

# NANOPHASE SEPARATED ANIONIC AMPHIPHILIC MODEL CONETWORKS BASED ON METHACRYLIC ACID

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Two series of model amphiphilic polymer conetworks were synthesized by group transfer polymerization (GTP). The first one contained methyl methacrylate (MMA) and the second one 2-butyl-1-octyl methacrylate (BOMA) as hydrophobic monomers. Methacrylic acid (MAA) was used as the hydrophilic monomer for both series. Network synthesis was performed by sequential monomer/cross-linker additions to form conetworks in a wide range of compositions and architectures. All conetwork precursors and the extractables were characterized in organic solvents by gel permeation chromatography and <sup>1</sup>H NMR. The polymer conetworks were investigated in terms of their degree of swelling in aqueous media and in THF. The nanophase separated structure was proved by atomic force microscopy and small-angle neutron scattering measurements for the triblock copolymer model conetworks.

**Keywords:** amphiphilic conetworks, GTP, nanophases, SANS, AFM.

## Introduction

Amphiphilic polymer conetworks (APCN) [1-5] represent an emerging class of soft materials. These special cross-linked polymer systems have some unique properties and great application potential. These materials comprise covalently bonded hydrophilic and hydrophobic polymer chains. Therefore, APCNs can swell in both aqueous and organic media, and may adsorb both polar and non-polar solutes. For most of APCNs nanophase separation occurs [4,5]. Possible applications of APCNs include uses as supports for enzymes, antifouling surfaces, matrices for the preparation of inorganic nanoparticles and for drug delivery, scaffolds for tissue engineering and for implantation and use in soft contact lenses [1,2]. Model conetworks are composed of polymer chains of well-defined molecular weight and composition [1,5]. Most of the APCNs reported in the literature so far cannot be considered as model conetworks because they comprise

chains, with broad length distributions between the cross-linking points [3,4].

Two series of amphiphilic model conetwork were synthesized by group transfer polymerization (GTP) [6]. The hydrophilic monomer was methacrylic acid (MAA) introduced via the polymerization of tetrahydropyranyl methacrylate (THPMA) followed by the removal of the protecting group by acid hydrolysis after the cross-linking reaction. The hydrophobic polymers were the glassy poly(methyl methacrylate) (PMMA) and the rubbery poly(2-butyl-1-octyl methacrylate) (PBOMA). The resulting two conetwork series were characterized gravimetrically in terms of their swelling behavior in water and tetrahydrofuran (THF) over the whole range of ionization. The nanophase separation of both the conetwork series was analyzed and proved by small-angle neutron scattering and atomic force microscopy.

## Experimental

**Conetwork Formation.** All the conetworks in this study were synthesized by GTP. The reactions were carried out at room temperature under N<sub>2</sub> atmosphere. 1,4-Bis(methoxytrimethylsilyloxymethylene)cyclohexane (MTSCH) and ethyleneglycol dimethacrylate (EGDMA) were used as initiator and cross-linker, respectively. Network syntheses were performed by sequential monomer/cross-linker additions. ABA triblock copolymer-based model conetworks were prepared with different compositions, and two less ordered conetworks were also synthesized.

**Gel Permeation Chromatography (GPC) and <sup>1</sup>H NMR.** GPC and <sup>1</sup>H NMR were used to determine the molecular weights (MWs) and compositions for all the conetwork precursors and the extractables.

**Measurements of the Degree of Swelling (DS).** The polymer conetworks were characterized in terms of their degree of swelling (DS) in aqueous media and in THF over the whole range of ionization. The DSs were calculated as the ratio of the swollen conetwork mass divided by the dry conetwork mass.

