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Three different types of quasi-model networks: synthesis by group transfer polymerization and characterization

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Summary

Group transfer polymerization (GTP) chemistry was employed for the preparation of polymethacrylate networks of controlled structure (quasi-model networks) of three different types: (a) regular quasi-model networks, in which all polymer chains were linked at their ends, leaving, in principle, no free chain ends, (b) crosslinked star polymer quasi-model networks, in which star polymers were interlinked via half of their chains, letting the other half free (dangling), and (c) shell-crosslinked polymer quasi-model networks, in which the outer part of the network contained polymer arms (dangling chains). Combination of hydrophilic and hydrophobic monomers led to amphiphilic networks whose aqueous swelling behavior was characterized gravimetrically.

Introduction

Randomly crosslinked networks, illustrated schematically in Figure 1a, represent the least perfect structure of networks in which the chains between the crosslinks (called the elastic chains) have a broad size distribution and the crosslink functionality (number of chains emanating from a crosslink) is not fixed. Due to these non-idealities and others (ring formation, entanglements, dangling chains) the mathematical description of these networks is very demanding [1,2]. However, this network structure is the most extensively studied [3], due to the ease of preparation and the low cost [4].

The other extreme is the perfect networks, called model networks [5], presented in Figure 1b. In these networks, the length of the elastic chains and the crosslink

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Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks", Prague, 10–14 July 2005 functionality are both well-defined (although defects cannot be totally excluded). Less attention has been paid to the study of this structure of networks as they are more difficult to synthesize and, therefore, more expensive. However, model networks lend themselves for the derivation of accurate structure-property relationships.

In-between these two extremes, the randomly crosslinked networks and the model networks, are the "almost perfect" networks or quasi-model networks, whose structure is drawn in Figure 1c. Quasi-model networks have well-defined lengths of the elastic chains but a broad distribution of the crosslink functionality, representing a compromise between structural perfection and ease of synthesis. This network structure is the object of our research [6]. In particular, we work on their synthesis using a "living" [7] polymerization technique and the characterization of their degree of swelling in water.

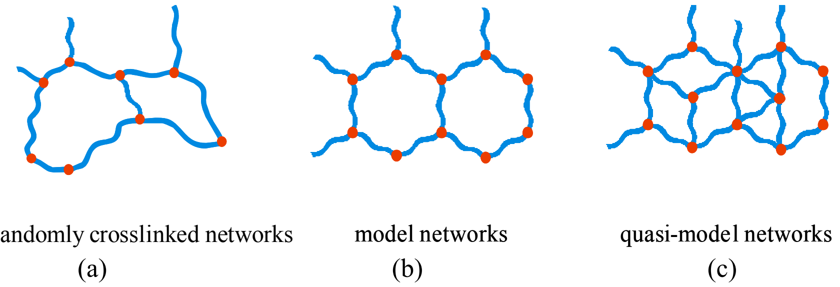
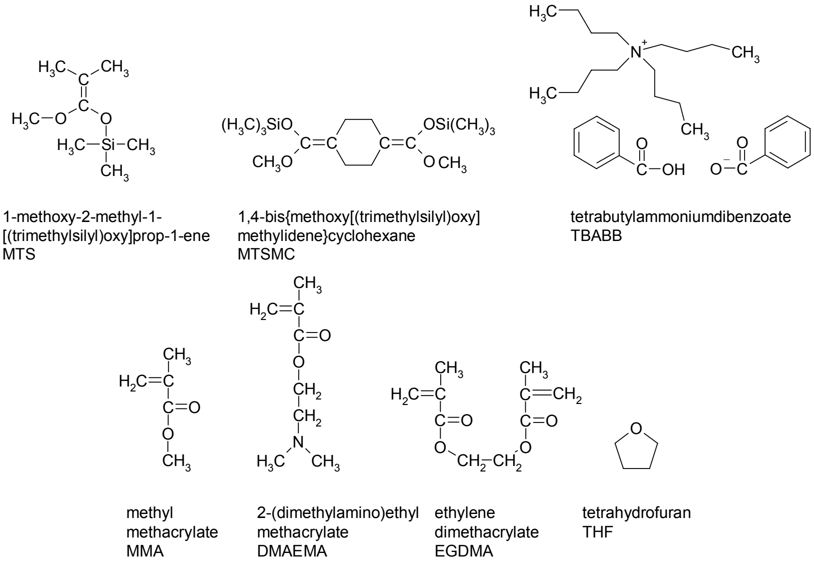


Figure 1. Three network structures with different degrees of perfection: (a) randomly crosslinked, (b) model, and (c) quasi-model.

Experimental Section

The network syntheses were performed using group transfer polymerization (GTP) [8, 9], a "living" polymerization method developed by Webster and co-workers at DuPont about 20 years ago. GTP is ideal for the controlled polymerization of methacrylates but it is limited to relatively low-molecular-weight (MW) products, typically below 50 000 g mol^{-1} for the linear chains. The networks were prepared by sequential addition of monomers and crosslinker in absolute tetrahydrofuran (THF), freshly distilled from a K/Na amalgam. Figure 2 shows the chemical structures, the names and the abbreviated names of the compounds used for the syntheses.

