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Synthesis and Characterization of Three-Component Polyelectrolytic Amphiphilic Model Networks

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Summary: Two hydrophilic monomers, 2-(dimethylamino)ethyl methacrylate (DMAEMA, ionizable) and methoxy hexa(ethylene glycol) methacrylate (HEGMA, non-ionic), and one hydrophobic monomer, *n*-butyl methacrylate (BuMA) were copolymerized via group transfer polymerization (GTP) to prepare eight equimolar, isomeric, amphiphilic terpolymer networks. The degree of swelling in acidic water of these networks varied, depending on network structure.

Keywords: amphiphiles; block copolymers; hydrogels; microphase separation; swelling

Introduction

Amphiphilic polymer networks are networks composed of both hydrophilic and hydrophobic monomer repeat units.[1] Although these networks absorb water, they do so in a lesser degree than their hydrophilic homopolymer counterparts. Thus, amphiphilic networks are not superabsorbents. However, amphiphilic networks absorb non-polar organic solvents such as hexane, something that hydrophilic homopolymer networks cannot do. Amphiphilic networks can *adsorb* hydrophobic drugs and hydrophilic drugs, and they can, therefore, be used for the delivery of a wide spectrum of drugs.

A particular type of amphiphilic networks is that of segmented amphiphilic networks, in which the hydrophilic and the hydrophobic units are placed in separate blocks or segments. This arrangement of units creates a large tendency for separation into hydrophobic and hydrophilic microphases. Figure 1 illustrates schematically four examples of segmented amphiphilic networks, where the hydrophobic units are painted black and the hydrophilic ones are colored white. In example (a), provided by Osada and co-workers,[2] the hydrophobic segments are introduced via a hydrophobic macromonomer, such as hexadecyl acrylate. The hydrophilic units are introduced through a low molecular weight monomer, while a cross-linker is required to freeze the structure into a three-dimensional

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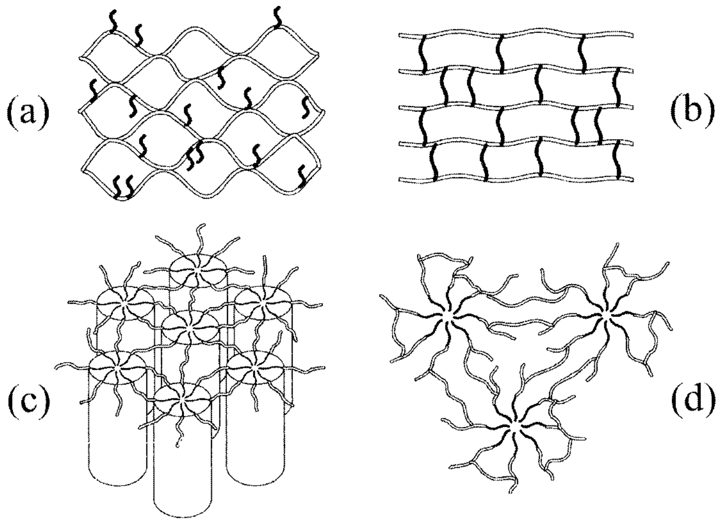

Figure 1. Various types of segmented amphiphilic networks synthesized recently.

network. In example (b), pioneered by the groups of Kennedy[3] and Iván,[4] the hydrophobic segments are introduced via a hydrophobic macrocross-linker, such as polyisobutylene dimethacrylate, prepared by "living" carbocationic polymerization. Example (c) has been presented by Antonietti and colleagues[5] and it is based on linear amphiphilic diblock copolymers of polybutadiene and poly(ethylene oxide) (PEO) prepared by anionic polymerization, dissolved in water at high concentration to form hexagonal structures, and cross-linked via γ-radiation to result in the formation of the network which preserved the hexagonal morphology. The last example is from the group of Hatton,[6] in which Pluronics, commercially available linear amphiphilic PEO-poly(propylene oxide)-PEO triblock copolymers, are dissolved in water, grafted with acrylic acid and cross-linked with ethylene glycol dimethacrylate (EGDMA).

