows the chemical formulas and names of all the above reagents.

2. Experimental

2.1. Materials

All the chemicals were purchased from Aldrich, UK.

Monomers: DMAEMA and EGDMA were commercially available.

Initiators: MTS was commercially available but MTSMC was in-house synthesized by the silylation of dimethyl 1,4-cyclohexanedicarboxylate, accomplished in a two step procedure [9]: the reaction of dimethyl 1,4-cyclohexanedicarboxylate with diisopropylamine and butyllithium in absolute tetrahydrofuran at −78°C, followed by the reaction of the mixture with trimethylsilyl chloride under the same conditions.

Catalyst: The polymerization catalyst was tetrabutylammonium bibenzoate (TBABB) and was synthesized by the reaction of tetrabutylammonium hydroxide with benzoic acid, according to Dicker et al. [8].

Polymerization solvent: The polymerization solvent was tetrahydrofuran (THF) which was dried by refluxing for three days over a potassium–sodium mixture.

2.2. 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 mg) of TBABB were transferred to the vial, which was immediately purged with dry nitrogen. Freshly distilled THF was subsequently transferred directly from the still into the vial via a glass syringe. DMAEMA and EGDMA were passed through basic alumina columns to remove inhibitors and protonic impurities. They were subsequently stirred over calcium hydride for three days in the presence of free-radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), and distilled under vacuum. They were stored over calcium hydride with added DPPH and distilled a second time prior to use. The initiators were distilled once prior to the polymerization, but they were neither contacted with calcium hydride nor passed through basic alumina columns because of the risk of hydrolysis. The dried catalyst powder was stored in a round-bottom flask under vacuum until use.

2.3. Synthesis

The gel syntheses involved the GTP of DMAEMA utilizing the MTSMC bifunctional initiator followed by the in situ polymerization of the EGDMA difunctional monomer (in an 8-fold molar excess with respect to the initiator, equivalent to a 4-fold molar excess with respect to initiator's active sites) which acts as a cross-linker. The star syntheses involved the GTP of DMAEMA utilizing the MTS monofunctional initiator followed by the in situ polymerization of the EGDMA difunctional monomer (in a 4-fold molar excess with respect to the initiator) which acts as a "microgel" formation agent. The reactions were carried out at ambient temperature (20°C) without thermostatting the polymerization reactor. The polymerization exotherm was monitored by a digital thermometer and was used to follow the progress of the reaction. A typical polymerization procedure is detailed below which describes the synthesis of gel MS191 with 100 monomer repeat units of DMAEMA between cross-links.

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 polymerization flask. 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. Subsequently, 0.19 mL of freshly distilled 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.

2.4. Characterization in organic solvents

GPC. Molecular weights (MWs) and molecular weight distributions (MWDs) of the linear polymer segments and of the star polymers were obtained by gel permeation chromatography (GPC) using a single Polymer Laboratories PL-Mixed ‘E’ column. 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 an ERC-7515A refractive index detector supplied by Polymer Laboratories. The calibration curve was based on six narrow MW (1400, 2400, 4250, 7600 and 22650 g mol^{-1}) linear poly(methyl methacrylate) standards supplied by Polymer Laboratories, which provided accurate MW calculations for the linear polyDMAEMAs but only qualitative estimates of the MWs of the DMAEMA star polymers.

^{1}H NMR spectroscopy. A Bruker 300 MHz instrument was used to acquire the proton NMR spectra of the bifunctional initiator and the star polymers in $CDCl_3$ using the residual non-deuterated solvent ($CHCl_3$) as an internal reference.

2.5. Characterization of the degree of swelling

The gels were taken out of the glass vial where polymerization and cross-linking took place by breaking the glass container after drawing a line on it with a diamond knife. The gels were then cut into smaller cubes of size 5–10 mm and were thoroughly washed from THF by placing them in bottles containing distilled, de-ionized water for four weeks and changing the water every 2–3 days. The mass of all water-swollen cubes was measured. The degree of swelling was determined by vacuum drying gel samples at 40°C and determining the dry gel mass. Subsequent swelling experiments at different pHs involved the re-equilibration of the gels in water after the addition of the appropriate volume (typically several drops) of solutions of 0.5 M HCl or 0.5 M NaOH and the measurement of the solution pH and gel mass one week later.

