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New Nanophase Separated Intelligent Amphiphilic Conetworks and Gels

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Summary: Amphiphilic conetworks (APCN) are new materials composed of covalently bonded otherwise immiscible hydrophilic and hydrophobic polymer chains. The amphiphilic nature of these new crosslinked polymers is indicated by their swelling ability in both hydrophilic and hydrophobic solvents. Special synthetic techniques have been developed for the preparation of these new unique materials, such as poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene (PHEMA-*l*-PIB), poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB) and poly(N,N-dimethylaminoethyl methacrylate)-*l*-polyisobutylene (PDMAEMA-*l*-PIB) (-*l*- stands for *linked by*). Due to their unique architecture, macrophase separation of the immiscible components is prevented by the chemical bonding in the conetworks. As a results, phase separation leads to nanodomains with usually 2-20 nm domain sizes as shown by AFM measurements. The nanophase separated morphology may also lead to smart temperature responsive gels with high mechanical stability, such as in the case of poly(N,N-dimethylaminoethyl methacrylate)-*l*-polyisobutylene APCNs as discovered during these studies. In another approach, poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene and poly(methacrylic acid)-*l*-polyisobutylene APCNs were prepared by a special two-step process. The new PMAA-*l*-PIB polyelectrolyte APCNs possess smart (intelligent) reversible pH-responsive properties in aqueous media. These unique conetwork structures and properties of these new emerging materials may lead to numerous new potential applications, such as smart materialk products, sustained drug release matrices, biomaterials, nanohybrids, nanotemplates etc.

Keywords: amphiphilic conetworks; gels; nanophases; smart materials; stimuli-responsive polymers

Introduction

Increasing polymer production these days is not only driven by everyday needs for commodity plastics, but more so by most of the state-of-the-art sciences and industrial

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processes (such as nanotechnologies, chip making, biomaterials etc.) which are in fact largely based on advanced polymer technologies. The rapid progress in these fields raises the demand for novel polymer materials with special, unprecedented structures and properties. Amphiphilic conetworks (APCNs)[1-20] belong to one such group of materials. These two-component networks are composed of polymer chains with opposite philicity, one of them being hydrophilic while the other one is hydrophobic. The schematic structure of an APCN is shown in Figure 1.

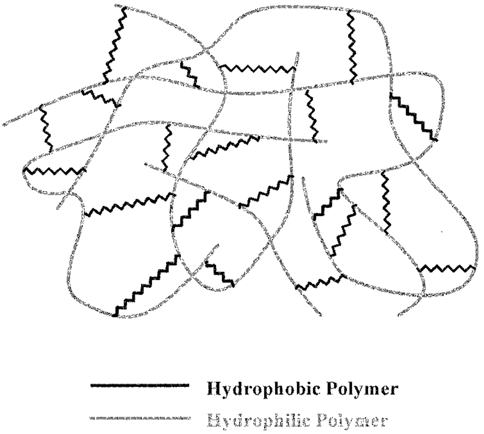


Figure 1. Schematic structure of an amphiphilic conetwork (APCN).

The otherwise immiscible, thermodynamically incompatible polymer moieties are connected via covalent bonding (the hydrophobic chains crosslink their hydrophilic counterparts or vice versa), preventing macroscopic phase separation. The amphiphilic behavior is represented by the ability of APCNs to swell in both aqueous and hydrophobic media. These new materials have already been known to exhibit various outstanding beneficial properties which make them suitable for special applications such as controlled drug release matrices,[1-3] nanocrystal production,[6] pervaporation membranes,[11] immunoisolatory devices,[12] biomaterials[13], enhanced biocatalysis[20] *etc.*

Synthesis of Amphiphilic Conetworks

APCNs have been prepared by various synthetic routes including chain coupling[9], group transfer polymerization[14] and Diels-Alder reactions[15] just to name a few, but the most widespread procedure is the so-called macromonomer method[1-8], the general scheme of which is shown in the top half of Figure 2. A bifunctional macromonomer (a polymer chain with a polymerizable functional group on each end) is copolymerized in a common solvent with a comonomer via free radical copolymerization. There are three important conditions that must be met in order to succeed with this reaction scheme[7]. First, the two moieties must be copolymerizable. Second, the chains should be connected with more than one crosslinking points in order to form a network. Third, it is crucial to avoid phase separation during the copolymerization process.

