

Morphology Studies and Potential Applications of Poly(N,N-dimethylacrylamide)-*l*-Polyisobutylene Amphiphilic Polymer Conetworks

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ABSTRACT

A series of poly(N,N-dimethylacrylamide)-*l*-polyisobutylene (PDMAAm-*l*-PIB) amphiphilic conetworks were synthesized from two incompatible polymers, i.e. hydrophilic PDMAAm and strongly hydrophobic PIB in a wide range of composition (38-80 m/m % PIB). Swelling experiments were carried out to determine the equilibrium swelling ratios which proved the amphiphilic nature of these new materials, and are in correlation with composition. Thermal analysis (DSC), small angle X-ray scattering (SAXS) and atomic force microscopy (AFM) measurements were carried out. Results show special phase separated morphology, where the size of the phases are in the nanometer range in all cases. Furthermore, the nanophases of the conetworks have composition dependent spatial arrangement. Successful synthesis of silver nanoparticles was achieved inside of the conetwork's hydrophilic phases resulting in a novel organic-inorganic nanohybrid material.

Keywords: hydrogel, amphiphilic, conetwork, silver, nanoparticle

1 INTRODUCTION

Well-defined heterogeneous polymeric structures have played an important role in polymer chemistry, material science and technology in recent years. One type of these promising materials belongs to amphiphilic polymer conetworks (APCN). Since the discovery of APCNs, this field of polymer chemistry has experienced a great development in terms of synthesis, characterization and applications [1]. APCNs are bi- or multicomponent polymeric materials consisting of covalently bonded hydrophilic and hydrophobic polymer chain segments. Because of their unique and novel advantageous properties significant attention has been paid to these type of materials. A number of potential applications has already been demonstrated, especially for biological fields, e.g. soft contact lenses [2], drug delivery systems [3], or

antimicrobial films [4]. Another very promising field is the use of APCNs as nanoreactors. This means that in one of the APCN's phase a chemical reaction can take place which results in nanoparticle formation inside the APCN [5]. Due to the fact that APCNs have such important and remarkable utilization, it is essential to understand their structure, properties and characteristics. Among the properties of APCNs the most significant is their amphiphilic character which originates from the different philicity of the building polymer segments. It is analyzed by swelling experiments in polar and non-polar solvents [6]. Other methods, such as thermoanalytical (TG, DSC) and imaging techniques (TEM, AFM) have provided important information about the structure and morphology of APCNs [7]. The periodicity and the size of the phases in APCNs have been examined by small angle X-ray scattering (SAXS) and spin-diffusion solid state NMR technique [8]. This study reports on the synthesis, morphological characteristics of PDMAAm-*l*-PIB APCNs, and on a potential utilization of these conetworks as nanoreactors as well.

2 EXPERIMENTAL

2.1 Materials

Methacrylate-telechelic polyisobutylene (MA-PIB-MA; $M_n=5000$ g/mol; $M_w/M_n=1.02$) was synthesized as described earlier [9,10], and it was applied as hydrophobic macromonomer. N,N-dimethyl acrylamide (Aldrich), the monomer of the hydrophilic polymer segment, was distilled under vacuum prior to use. Azo-bis-isobutyronitrile (Aldrich) initiator was recrystallized from methanol before use. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. Silver nitrate, dimethylformamide (DMF) (Aldrich) and other solvents and reagents were used as received.

2.2 Methods

Synthesis of PDMAAm-*l*-PIB APCNs

A series of PDMAAm-*l*-PIB APCNs was synthesized by the macromonomer method [10]. In this reaction a free

radical copolymerization occurs between the hydrophilic monomer (N,N-dimethyl acrylamide) and the hydrophobic macromonomer (methacrylate-telechelic polyisobutylene). Polyisobutylene was dissolved in distilled THF and mixed with N,N-dimethyl-acrylamide. Subsequently AIBN was added, and the reaction mixture was poured into a teflon mold (under inert atmosphere) in which the cross-linking reaction took place. The mixture was kept at 65 °C for 72 hours. After the cross-linking reaction the samples were purified by extraction and were dried until constant weight under reduced pressure. The composition of the resulting APCN samples was determined by elemental analysis (see Table 1).

Amount of PIB in the reaction [m/m%] (M=5000 g/mol)	Molecular weight of PDMAAm M _c [g/mol] *	Composition by elementary analysis		Sample
		PIB [m/m%]	PDMAAm [m/m%]	
30	4100	38	62	MP 38
40	3180	44	56	MP 44
50	2130	54	46	MP 54
60	1670	60	40	MP 60
70	930	73	27	MP 73
80	550	82	18	MP 82

*M_c: Average molecular weight between PIB crosslinks

Table 1. Sample codes, feed ratio of MA-PIB-MA, and composition and M_c of PDMAAm-*l*-PIB APCN samples.