3. Results and discussion

3.1. Synthetic strategy

The synthesis of the linear segments between cross-links was accomplished by the GTP of DMAEMA, initiated by a bifunctional initiator which leads to polymer growth at both ends of the chain. Subsequently, cross-linking took place in situ by the polymerization of a difunctional methacrylate which led to the interconnection of the ends of the linear chains to a network. Although this method of synthesis precludes an exact number of chains per cross-link, it constitutes a very convenient procedure for gel synthesis which is not limited by requirements of exact stoichiometry between the cross-linker and the chain ends, as with the method of network formation from the reaction between multifunctional isocyanates and telechelic polymers, employed in our previous approach [5].

The preparation of gels using a bifunctional initiator and a difunctional monomer has already been employed with anionic polymerization [3,10], but, to the best of our knowledge, it is the first time it is applied with GTP. It is noteworthy, however, that bifunctional GTP initiators have been prepared and used for the synthesis of homopolymers [9] and linear symmetric ABA triblock copolymers [7,11].

3.2. Synthesis of star polymers

Model networks always have structural imperfections [3], including singly attached chains and loops, which are, however, difficult to characterize. In an effort to minimize these imperfections in our networks we performed preliminary studies on star polymers prepared by the same method as that used for the gels. The only synthetic difference was the use of a monofunctional rather than a bifunctional initiator used for the preparation of the gels. The molecular weight homogeneity of star polymers can be readily characterized using GPC because, unlike gels, star polymers are soluble. The GPC chromatograms of our star polymers exhibited two peaks, one due to the star polymer and the second due to some of the constituting linear polymer which had remained unattached (free arm). Incomplete incorporation of the linear polymers into the stars is due to increased solution viscosity, lower chain mobility and possible chain termination / chain transfer. We wish to stress at this point that, due to the use of linear calibration standards, the MWs determined by GPC are only rough estimates of the true MW of star polymers (SEC LALLS not yet available in our laboratory).

The unattached linear polymer contributes to the heterogeneity of the star polymer sample. The corresponding situation in networks would be chains attached only at one end or even totally unattached linear chains. Thus, we decided to identify the conditions under which the amount of free arm is minimized in the star polymers, and use these optimal conditions to prepare the networks. We investigated the effect of cross-linker to initiator loading, of monomer concentration and of linear polymer molecular weight on the relative sizes of the chromatographic peaks due to star polymer and to free arm.

Effect of cross-linker to initiator charge. This is a very

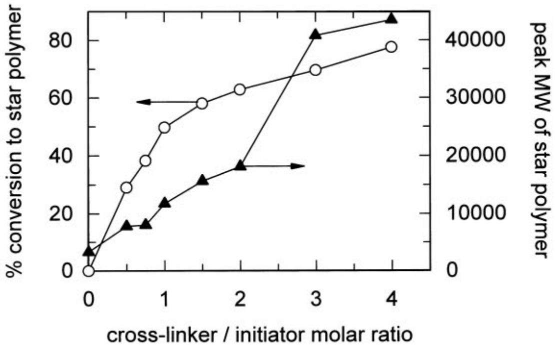

Fig. 2. Dependence of the percentage of star polymer and of the star polymer MW on the EGDMA/MTS molar ratio.

important quantity because it determines the average number of arms in a star polymer. Thus, for a linear polymer system initiated with a monofunctional initiator such as MTS and connected to star polymers using a di-vinyl cross-linker such as EGDMA, we should expect that when the EGDMA/MTS molar ratio is 0.5 (1:2) the linear polymers would dimerize (“star” polymer with two arms) because 1 EGDMA molecule (which is difunctional) corresponds to two linear chains [12]. When the EGDMA/MTS ratio is 0.67 (2:3), then, on the average, tri-arm star polymers will result. This can be rationalized by considering that the first (out of the two) EGDMA molecule will form a linear dimer with the 2 (out of 3) linear polymers, while the second EGDMA molecule will react with the third linear polymer. The remaining vinyl functionality of the latter species will combine with the dimer, giving a trimer (tri-arm star polymer). If the molar ratio of EGDMA-to-MTS is 1:1 (or greater than 1), then a network (gel) rather than a star polymer will form. This is so because each linear polymer will be connected, on the average, to one EGDMA molecule. This adduct will still have an available vinyl functionality to further react. Because every adduct has this extra reactive functionality, every linear chain will be able to react to another, eventually giving a network. The formula summarizing the above calculations is [12]:

$$\text{Number of arms in star polymer} = 1/(1 - \text{EGDMA/MTS}) \qquad (1)$$

In practice, however, the predictions of this simple formula are not precise due to the side-reactions of the polymerization process (e.g. chain transfer and termination reactions) on the one hand, and due to the statistics [5,10] of the cross-linking procedure (Poisson distribution on low numbers of cross-linker molecules), on the other. We illustrate the latter issue by giving an example. If one mole of linear chains reacts with one mole of EGDMA molecules, then Poisson statistics dictates that 36% of the chains would acquire zero EGDMA molecules, 36% would acquire 1 EGDMA molecule, 18% two EGDMA molecules, 6% three EGDMA molecules, 1.5% four EGDMA molecules etc. This distribution is created because a “living” chain can react with more than one EGDMA molecules, and because this combination procedure is random. Moreover, high EGDMA/MTS loadings rarely lead to network formation because the arms of the star polymers sterically prevent the interconnection of the cores of the star polymers (our “arms-first” synthetic procedure directs the “living” centers in the core of the star polymer).

Thus, a relatively high (greater than 1) EGDMA/MTS molar ratio is required to minimize the percentage of the unattached (to the EGDMA cross-linker) linear chains imposed by Poisson distribution statistics. Fortunately, this high ratio does not usually lead to network formation due to the steric hindrances mentioned above — network formation is observed when the degree of polymerization of the arms is low, generating poorer steric protection.

Fig. 2 presents the percentage of star polymer as a function of the EGDMA/MTS molar ratio. The second y-axis shows the peak MW (rough GPC estimate) of the star polymer. In these experiments, the arms had a degree of polymerization of 20 and the initial monomer concentration was 25%. The data in the figure suggest that the percentage of star polymer increases (and, therefore, the percentage of unattached arm decreases) with the EGDMA/MTS molar ratio, reaching 80% star polymer when the EGDMA/MTS molar ratio is 4. The curve in the figure is concave down, presenting a slow increase in the percentage of star polymer above an EGDMA/MTS molar ratio of 2. Thus, we considered that an EGDMA/MTS molar ratio of 4 is optimal for star polymer synthesis because the conversion to star polymer is sufficiently high. Higher cross-linker/initiator molar ratios would increase the conversion to star polymer but, at the same time, they would introduce more amount of hydrophobic cross-linker in the network. In their studies of star polymer synthesis by GTP, Simms and Spinelli also used a 4:1 EGDMA/MTS molar ratio [13,14]. These investigators also observed unattached arms whose percentage varied between 29 and 60% [14]. It is noteworthy that the preparation of star polymers by “living” cationic polymerization left no unattached arm (DP of arm = 40) [15], probably reflecting the greater “living” character of this method compared to GTP.

The elected 4:1 EGDMA/MTS molar ratio for star polymer synthesis corresponds to an 8:1 EGDMA/MTSMC molar ratio for network synthesis because one MTSMC molecule is equivalent to two MTS molecules (see Fig. 1). Thus, all networks of this study were prepared using an 8:1 cross-linker/initiator molar ratio.

The peak MW of the star polymers, also shown in Fig. 2, increases with the cross-linker/initiator ratio. The MW reaches 44000 when the cross-linker/initiator ratio is 4. Dividing by the arm MW of 3300, we can get a rough estimate of the average number of arms per star polymer which, in this case, comes out to be 13.5. Static light scattering measurements, however, have revealed that GPC underestimates the MW of star polymers which are more compact than their linear precursors [16]. A correction

Table 1
GPC Characterization of gel precursor polymers

Sample	Theory		Observed by GPC[a]	
name	Formula[b]	MW[c]	M_n	M_w/M_n
MS188	$DMAEMA_{10}$	1766	1980	1.35
MS189	$DMAEMA_{20}$	3336	4640	1.15
MS190	$DMAEMA_{50}$	8046	6870	1.12
MS191	$DMAEMA_{100}$	15896	13500	1.10

[a] In THF using PMMA MW standards.

[b] Number of monomer units.

[c] Weight from initiator fragment (196 g mol^{-1}) included.

factor of 2.5 has been proposed [14], which will raise the estimated number of arms from 11 to 33.5.

Effect of monomer concentration. It is known that the "livingness" of GTP increases with the monomer concentration. That is why the amount of monomer loaded in GTPs often reaches concentrations of up to 50%. Thus, we investigated star polymer formation at 50% monomer concentration. The results of this study were disappointing because, in most cases, undesired gel formation took place. This is probably due to the fact that there is excessive overlap between the "living" cores at these high concentrations, which leads to interconnection of the star polymers and gelation. If we prepare networks at this high monomer concentration, additional non-ideal connections between the cross-links (cores) would be probably formed, which would drastically reduce the degree of swelling. Thus, we kept the monomer concentration for network synthesis at the relatively low value of 25%.