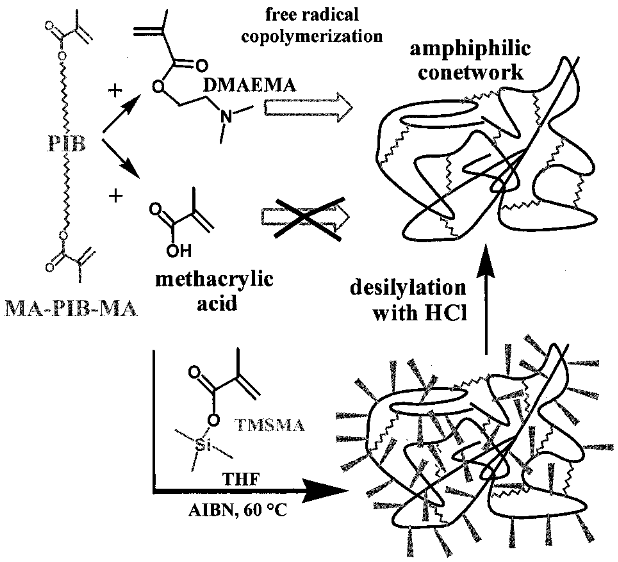


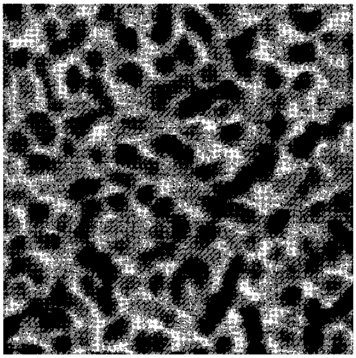
Figure 2. Synthetic routes for obtaining amphiphilic conetworks by the macromonomer method.

In this study we report on the successful synthesis and some interesting properties of different APCNs, containing poly(2-hydroxyethyl methacrylate) (PHEMA), poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) and poly(methacrylic acid) (PMAA) as hydrophilic components and polyisobutylene (PIB) as hydrophobic moiety. Methacrylate-telechelic bifunctional macromonomer of the latter was prepared via quasiliving carbocationic polymerization[21] of isobutylene from a bifunctional *t*-butyl dicumyl chloride initiator. Functionalization was achieved by terminating the polymerization reaction with allyltrimethylsilane resulting in allyl-telechelic PIB.[22] This was followed by a three-step endgroup modification: first, hydroboration of the terminal double bonds with 9-borabicyclo[3.3.1]nonane (9-BBN), then oxidation with H_2O_2 leading to primary hydroxyl termini,[22,23] and finally esterification with methacryloyl chloride.[1,2] The resulting methacrylate-telechelic polyisobutylene (MA-PIB-MA) was used as macromolecular crosslinker for obtaining the desired conetworks.

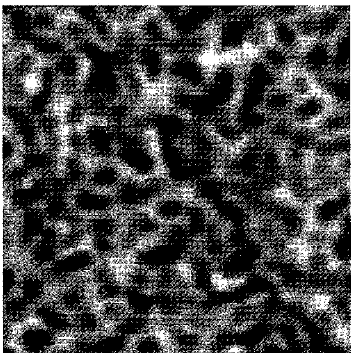
However, it is not possible to obtain APCNs directly via the macromonomer method if the comonomer happens to be 2-hydroxyethyl methacrylate (HEMA) or methacrylic acid (MAA) as these monomers are too hydrophilic to have a common solvent with PIB. To prevent phase separation, HEMA and MAA had to be made hydrophobic by protecting the polar functional group with a trimethylsilyl group. This way both the bifunctional macromonomer and the comonomer could be dissolved in tetrahydrofuran and a conetwork was formed via azo-isobutyronitrile (AIBN)-initiated free radical copolymerization. The unwanted trimethylsilyl protecting groups were removed by quantitative hydrolysis with dilute HCl solutions, and thus amphiphilic conetworks containing covalently bonded immiscible polymer chains were formed. APCNs were synthesized in a wide range of compositions (generally between 20 and 80 m/m% PIB) by using this generally applicable synthetic method; deprotection and successful conetwork formation were confirmed by elemental analysis.