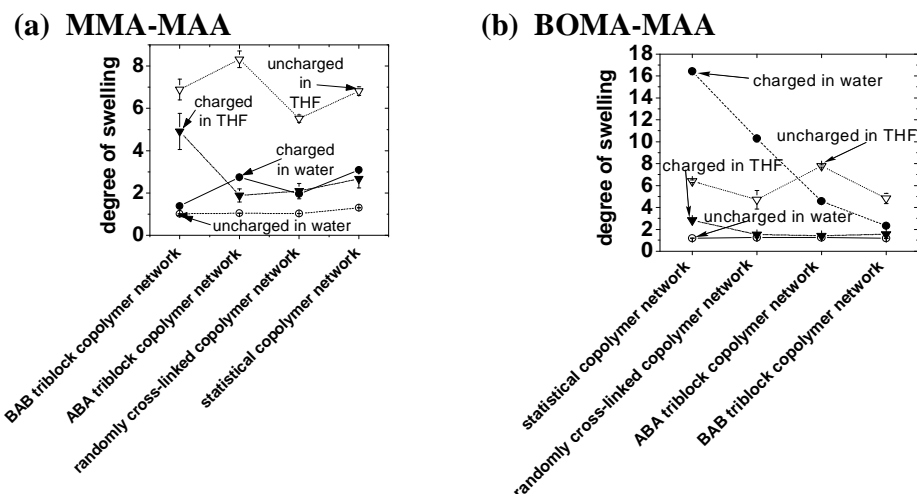


Figure 1. Effect of conetwork architecture on the degrees of swelling of the conetworks in water and in THF at their uncharged and fully charged states.

*Small-Angle Neutron Scattering (SANS).* All the (hydrolyzed and uncharged) conetworks of this study were characterized using SANS in  $D_2O$ . SANS measurements were performed on the 30 m NG7 instrument at the Center for Neutron Research of the NIST.

*Atomic Force Microscopy (AFM).* AFM images of the dried microtomed samples (hydrolyzed and uncharged) were recorded with a Nanoscope III scanning probe microscope from Digital Instruments.

## Results and discussion

The first step for the preparation of block and statistical copolymer-based model conetworks was the synthesis of the corresponding linear copolymers with well-defined chain length. The MW, molecular weight distributions (MWD) and composition of these copolymer chains were investigated by GPC and  $^1H$  NMR. The determined precursor MWs and compositions were found to be quite close to the expected values and the MWDs were narrow.

The DSs in water and THF follow exactly the opposite pH dependencies. In water, all the conetworks start to swell above pH 7 and the DS increases with the pH due to the ionization of the weakly acidic MAA units, confirming the importance of electrostatics in swelling. In THF, the conetworks showed the opposite behavior. In particular, the DSs in THF decrease as the ionization of the MAA units in the conetworks increase. This is due to the incompatibility of THF with the ionized MAA units.

The DSs of the two conetwork series in water and in THF in the ionized and nonionized states of the MAA units strongly depend on composition. The composition dependence of the DSs can be interpreted according to the compatibility of the conetwork units. The MMA, the BOMA and the uncharged MAA units were compatible

with THF and not compatible with water. In the fully charged states of the MAA segments in water, the DS was barely depending on composition. For charged MAA in THF, the conetworks produce low DSs.

Figure 1 displays on the effect of conetwork architecture on the DSs. There is no significant dependence of the DS on the architecture in the case of uncharged MAA units in either of the solvents because of the full compatibility or incompatibility of the monomer units with the solvent (as described before). For fully charged MAA units in water, the architecture had a significant influence on the DSs. The architecture dependence of the DSs can be attributed to the different phase behavior of the two triblock copolymer-based model conetworks compared to the less ordered conetwork structures. In particular, the statistical copolymer model conetwork swells more than the other three types of conetworks because the randomly distributed solvated units drag along the nonsolvated units, forcing them to contribute also to swelling. In the triblock copolymer-based model conetworks, there is phase separation, resulting in the shrinkage of one type of blocks (hydrophobic MMA and BOMA in water or  $Na^+MA^-$  salt in THF) and to lower DSs.

Figure 2 shows the SANS profiles of all the APCNs in the uncharged state in  $D_2O$ . Figures 2a and 2c illustrate the effect of conetwork composition, while Figures 2b and 2d present the effect of conetwork architecture. For the MMA series only the higher MAA-containing conetworks show maxima indicating scattering domains. For these triblock copolymer-based conetworks the average distance between the scattering centers (as  $2\pi/q_{max}$ ) calculated to be in the range of 8.5-9 nm.