The work of our research team on segmented amphiphilic networks involves their synthesis by group transfer polymerization (GTP),[7-10] a "living" polymerization technique that secures precise chain lengths and well-defined copolymer composition, leading to "model" network formation.[11] The network preparation employs sequential monomer and cross-linker additions, allowing the polymerization and cross-linking to take place in a "one-pot" procedure. Two different methodologies have been devised, resulting in two different amphiphilic network structures: (a) regular amphiphilic model networks[12,13] and (b) cross-linked star amphiphilic model networks,[14] illustrated in Figure 2. In Figure 2(a)

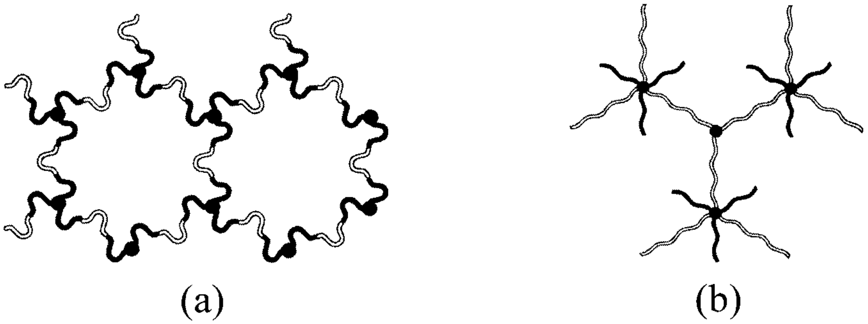

Figure 2. The two types of segmented amphiphilic model networks prepared by GTP.

all chains are end-linked and the network formed has, in principle, no dangling chains. In Figure 2(b), "in-out" star polymers are prepared first and are subsequently cross-linked, leading to a network with two types of cross-links: the primary cross-links and the secondary cross-links. Only elastic chains emanate from the secondary cross-links, whereas an equal number of elastic and dangling chains emanate from the primary cross-links.

The present work involves regular amphiphilic model networks composed of three rather than two different types of monomer repeat units. The chemical structures and names of the three monomers, the cross-linker and the initiator used in the synthesis are shown in Figure 3. 2-(dimethylamino)ethyl methacrylate (DMAEMA, ionizable) and methoxy hexa(ethylene glycol) methacrylate (HEGMA, non-ionic) were the two hydrophilic monomers used, while *n*-butyl methacrylate (BuMA, nonionic) was the hydrophobic monomer employed. Ethylene glycol dimethacrylate (EGDMA) was used as the cross-linker, whereas 1,4-bis(1-trimethylsiloxy-1-methoxy-methylene)cyclohexane (MTSMC) served as the bifunctional GTP initiator. Tetrabutylammonium bibenzoate (TBABB) was employed as the GTP catalyst.

Experimental Section

The MTSMC initiator[15] and the TBABB catalyst[9] were prepared following published procedures. Pentablock terpolymer-based model networks were synthesized using sequential additions of monomers and cross-linker under GTP conditions.[12,13] The statistical terpolymer-based model network (random) was prepared by the simultaneous addition of the three monomers followed by the addition of cross-linker, whereas the

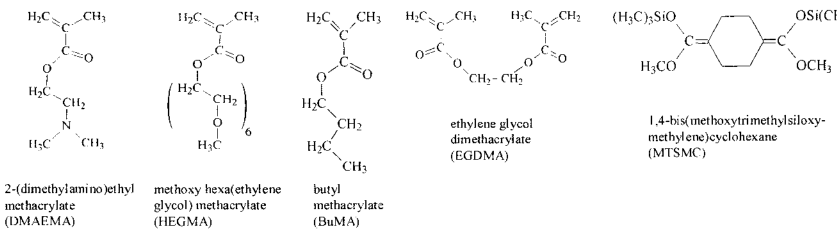

Figure 3. Chemical structures and names of the main reagents used for the polymerization.

randomly cross-linked statistical terpolymer network (random-random) resulted from the simultaneous copolymerization of the cross-linker as well as the three monomers, triggered by the addition of the initiator, which, in this case, was the last reagent to be added. The linear precursors to the networks were characterized in terms of their molecular weights (MWs) and composition using gel permeation chromatography (GPC) in tetrahydrofuran (THF) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy in $CDCl_3$. The network degrees of swelling (DSs), defined as the network wet mass divided by the network dry mass (obtained by drying in a vacuum oven), were determined gravimetrically in water (different values of pH) and in THF. The fraction of ionization of the DMAEMA units at each pH was estimated as the ratio of the HCl equivalents added divided by the number of equivalents of the DMAEMA monomer repeat units present in the network sample. The number of DMAEMA equivalents was calculated from the dry mass of the network sample and the network composition.