Nanostructured Morphology of Amphiphilic Conetworks

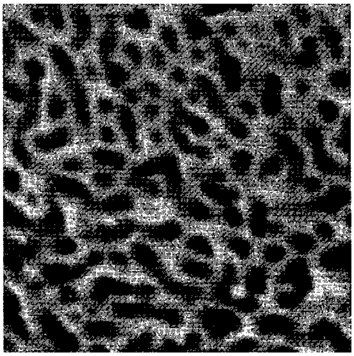
Figure 3 shows a typical series of AFM (Atomic Force Microscopy) images of sectioned poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene (PHEMA-*l*-PIB) (-*l*- stands for *"linked by"*). The dark areas correspond to PIB whereas the areas with lighter shades belong to PHEMA phases. As indicated by these images the morphology and average domain sizes depend on the composition of APCNs. At low PIB content, spherical PIB domains of about 13 nm diameter are dispersed in the PHEMA matrix. When increasing the PIB content (and with it the crosslinking density), the PIB phase appears as elongated domains with decreased sizes. At around 50-70 % PIB content, a so-called cocontinuous morphology is observed. At high PIB contents, elongated and dispersed PHEMA phases of around 5 nm domain sizes can be seen. It is evident that this nanostructured morphology will play a key part in all possible applications of APCNs.



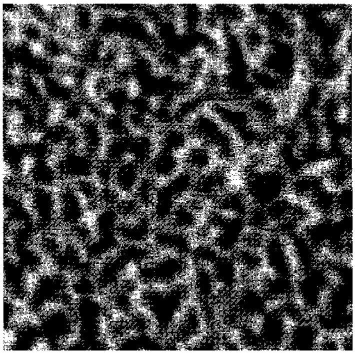
27% PIB 73% PHEMA



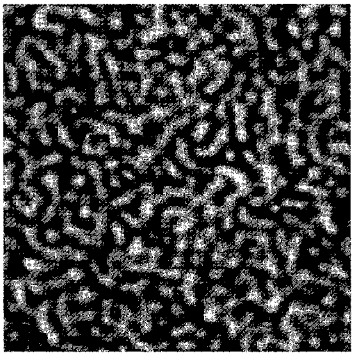
35% PIB 65% PHEMA



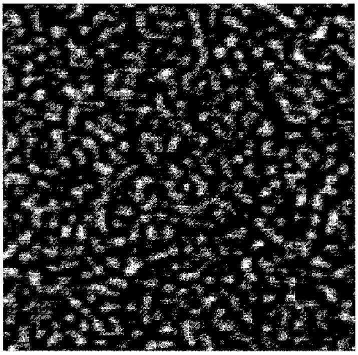
50% PIB 50% PHEMA



63% PIB 37% PHEMA



69% PIB 31% PHEMA



77% PIB 23% PHEMA

Figure 3. AFM images of poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene (PHEMA-*l*-PIB) amphiphilic conetworks (250 x 250 nm).

Smart pH-responsive Swelling of PMAA-*l*-PIB Amphiphilic Conetworks

Figure 4 shows the equilibrium swelling ratios of poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB) APCNs in hydrophobic (hexane) and aqueous media as a function of PIB content. Via solvation of the polymer chains of appropriate philicity, the gels swelled in both solvents. The swelling ratios depend on composition. Higher PIB content increases the swelling capacity in hexane and decreases swelling in aqueous media. Considerable difference was observed between swelling degrees achieved under acidic conditions as opposed to those in alkaline solutions. Obviously this effect can be attributed to the deprotonation of the polyacid and related processes (*e.g.* osmotic pressure of counterion *etc.*). It is also important that the volume of response to pH shift can be varied arbitrarily through composition parameters producing controlled swelling behavior. The polymer segments of the non-swelling polymer moiety remain unsolvated (*e.g.* polyisobutylene in aqueous media), which serves as a strong, supple frame preventing the solvated component from over-expanding. Macroscopically, this will keep the APCN gels from over-swelling and consequently disintegrating (which is what a conventional hydrogel is prone to under identical conditions) resulting in overall superior mechanical properties. This mechanical stability enables APCNs to reversibly react to swelling-deswelling cycles.

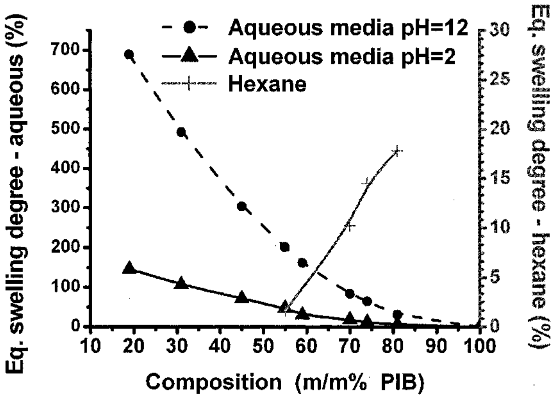


Figure 4. Equilibrium swelling of PMAA-*l*-PIB APCN in hydrophobic (hexane) and aqueous media.