More specifically, we studied two star polymer systems at 50% monomer concentration, one with an arm DP of 20 and the other with an arm DP of 100. For both systems, we varied the cross-linker to initiator molar ratio from 0.5 to 4. For the DP 20 system, we observed gelation for all values of cross-linker to initiator loadings. For the DP 100 system, we observed gelation in all cases except at the lowest loading of EGDMA/MTS of 0.5:1, at which point the star polymer formation was low, at 10%. This absence of gelation can be attributed to the better steric stabilization in the case of the stars with the longer arms (and to the smaller amount of EGDMA).

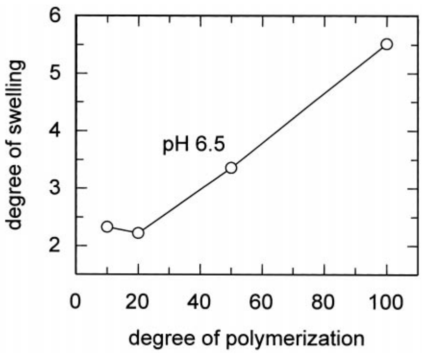

Fig. 3. Dependence of the aqueous degree of swelling of the model networks on the degree of polymerization of the linear segments between cross-links at pH 6.5 where the networks are uncharged.

Effect of polymer MW. Finally, we investigated the effect of the arm length on the quality of the star polymers. Thus, we prepared star polymers based on linear segments with DPs 5, 10, 20 and 50. The monomer concentration was about 15% and the EGDMA/MTS molar ratio was 4, in all cases. The smaller star polymer (DP 5) gave a gel because of the poor steric stabilization of the "living" core, as explained above. For the other cases, no gelation was observed but the amount of star polymer decreased from 87, to 82 and to 63% for the stars with arm DP of 10, 20 and 50, respectively. This is the expected trend: larger polymers confer a higher solution viscosity, have a lower chain mobility and are more prone toward chain termination due to lower initiator concentrations. Regarding the size of the linear segments, a practical limit for GTP is around a MW of 20000 (DP ~ 200), while a higher MW limit of 60000 has been observed for anionic polymerization [3].

3.3. Synthesis of networks

Table 1 displays the MW characteristics of the linear segments of the networks, as determined by GPC. The experimental number average MWs, M_ns, are close to the theoretical MWs expected from the monomer to initiator loadings. The polydispersity indices, M_w/M_n, decreased with the polymer MWs, which can be attributed to the reduced chain transfer for longer chains [17] or to the equilibrium between active and dormant species [18]. The monomer concentration and cross-linker to initiator ratio during network synthesis were those determined in the star polymer synthesis optimization study. Thus, the monomer concentration was kept at 25%, while the EGDMA/MTSMC molar ratio was fixed at 8:1.

3.4. Gel swelling in water

Fig. 3 shows the degree of swelling in pure water of the networks as a function of the degree of polymerization. The equilibrium solution pH was measured to be around 6.5 for all samples. Given the experimentally measured effective p*K* of all the gels of 5.2, the gels are not ionized in pure water (pH 6.5) [5], which is consistent with the fact that no acid has been added to the gels. For comparison, linear (not cross-linked) homopolyDMAEMA presents an effective p*K* of 7.4 [5].

The degree of swelling increases with the degree of polymerization, which can be attributed to the weaker retractive force in the case of the networks with segments of higher degrees of polymerization. A second contributing factor to this trend might be the lower percentage content in hydrophobic cross-linker in the networks of higher degree of polymerization. It is reminded that the molar ratio of

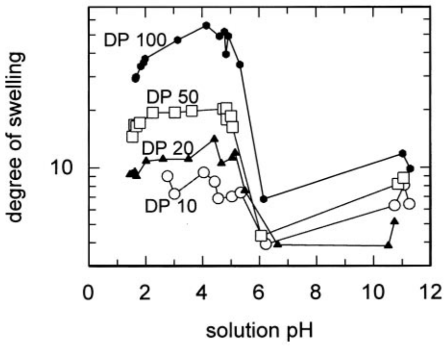

Fig. 4. Dependence of the aqueous degree of swelling of the model networks on the solution pH. Data for all four networks are shown, having linear segments between cross-links with degrees of polymerization 10, 20, 50 and 100.

cross-linker to initiator was kept constant for all networks. Thus, the network with the longest segments between cross-links contains the lowest percentage of cross-linker. The shape of the curve in the figure is a straight line (ignoring the point at DP 10), which is consistent with theoretical exponents of power-law fits of the degree of swelling versus degree of polymerization for uncharged networks, ranging from 0.6 [19] to 1.25 [20]. Experiments with poly(ethylene oxide) model networks in water and organic solvents also present an almost linear relationship between degree of swelling and degree of polymerization [21].