Results and Discussion

Table 1 shows the MWs and compositions of the linear terpolymer precursors to the networks. There are no data for the random-random network precursor because, for this synthesis, gelation takes place immediately. The theoretical MW is the same (around 7000 g mol^{-1}) for all the linear terpolymer precursors because they are isomers. The experimental number average MW, M_n, for all the terpolymers is in good agreement with the theoretical one, although the former is slightly higher than the latter due to partial initiator deactivation. The MW distributions are narrow with polydispersity indices (M_w/M_n) around 1.1. The comonomer composition for all terpolymers is close to the theoretical one, 33.3 % mol (equimolar terpolymers).

Table 1. Molecular weights and compositions of the linear terpolymer precursors.

Polymer formula[a]	theor MW	GPC results M_n	GPC results M_w/M_n	% mol composition H-Bu-D theoretical	% mol composition H-Bu-D by ^{1}H NMR
Bu$_5$-*b*-D$_5$-*b*-H$_{10}$-*b*-D$_5$-*b*-Bu$_5$	6690	7520	1.10	33.3-33.3-33.3	N/D[b]
D$_5$-*b*-Bu$_5$-*b*-H$_{10}$-*b*-Bu$_5$-*b*-D$_5$	6690	7210	1.09	33.3-33.3-33.3	35-34-31
Bu$_5$-*b*-H$_5$-*b*-D$_{10}$-*b*-H$_5$-*b*-Bu$_5$	6690	7130	1.11	33.3-33.3-33.3	36-33-31
H$_5$-*b*-Bu$_5$-*b*-D$_{10}$-*b*-Bu$_5$-*b*-H$_5$	6690	7810	1.14	33.3-33.3-33.3	34-35-31
D$_5$-*b*-H$_5$-*b*-Bu$_{10}$-*b*-H$_5$-*b*-D$_5$	6690	7105	1.11	33.3-33.3-33.3	34-35-31
H$_5$-*b*-D$_5$-*b*-Bu$_{10}$-*b*-D$_5$-*b*-H$_5$	6690	7975	1.16	33.3-33.3-33.3	36-35-29
(H-*co*-D-*co*-Bu)$_{10}$	6690	9420	1.12	33.3-33.3-33.3	36-32-32
(H-*co*-D-*co*-Bu)$_{10}$-*co*-E$_8$	N/A[c]	N/A	N/A	N/A	N/A

[a] Bu: BuMA, D: DMAEMA, H: HEGMA, E: EGDMA
[b] not determined
[c] not available

The pH dependence of the aqueous DSs of the network based on the pentablock terpolymer DMAEMA$_5$-*b*-BuMA$_5$-*b*-HEGMA$_{10}$-*b*-BuMA$_5$-*b*-DMAEMA$_5$ is shown in Figure 4. The DSs increase with a reduction in the pH (below pH 7) because this induces

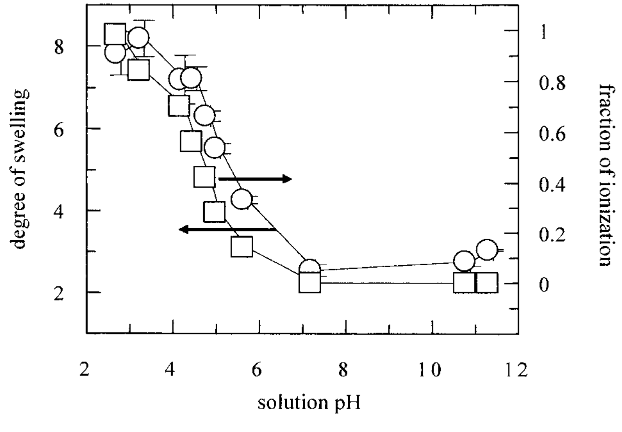

Figure 4. Effect of pH on the degree of swelling and fraction of ionization of the network based on the pentablock terpolymer DMAEMA$_5$-*b*-BuMA$_5$-*b*-HEGMA$_{10}$-*b*-BuMA$_5$-*b*-DMAEMA$_5$.

