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Randomly cross-linked homopolymer networks: synthesis by group transfer polymerization in solution and characterization of the aqueous degree of swelling

Stella C. Hadjiyannakou, Edna N. Yamasaki, Costas S. Patrickios*

Department of Chemistry, University of Cyprus, P.O. Box 20537, Nicosia 1678, Cyprus

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Abstract

Randomly cross-linked homopolymer networks of 2-(dimethylamino)ethyl methacrylate (DMAEMA) of various average degrees of polymerization (DPs) between cross-links were synthesized by group transfer polymerization (GTP) in tetrahydrofuran (THF), using 1-methoxy-1-(trimethylsiloxy)-2-methyl propene (MTS) as the initiator, ethylene glycol dimethacrylate (EGDMA) as the cross-linker (eight-fold molar excess with respect to the initiator), and tetrabutylammonium bibenzoate (TBABB) as the catalyst. Networks with monomer-to-initiator molar ratios of 5, 10, 20, 50, 100 and 200 were synthesized successfully, while an attempted synthesis with a monomer-to-initiator molar ratio of 500 did not produce a network. The networks were characterized in terms of their degree of swelling (DS) in water and the effects of DP, pH, salt concentration and temperature were investigated. Moreover, the aqueous degrees of swelling determined in this study of random networks were compared to the aqueous degrees of swelling of model networks also synthesized by GTP and using a similar procedure.

Keywords: Group transfer polymerization; 2-(dimethylamino)ethyl methacrylate; Hydrogels

1. Introduction

Synthetic hydrogels [1,2], cross-linked hydrophilic synthetic polymers (synthetic polymer networks), are versatile materials with a growing number of novel applications [3]. Despite their usefulness, the structure of most synthetic hydrogels is poorly controlled. Networks with controlled structure are called model networks [4] and, unlike conventional (randomly cross-linked) networks, the polymer chains between cross-link points have a precise length. This can be achieved with the use of a 'living' [5] polymerization technique such as anionic polymerization. Much work has been done with hydrophobic model networks, but very little with model hydrogels [4]. We have recently used group transfer polymerization (GTP) [6–8] to produce hydrophilic homopolymer [9,10] and amphiphilic copolymer [11] model networks of different molecular weights (MWs) and various copolymer architectures. The characterization of our homopolymer model networks [10] provided degrees of swelling which increased with the homopolymer size (chain length between cross-links), as expected. Moreover, since these networks comprised monomer repeat units of a weak base, the degree of swelling (DS) increased with the degree of ionization.

The present study expands on our previous work and employs the same living polymerization method, GTP, to prepare randomly cross-linked rather than model networks. Such randomly cross-linked polymer networks have usually been produced using free radical polymerization methods [1,2] and, to the best of our knowledge, this is the first report describing the use of GTP to synthesize randomly cross-linked polymer networks. A series of polymer networks covering a broad range of average MWs between cross-links were produced and characterized in terms of their aqueous swelling properties. The hydrophilic monomer repeat unit employed in the present as well as in the previous studies [9–11] was 2-(dimethylamino)ethyl methacrylate (DMAEMA), and its chemical formula is shown in Fig. 1. The same figure also displays the structures of the divinyl cross-linker, ethylene glycol dimethacrylate (EGDMA), and of the initiator, 1-methoxy-1-(trimethylsiloxy)-2-methyl propene (MTS), used for the network synthesis.

* Corresponding author.

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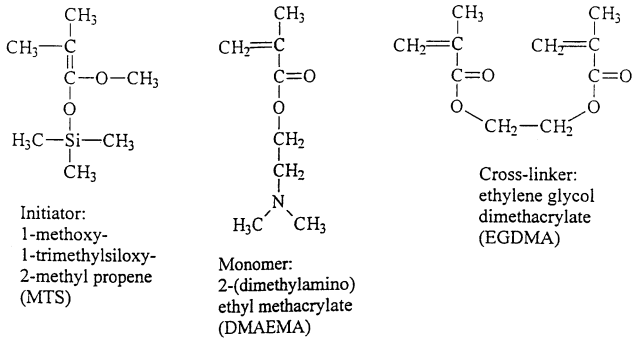

Fig. 1. Chemical formulas and names of the monomer, cross-linker and initiator used for the polymer network synthesis.

2. Experimental

2.1. Materials

All the chemicals were purchased from Aldrich, Germany. The monomer, DMAEMA, the cross-linker, EGDMA, and the initiator, MTS, were commercially available. 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]. The polymerization solvent was tetrahydrofuran (THF), which was dried by refluxing for three days over calcium hydride.