MTS (commercially available) and MTSMC (commercially unavailable, prepared following literature, [10]) are the two GTP initiators used. They are both silicon-containing acetals. MTS is a monofunctional initiator, allowing chain growth only in one direction. MTSMC is structurally the dimer of MTS and it is a bifunctional initiator, allowing growth from both chain ends. TBABB, an onium salt, is the GTP catalyst [11], which reacts with the initiator to provide the enolate anion, the GTP active site. GTP propagates through the nucleophilic attack of the enolate anion on the methacrylate monomer by a Michael-type addition [12]. One hydrophobic (MMA) and one hydrophilic (DMAEMA) monomers were used for the syntheses. DMAEMA bears a tertiary amine group in the pendant, which gets positively charged below pH 7. EGDMA was the dimethacrylate crosslinker used to interconnect the chains to a network. THF served as the polymerization solvent.



1-methoxy-2-methyl-1-[(trimethylsilyl)oxy]prop-1-ene
MTS

1,4-bis{methoxy[(trimethylsilyl)oxy] methylidene}cyclohexane
MTSMC

tetrabutylammoniumdibenzoate
TBABB

methyl methacrylate
MMA

2-(dimethylamino)ethyl methacrylate
DMAEMA

ethylene dimethacrylate
EGDMA

tetrahydrofuran
THF

Figure 2. Initiators, catalyst, monomers, crosslinker and solvent used for the synthesis of quasi-model networks by GTP.

Three different types of quasi-model networks were prepared by using either the monofunctional or the bifunctional initiator and employing different sequences of monomer and crosslinker additions. The final step in the network synthesis involved the addition of EGDMA crosslinker (or its mixture with a monomer), which resulted in gelation within seconds. The networks were taken out of the polymerization flasks or vials, washed in THF for one month, cut into pieces, weighed, dried for one week in a vacuum oven at room temperature, reweighed and transferred to water. A calculated amount of HCl (or NaOH) was added to each network sample to induce the ionization of the DMAEMA units in the networks to different degrees, covering the pH range from 2 to 12, and were left standing for one month for equilibration. The degrees of swelling (DSs) of the networks were calculated as the ratio of the moist network mass divided by the dry network mass, both measured gravimetrically.

Results and discussion

Network Preparation and Structure

Figure 3 illustrates schematically the addition sequences employed for the preparation of the three types of quasi-model networks. The synthesis of the first type [6,13,14] involved the use of the bifunctional GTP initiator MTSMC, which, upon monomer addition, resulted in the formation of linear homopolymers active at both ends. Subsequent EGDMA addition led to freezing of the structure to a network with no dangling ends (in principle) but only elastic chains. This was the simplest type of quasi-model networks we prepared.

The second and third network types employed the monofunctional GTP initiator MTS, and the first synthetic step for their preparation involved monomer addition, resulting in linear homopolymers active only at one end. These primary chains would later constitute the dangling chains for both of these network types. The synthesis of the second network type [15, 16] involved the subsequent addition of EGDMA crosslinker, resulting in the formation of “arm-first” star polymers with a broad distribution in the number of arms, typically from 15 to 30, but with a narrow distribution in the arm length. Star polymers [17] represent a very interesting compact polymer structure, with cost and degree of perfection intermediate between those of dendrimers and hyperbranched polymers. The cores of these “arm-first” star polymers would be the primary cores of the final networks. Monomer addition to the “arm-first” star polymers led to their conversion to “in-out” star polymers in which the number of arms doubled due to the “livingness” of the technique (conservation of the active sites). The secondary arms formed in this synthetic stage would later become the elastic chains of this network type. The polymerization was completed by the addition of EGDMA crosslinker for a second time, leading to network formation. This type of quasi-model networks was named crosslinked star polymer networks (CSPNs) to indicate the origin of these networks from star polymers. The cores formed by the second EGDMA addition were the secondary cores of the CSPNs. Because of the synthetic procedure detailed above, CSPNs had an equal number of elastic and dangling chains. Both elastic and dangling chains emanated from the primary cores, while only elastic chains emanated from the secondary cores.

As mentioned above, the first synthetic step for the preparation of the third network type was the synthesis of linear homopolymers active at one end, as with the second type. The second and final synthetic step for the preparation of the third network type represented a merging of the second, third and fourth addition steps employed for the second network type. Thus, a monomer/crosslinker mixture was added to effect the formation of the third network type. This network type had a large number of dangling chains in the network cavity (chosen to be called the core), making the network shell