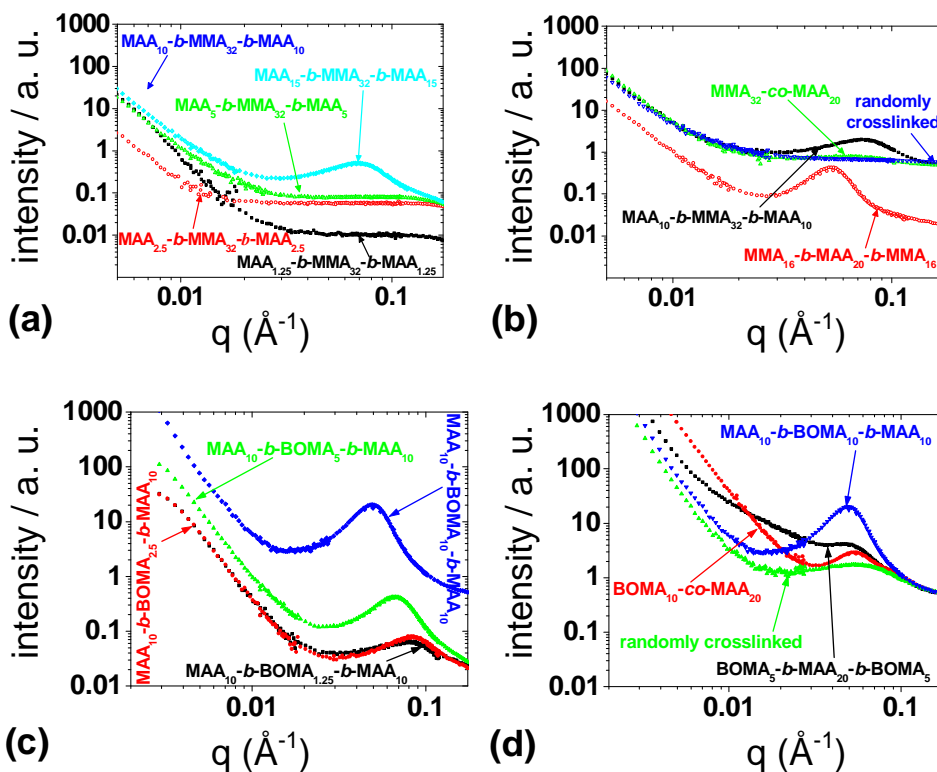


Figure 2. SANS profiles of APCNs in  $D_2O$  in the uncharged state.

For the BOMA conetwork series all SANS profiles exhibited single peaks, consistent with conetwork nanophase separation. In particular, the spacing between the scattering centers varied from 7.7 nm to 12.8 nm as the  $M_n$  of the linear copolymer precursors of the conetworks increased. The absence of higher harmonics could be attributed to the polydispersity of the scattering centers or/and to their short-range liquidlike order [7,8].

Figures 2b and 2d show the SANS profiles of the four isomeric APCNs having different architectures. In the case of MMA series only the two triblock copolymer and the statistical copolymer model conetworks, while in the case of the BOMA series all scattering curves exhibit maxima, manifesting the presence of scattering centers. However, the peak of the randomly cross-linked APCN was very weak, possibly reflecting some correlation between EGDMA cross-linker residues or BOMA unimolecular micelles. The peaks of the three other APCNs were located approximately at the same  $q$ -values, suggesting similar distances between the scattering centers of these isomeric APCNs.

Figures 3a and 3b and Figures 4a and 4b display AFM images for the equimolar triblock and statistical copolymer-based model APCNs. The images were measured in phase mode, which distinguishes between hard (bright) and soft (dark) phases.

The model conetwork based on the triblock copolymer  $MAA_{10}$ - $b$ - $MMA_{32}$ - $b$ - $MAA_{10}$  displays large spherical domains of a size of 40 nm, while the  $MAA_{20}$ - $co$ - $MMA_{32}$  copolymer based model conetwork exhibits smaller and elongated domains of a broadly distributed size in a range of 4-20 nm with the average of some 10 nm. The domain size of 40 nm in the former conetwork is larger than the characteristic size of 9 nm determined by SANS. This indicates that the contrast difference between the phases is not high enough to see distinguishable morphologies in the higher resolution. Note that both polymer phases are below their glass transition temperatures ( $T_g$ ). The SANS measurements can give complementary information to AFM. The domain size of 10 nm in the statistical copolymer model conetwork corresponds to the EGDMA cores, and this is in perfect agreement with the SANS measurements.