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 250 mL round bottom flasks, fitted with a rubber septum. Catalytic amounts (~10 mg) of TBABB were transferred to the flask, which was immediately purged with dry nitrogen. Freshly distilled THF was subsequently transferred directly from the still into the flask 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 a 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 initiator was distilled once prior to the polymerization, but it was neither contacted with calcium hydride nor passed through a basic alumina column 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 network synthesis involved simultaneous GTP of DMAEMA and EGDMA (in an eightfold molar excess with respect to the initiator) using the MTS monofunctional initiator. 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 used to follow the progress of the reaction. A typical polymerization procedure is detailed below which describes the synthesis of the network with a DMAEMA/MTS molar ratio of 100 (nominal degree of polymerization, DP, of 100).

To a 250 ml round bottom flask kept under a dry nitrogen atmosphere, sealed with a rubber septum, and containing ~10 mg TBABB (20 μmol, 0.58 mM in final reaction volume) and a stirring bar, were added via glass syringes 25 mL of freshly distilled THF followed by 8.4 ml of freshly distilled DMAEMA (7.8 g, 50 mmol, 1.5 M) and 0.76 ml EGDMA (0.79 g, 4.0 mmol, 0.12 M). To this was rapidly added under stirring 0.1 ml MTS (0.086 g, 0.49 mmol, 0.014 M) which triggered the polymerization and cross-linking reactions, causing an increase in temperature from 22 to 50°C and gelation within 1 min. Similar exotherms were observed in the other polymerizations where the molar ratio of DMAEMA to MTS was varied (mainly by varying the amount of MTS and keeping the amount of DMAEMA constant) to achieve the desired range of nominal DPs: 5, 10, 20, 50 and 100. For the network with nominal DP 200 the exotherm was lower, from 21 to 39°C and gelation occurred 20 min after the addition of the initiator. Efforts to prepare the network with a monomer to initiator molar ratio of 500 failed (no exotherms or gelation were observed).

2.4. Characterization of the degree of swelling

After the synthesis, the networks were cut and taken out of the polymerization flasks, rinsed in water for four weeks, with the water being changed every 3–4 days. Pieces from each gel were placed in vials where the appropriate conditions of pH or salt concentration were achieved by adding the appropriate amount of HCl, NaOH or NaCl. The DS at equilibrium, defined as the wet network mass at equilibrium (typically stabilized after one week but measured after three weeks) divided by dried network mass, was calculated after measuring both the masses gravimetrically in triplicate. Dry network samples were obtained by drying overnight in a vacuum oven at 40°C.

2.5. Calculation of the hydrogen ion titration curves

The effective p*K*s of the networks were read out of the hydrogen ion titration curves, as the pH at 50% ionization. The hydrogen ion titration curves were plots of the degree of ionization vs. the solution pH. The latter was simply measured using a pH-meter, while the former was calculated as the mole ratio of added HCl divided by the DMAEMA repeat units present in each sample. In the calculations, it was assumed that all protons from HCl go to the DMAEMA units and none to the aqueous solvent, justified at non-extreme pH values, as in the present case with pH~2–12.

3. Results and discussion

3.1. Network synthesis

There is one important difference between the polymerizations in this study and classical GTP [6–11]. This is the addition of the initiator last (in GTP the initiator is usually added before the monomers are added dropwise), which was necessitated by the preparation of networks (see also following paragraph). Addition of the monomer/cross-linker mixture to the initiator would compromise the conversion because, given the high speed of GTP, the first amounts of the monomer/cross-linker mixture would cause gelation which would render difficult any subsequent polymerization. In contrast, addition of the initiator to the monomer/cross-linker mixture provides a better chance for complete mixing before the polymerization starts. On the other hand, sequential addition of the three reagents, monofunctional initiator, monomer and cross-linker, in this order, would not produce networks but star polymers [10]. However, sequential addition of *bifunctional* initiator, monomer and cross-linker would result in the synthesis of model networks [10,11].

The present synthetic strategy for the preparation of random networks is similar to that usually employed for the synthesis of randomly cross-linked hydrogels using free radical polymerization, in which the monomer and divinyl cross-linker are polymerized simultaneously [1,2]. However, the gelation in the GTP system is completed within one minute, compared to 5–30 min typically required for an ammonium persulfate-initiated system accelerated with tetramethyl ethylene diamine (TEMED) catalyst [1]. Moreover, the constant number of polymer active sites will confer better control over the network structure in the present system [12,13] than in the case of conventional free radical polymerization where extensive intramolecular cross-linking and cyclization are known to take place [14]. It is possible, however, that some intramolecular cross-linking and cyclization processes take place in the GTP system as well.