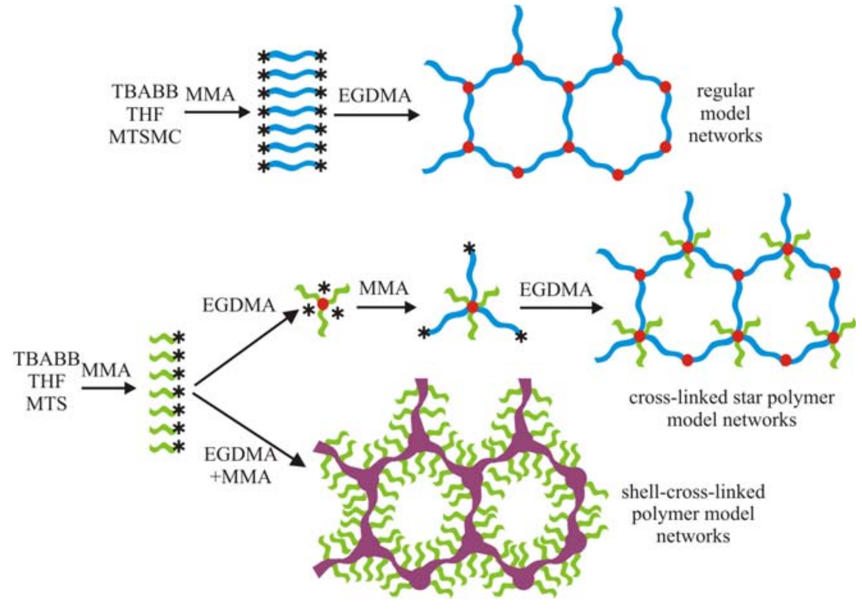


Figure 3. The three different types of quasi-model networks prepared: (a) regular type, (b) crosslinked star type, and (c) shell-crosslinked type.

composed of the monomer/crosslinker mixture. This type of networks was given the name shell-crosslinked polymer networks (SCPNs), a term coined after shell-crosslinked micelles (micelles covalently frozen at their periphery) developed by Wooley and co-workers [18].

A combination of hydrophilic and hydrophobic monomers would result in the formation of amphiphilic conetworks [19].

Degrees of Swelling

Figure 4 presents the pH-dependence of the degrees of swelling (DSs) in water of an amphiphilic shell-crosslinked quasi-model polymer network with the formula MMA_{30}-*b*-($DMAEMA_{30}$-*co*-$EGDMA_6$), equimolar in DMAEMA and MMA. The DSs increased as the pH decreased below pH 6. Under these conditions, the DMAEMA tertiary amine units became ionized, creating Coulombic repulsions between the charged segments and establishing osmotic pressure due to the accumulation of chloride counterions, both of which promoted swelling [20]. The DS vs. pH curve followed the degree of ionization vs. pH curve, also shown in the Figure, confirming the electrostatic nature of swelling in this system.

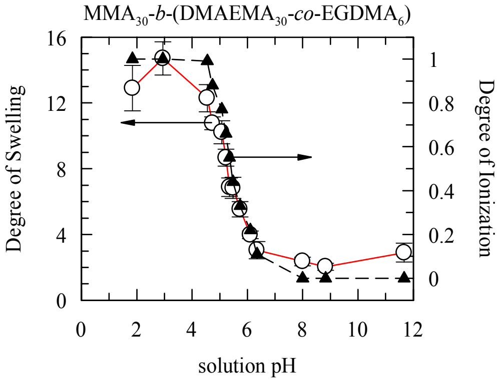


Figure 4. Degrees of swelling and ionization as a function of pH for the MMA_{30}-*b*-($DMAEMA_{30}$-*co*-$EGDMA_6$) amphiphilic shell-crosslinked quasi-model polymer conetwork.

Table 1 shows the aqueous DSs at neutral pH and at acidic pH (at the swelling maximum) for the above-mentioned amphiphilic shell-crosslinked quasi-model polymer network and also for equimolar DMAEMA-MMA amphiphilic quasi-model polymer networks of the regular type and of the crosslinked star type.

Table 1. Aqueous degrees of swelling in the neutral and the fully ionized state of equimolar DMAEMA-MMA amphiphilic quasi-model polymer networks of the three different types.

Network type	Network chemical formula	Degree of swelling	
		neutral	ionized
regular	$EGDMA_4$-b-MMA_{10}-b-$DMAEMA_{20}$-b-MMA_{10}-b-$EGDMA_4$	2.5	6.5
crosslinked star	MMA_{50}-b-$EGDMA_4$-b-$DMAEMA_{50}$-b-$EGDMA_4$	1.9	10.5
shell-crosslinked	MMA_{30}-b-($DMAEMA_{30}$-co-$EGDMA_6$)	2.4	15.0

For all three networks, the DSs were higher in the ionized state than in the neutral, increasing from about 2 to approximately 10. The differences in the DSs of the three ionized networks may reflect structural differences relevant to the network type, but may also be due, in part, to differences in the lengths of the various chains.

Conclusions

GTP has been used successfully to prepare three different types of almost-perfect (quasi-model) polymer networks: regular type, crosslinked star type, and shell-crosslinked type. The synthesis was achieved by simply devising variations in the order / combination of monomer(s) and crosslinker additions. Amphiphilic networks were obtained by combining a hydrophilic and a hydrophobic monomer. Representative samples of these different types of amphiphilic networks exhibited qualitatively the same behavior in water, with large increases in swelling upon network ionization.

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