Fig. 4 shows the aqueous degrees of swelling of all gels as a function of the solution pH. The trends in the degree of swelling are dictated by the ionization behavior of the weakly basic tertiary amine units of DMAEMA which are uncharged at high pH but get charged at low pH. Above pH 6 the degree of swelling is almost constant and the same as that in pure water. In this pH region, the DMAEMA units are completely unprotonated and uncharged and the gels exhibit their minimum degree of swelling. In contrast, below pH 6, the degree of swelling increases due to the protonation and ionization of the DMAEMA units whose necessary counterions increase the osmotic pressure and lead to gel expansion. This behavior has also been observed in both polyelectrolytic model networks [4,5] and polyelectrolytic random networks [22].

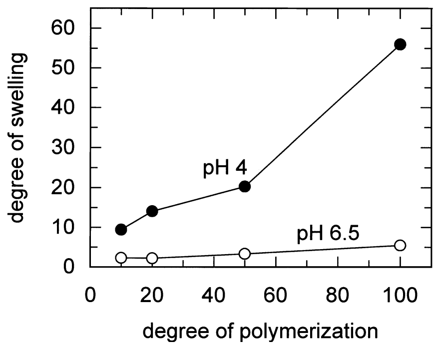

Fig. 5. Dependence of the aqueous degree of swelling of the model networks on the degree of polymerization of the linear segments between cross-links at pH 4 where the networks are fully ionized. The data at pH 6.5 are also shown.

We have observed that all gels below pH 6 break into small pieces of size ~1 mm (the original gel size is 5–10 mm). This has also been reported by Flory [23] on ionized poly(methacrylic acid) gels, who proposed that the strong electrostatic repulsion causes the rupture of the backbone carbon–carbon bonds.

Fig. 5 shows the dependence of the degree of swelling on the degree of polymerization of the linear segments between cross-links for the ionized networks ($\mathrm{pH} = 4$). For comparison, the degrees of swelling of the neutral networks ($\mathrm{pH} = 6.5$) from Fig. 3 are also plotted. As expected, the degree of swelling of the ionized networks also increases with the degree of polymerization. This dependence is almost linear, in good agreement with the results of Shefer and co-workers [4], and satisfactorily consistent with the theoretical exponent of 1.5 derived by Flory [23] for the aqueous swelling of networks in the absence of salt (as in our experiments).

Using the values of the degrees of swelling at pH 4 and assuming that, under these conditions, the chains are fully stretched (which can be realistic in this salt-free environment [23]), we can get a rough estimate of the average number of arms per cross-link in each network. Performing such a calculation for the system at hand, we derived the formula:

$$\text{Number of arms in network} = 0.1257 \times \mathrm{DP}^2/(\text{degree of swelling}) \qquad (2)$$

Thus, we estimated for the networks with linear segment DP 10 and 20 that the average number of arms per cross-link is 1.3 and 3.6, respectively, which are unrealistically low values. For the networks with segment DP 50 and 100, the estimated numbers of arms were 15.5 and 22.5, respectively, which must be compared with the value of 33.5 determined for star polymers using GPC (see Fig. 2).

4. Conclusions

Polyelectrolytic model networks based on homopolymers of DMAEMA were prepared by GTP. The synthesis involved the utilization of a bifunctional initiator for the formation of the linear segments, and the final addition of a difunctional monomer which acted as a cross-linker and promoted the interconnection of the linear segments to a network. To the best of our knowledge, the present work provides the first example of model network synthesis by GTP. Although anionic polymerization has been used in a similar way to prepare model networks, those products were never of a polyelectrolytic nature but most usually nonionic hydrophobic and more rarely nonionic hydrophilic. The aqueous degree of swelling of the DMAEMA networks was measured and found to exhibit the expected trends: it increased with the degree of ionization of the monomer repeat unit and with the degree of polymerization of the linear segments between cross-links. Future work will involve the preparation of homopolymer model networks based on different ionic monomers as well as the preparation of copolymer model networks.

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