Although of a less regular structure than the model networks of our previous study [10], the synthesis of the present networks is more convenient, requiring only a commercially available *monofunctional* initiator, as opposed to the non-commercially available *bifunctional* initiator necessary for the model network preparation. Fig. 2 illustrates the structures of randomly cross-linked and model networks. In the former case, there is a broad distribution in the chain lengths between cross-links, while in the latter case the chain lengths between cross-links are precisely defined. The highest nominal DP reached for the networks of this study was 200. Efforts to prepare the network with a nominal DP of 500 were unsuccessful. This can be attributed to the molecular weight (MW) limits of the 'livingness' of GTP [7] and to the neutralization by ubiquitous impurities of the very small amount of initiator

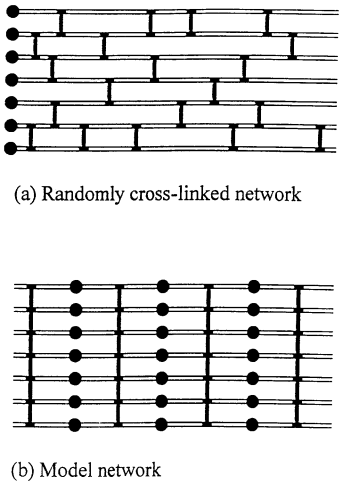

Fig. 2. Schematic representations of the structures of a randomly cross-linked (a) and a model (b) homopolymer network. The black dots represent the initiator fragments, while the black vertical segments the cross-linker.

required in this case. Even for the network with nominal DP 200, the exotherm was 10°C lower than those of the other networks and gelation was much slower, taking 20 times longer than with the smaller networks. Thus, the limits of GTP may have been reached with the network with DP 200.

3.2. pH-Dependence of the degree of swelling in pure water

Fig. 3 shows the aqueous DS of the networks with nominal DPs 5, 10, 20, 50, 100 and 200, as a function of the solution pH, without added salt. The error bars corresponding to a 95% confidence interval on three measurements of the DS are also presented. The gels with the smaller nominal DPs (5, 10, 20 and 50) are shrunk in pure water (pH~7) and alkaline conditions (pH>7), but swell under acidic conditions (pH<7). Within the group of these four gels, the curves of the gels with higher nominal DPs are systematically shifted to higher DS. The error bars for the DS of the curves with DP 5, 10 and 20 are smaller than the size of the symbols, while the error bars for the curve with DP 50 are slightly larger than the symbol size. The gels with

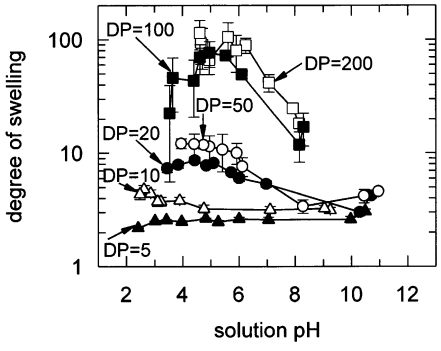

Fig. 3. pH-dependence of the DS of the polymer networks in salt-free water. The error bars correspond to a 95% confidence interval on three measurements.

the highest nominal DPs (100 and 200) swell gradually from pH 9 to lower pHs. Moreover, the DS of the two gels are rather similar, independent of their nominal DP. However, large error bars appear for the DSs of these two gels, particularly at low pH values where the DSs are highest. This less well-defined behavior of these two gels may be due to their very low cross-linking density and possible imperfections in their structure. However, the DS of the gels with nominal DP 100 and 200 are much higher than those of the gels with lower nominal DPs, as expected. The increase of swelling of all gels under acidic pH conditions can be attributed to the monomer repeat unit of the networks, DMAEMA, which is a weak base, becoming ionized at pH<7. The swelling of these materials under these conditions of pH is due to the osmotic pressure created by the counterions to the protonated tertiary amine monomer repeat units as well as to the electrostatic repulsive forces between the like charges [15].

The DMAEMA homopolymer model networks of our previous study [10] exhibited qualitatively the same behavior as the randomly cross-linked networks of this study, and swelled at pH<6. However, the swelling transition occurred within less than one pH unit in the model networks compared to more than two pH units in the random networks. This reflects the more perfect structure of the model networks (see Fig. 2) in which the constant length of the segments between cross-links may impart some cooperativity for the pH-expansion of these networks.