the ionization of the tertiary amine DMAEMA units. A charge in the DMAEMA units results in the build-up of Coulombic repulsions between the polyelectrolyte chains, and an introduction of chloride counterions which create an osmotic pressure, both of which promote network swelling. The charge-driven mechanism of the swelling is confirmed by the shape of the fraction of ionization vs. pH curve, also shown in Figure 4, which almost coincides with the DS vs. pH curve.

The aqueous DSs of the other networks exhibited a similar pH dependence. Figure 5 shows the DSs of all networks in neutral water (minimum DS in water), in acidic water (maximum DS in water) and in THF (DMAEMA units were uncharged). In neutral water, all networks display the same DSs which are low with values between 2 and 3. The poor swelling can be attributed to the collapsed state of the hydrophobic BuMA units and the uncharged state of the DMAEMA units under these conditions. The DSs in THF, a non-selective solvent (THF was the synthesis solvent), are higher than those in neutral water but there is still no differentiation among the networks. In acidic water, most of the networks present a maximum DS because of the ionization of the DMAEMA units. In the networks exhibiting the highest swelling under these conditions, and, in particular, the random and the random-random, the hydrophobic BuMA units are not collapsed because

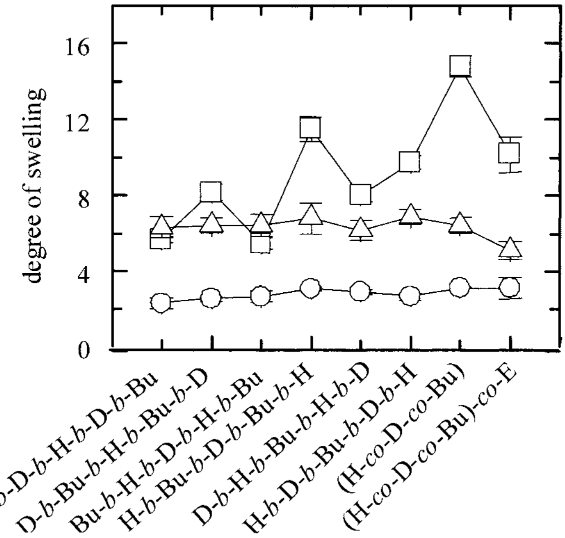

Figure 5. Effect of network structure on the swelling in tetrahydrofuran (triangles) and in neutral (circles) and acidic (squares) water.

they are randomly distributed in the polymer chains. In contrast, in those presenting the lowest swelling, particularly in the networks based on BuMA$_5$-*b*-DMAEMA$_5$-*b*-HEGMA$_{10}$-*b*-DMAEMA$_5$-*b*-BuMA$_5$ and BuMA$_5$-*b*-HEGMA$_5$-*b*-DMAEMA$_{10}$-*b*-HEGMA$_5$-*b*-BuMA$_5$, the BuMA units are collapsed leading to microphase separation which reduces the effective length of the elastic chains. In these two networks, there is a particular trend for microphase separation for two reasons. First, the BuMA units are placed in blocks. Second, these blocks are end blocks in the pentablock terpolymer, and they are, therefore, next to the EGDMA hydrophobic cross-linker units, thus further enhancing the drive for microphase separation. The reduced aqueous swelling of networks based on amphiphilic block copolymers has been shown theoretically using thermodynamic models.[16,17]

Conclusion

GTP has been successfully employed to prepare eight isomeric amphiphilic networks based on equimolar terpolymers. Six of the networks comprised ABCBA pentablock terpolymers, which were the six possible block sequence isomers of symmetrical ABCBA pentablocks. The other two were composed of statistical terpolymers (random distribution of the three monomer repeat units), with the one network having the cross-links placed at precise distances, and the other network having the cross-links randomly distributed. Maximum swelling of the networks was observed in acidic water where the tertiary amine units became ionized, and depended on the monomer distribution which governs microphase separation of the networks in water.

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