Figure 5 shows the swelling behavior of a PMAA-*l*-PIB APCN in alternating environments of pH = 2 and 12. It can be seen that the process could be repeated several times without noticeable change in either swelling factors (extent, speed *etc.*) or gel structure, which indicates the aptitude of APCNs for responsive behavior. It should also be noted that compared to the swelling an APCN containing sulfonic acid groups[18], the swelling degree of PMAA-*l*-PIB APCNs is apparently 2-3 times higher.

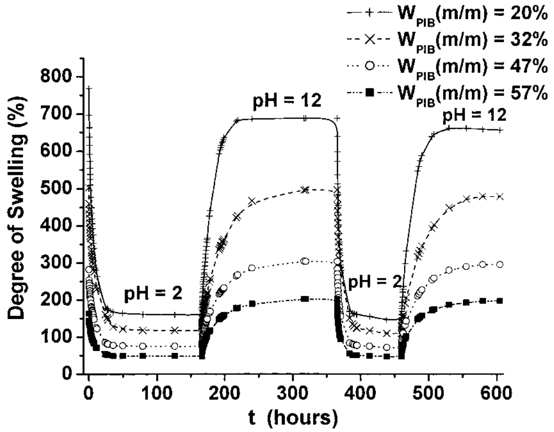


Figure 5. Swelling cycles of PMAA-*l*-PIB amphiphilic conetworks by altering pH between 2 and 12 in aqueous environment.

Intelligent Thermal Behavior of PDMAEMA-*l*-PIB Amphiphilic Conetworks

A large number of polymers, including poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) are known to possess lower critical solution temperature (LCST). Swollen hydrogels of such polymers usually become reversibly opaque above LCST, i. e. optical clarity is restored by lowering the temperature below the LCST. However, there are hydrogels of polymers with LCST which do not change their transmittance by increasing the temperature above or decreasing below the LCST. PDMAEMA, with an LCST of around 45 °C, is one such polymer.

The optical behavior of PDMAEMA homopolymer hydrogel and a series of PMDMAEMA-*l*-PIB amphiphilic conetworks has been investigated by us. It has been found that certain (otherwise optically clear) PMDMAEMA-*l*-PIB APCNs swollen in water become opaque by raising the temperature above the LCST of PDMAEMA. Figure 6 shows the instantaneous change in transmittance as a function of PDMAEMA content when changing the temperature from 40 °C to 60 °C. Apparently the phenomenon only appears in a certain composition range, which indicates that it is a result of structural effects stemming from the (nanoscopic) arrangement of the two constituents. As in the case of the swelling behavior of the the PMAA-*l*-PIB APCNs, this process is also thoroughly reversible, and its extent is controllable as well via composition factors.

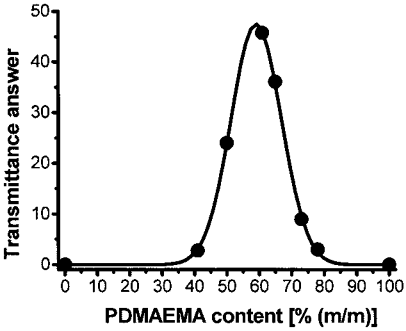


Figure 6. Change in transmittance of PDMAEMA-*l*-PIB gels by temperature shift from 40 °C to 60 °C.

Conclusion

Poly(2-hydroxyethyl methacrylate)-*l*-polyisobutylene (PHEMA-*l*-PIB), poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB) and poly(N,N-dimethylaminoethyl methacrylate)-*l*-polyisobutylene (PDMAEMA-*l*-PIB) amphiphilic conetworks (APCNs) were successfully synthesized. Due to the prevention of macroscopic phase separation, APCNs possess unique nanophase separated morphology. Owing to their distinct structure, these materials exhibit some exceptional properties with regard to mechanical properties and reversible responsive behavior. PMAA-*l*-PIB APCNs were shown to exhibit pH-responsive swelling while PDMAEMA-*l*-PIB APCNs displayed smart temperature-responsive obscurement. The characteristics of both responses were found to be a function of composition, which warrants control over these effects. According to prevalent definition, materials that give well-defined and reversible response to external action or trigger are dubbed intelligent (smart, responsive) materials. Typical such actions are mechanical effects, changes in species concentration/pH, electromagnetic effects/light/heat etc., and these materials are sought as potential sensors, actuators, biomaterials, drug delivery systems and so on. By this definition, the aforementioned APCNs doubtless qualify as intelligent materials, the responses of which (to pH or temperature shift) can be preset via composition variables.

Acknowledgements

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