The conetwork based on the triblock copolymer  $MAA_{10}$ - $b$ - $BOMA_{10}$ - $b$ - $MAA_{10}$  (Figure 4a) presented large and spherical domains of a size of approximately 40 nm (domain sizes ranged from 28 to 55 nm), whereas the other conetwork exhibited smaller and elongated domains like in the case of MMA series conetworks (average 10 nm). The domain size of 40 nm in the former conetwork is larger again than the characteristic size (13 nm) determined by SANS. Note that in the case of BOMA series one polymer phase (the MAA) was below its  $T_g$ .

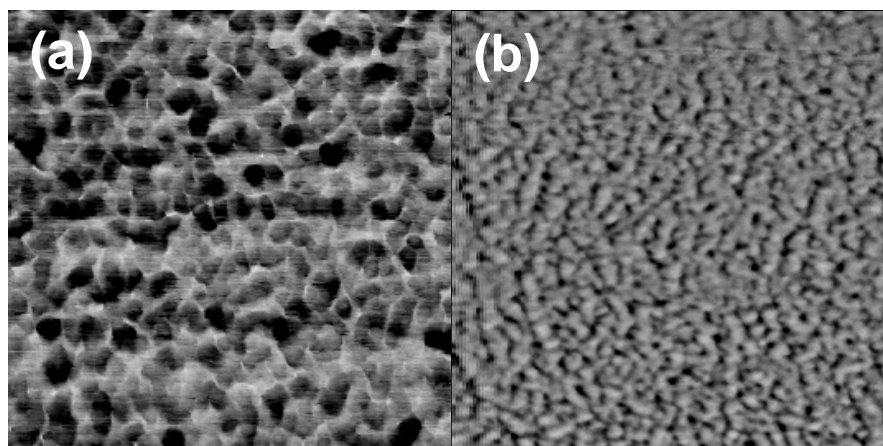


Figure 3. AFM phase mode images for (a) the ABA triblock copolymer-based and (b) the statistical copolymer-based MMA-MAA model conetworks. Each image has dimensions 500 nm x 500 nm.

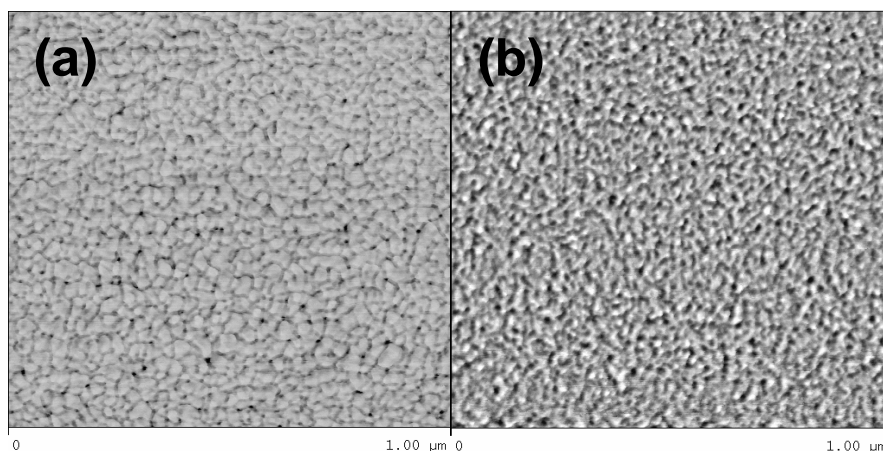


Figure 4. AFM phase mode images for (a) the ABA triblock copolymer-based and (b) the statistical copolymer-based BOMA-MAA model conetworks.

The SANS measurements gave again complementary information to AFM. The domain size of 10 nm in the statistical copolymer model conetwork corresponds to the EGDMA cores and is in good agreement with the SANS measurements (scattering center spacing of 12 nm).

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