To examine how ionization affects the DS, we determined the hydrogen ion titration curves of the random networks and calculated the effective p*K*s (pH at 50% ionization), which ranged between 5.4 and 6.0. This is similar to the values determined for the corresponding model networks [10,11]. It is reminded that the p*K* of the DMAEMA monomer is 8.5, and that of the linear (not cross-linked) polymer is about 7.5. The difference in the p*K* values between the monomer and the linear polymer is due to the increased difficulty for further ionization in the latter case due to the repulsion between the polyelectrolyte charge and the incoming proton, while the p*K* difference between the linear polymer and the networks is due to counterion partitioning between the gel and the supernatant [16,17]. Examination of Fig. 3 can reveal that the onset of swelling of the networks below pH 6 is consistent with their measured p*K* values of ~5.5.

3.3. Dependence of the degree of swelling on the nominal degree of polymerization

Fig. 3 was used to construct Fig. 4, which shows the aqueous DSs in the absence of added salt as a function of the nominal DP of the networks at two different pH values. The DSs at pH 4 are higher than those at pH 6.3, due to network ionization at the former pH value. At both pHs the DS increases approximately linearly with the nominal DP between cross-links. This can be attributed to the reduction

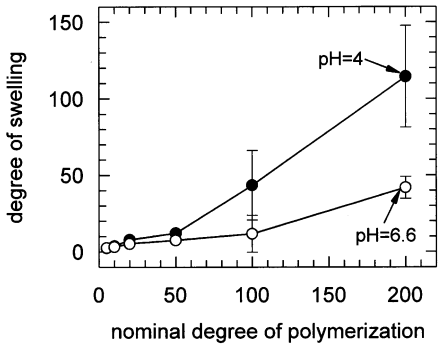

Fig. 4. Dependence of the aqueous (salt-free) DS on the nominal DP of the networks at two different values of pH. The 95% confidence intervals on the DS are also shown.

of the cross-link density with the nominal DP. It is also possible that the smaller percentage of hydrophobic cross-linker in the networks with higher nominal DPs further favors their swelling. Approximately linear dependencies of the DSs on DPs were also observed with model networks [10] at both the ionized and non-ionized state. For non-ionic poly(ethylene oxide) model networks in water and organic solvents an almost linear relationship between DS and DP was observed too [18], while theories on uncharged networks predict power-law exponents of DS vs. DP ranging from 0.6 [19] to 1.25 [20]. Ionized poly(acrylic acid) model networks showed a linear dependence of DS on DP [21], while the theoretical exponent in this case is 1.5 [22].

The values of the DSs of the randomly cross-linked networks are similar to those of the model networks of our previous study [10]. For example, the DS at pH 4 of the random network with DP 100 is 45, while that of its model network counterpart at the same pH is 55. The values of the DSs at pH 6.6 are 10 and 6, for the random and model networks with DP 100, respectively. Thus, the network architecture does not seem to have a great effect on the DS.

3.4. Effects of salt concentration and temperature on degree of swelling

Finally, the effects of salt concentration and temperature on the DS of the networks were investigated (data not shown). The salt concentration was varied between 0 and 1 M NaCl, without pH adjustment (almost neutral gels, pH~6.5). The DS of all gels dropped abruptly down to ~5 when the salt concentration was increased from 0 to 0.01 M NaCl, probably reflecting the screening of the small number of charges in the networks at this pH by the electrolyte. The DS remained approximately constant from 0.01 to 1 M NaCl. The DS of the network with a nominal DP 100 was studied both as a function of temperature (20–45°C) and pH (3–8), without added salt. For all the values of pH investigated (3.2, 4.7, 5.1, 5.9, 6.5, 8.1), the increase in temperature caused an almost linear reduction in the DS.

In particular, the DSs at 45°C were approximately 40% lower than those at 20°C. The observed effect of temperature on the aqueous DS of the networks is consistent with the precipitation of linear DMAEMA homopolymer in warm water solution (cloud point of neutral polyDMAEMA is about 40°C).

4. Conclusions

We have explored the synthesis of randomly cross-linked homopolymer networks of DMAEMA using a living polymerization technique, GTP. Although the structure of these networks is probably similar to that obtained by free radical polymerization, the present synthesis has the advantage of rapid gelation, of about 1 min. These networks swell in water, with the DS increasing as the nominal DP increases, and as the pH, salt concentration and temperature decrease. Although the values of the DSs of these networks were similar to those of model networks also prepared by GTP, the pH-induced expansion of the random networks was not as sharp as that of the model networks which have a more controlled structure.

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