2.3 Characterization

Differential Scanning Calorimetry (DSC). DSC thermographs of the conetwork samples were recorded by a Mettler TA4000 thermal analyzer with DSC 30 cell equipment in the -100-150°C temperature range under nitrogen with a heating rate of 10°C/min, and the second heating line was evaluated.

Small Angle X-ray Scattering (SAXS). The SAXS measurements were performed in an evacuated compact camera (Anton Paar KKK). As X-ray source, Cu K α radiation with a wavelength of 0.154 nm was used. Scattered intensity was recorded by a scintillation counter in a step-scanning mode.

Atomic Force Microscopy (AFM). The surfaces of dried samples were microtomed at room temperature with a diamond knife from Diatome and a Microtom ULTRACUT UCT (Leica), removing about 100 nm of the surface. AFM images of the microtomed samples were recorded with a Nanoscope III scanning probe microscope (Digital Instruments).

Transmission Electron Microscopy (TEM). TEM measurements were carried out with a LEO 912 Omega equipment using acceleration voltage of 120 kV. Sections of samples with 60-100 nm thicknesses were cut with a microtome for obtaining TEM pictures.

3 RESULTS AND DISCUSSION

3.1 Characterization of the conetworks and morphology investigations

The amphiphilic character of the PDMAAm-*l*-PIB conetworks was investigated by swelling experiments in both polar (water) and non-polar (n-hexane) solvents. As clearly visible in Figure 1, higher the polyisobutylene content higher the equilibrium swelling ratio of the conetwork samples in n-hexane. In contrast, when the APCNs were swollen in water, the lower polyisobutylene content resulted in higher equilibrium swelling ratios.

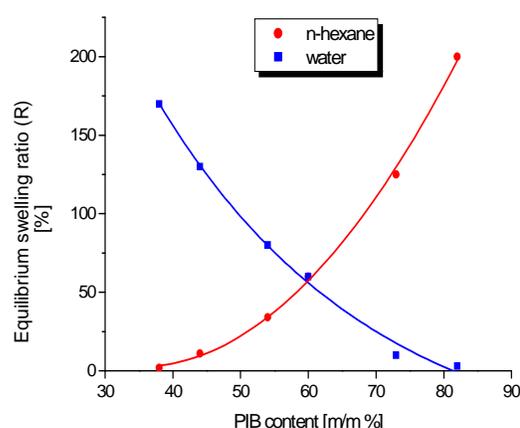


Figure 1. Equilibrium swelling ratios of PDMAAm-*l*-PIB conetworks in water and in n-hexane.
(R = mass of swollen conetwork/mass of dry sample [%])

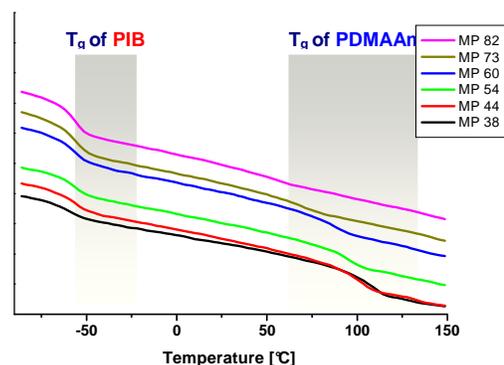


Figure 2. DSC analysis of PDMAAm-*l*-PIB conetwork samples.

Differential Scanning Calorimetry (DSC) measurements were made in order to characterize the thermal behaviour of the PDMAAm-*l*-PIB APCNs (Fig. 2). It can be seen from the DSC curves that the conetworks have two glass transition temperatures. This result indicates that the conetworks have two separated phases. In the temperature range around -60 °C, the glass transition of the polyisobutylene phase appears, while the other glass transition at around 100 °C corresponds to the poly(N,N-dimethyl-acrylamide) phase.

The special phase separated morphology was further studied by Atomic Force Microscopy (AFM). Phase mode AFM images can be seen in Figure 3. In these pictures, the polyisobutylene phase has darker brown color while the poly(N,N-dimethylacrylamide) phase has brighter yellow color. What is visible from the images is that the conetworks possess different morphologies depending on composition. In case of the low polyisobutylene content (MP38) separated sphere-like polyisobutylene phases are visible which are surrounded by the poly(N,N-dimethylacrylamide) matrix. When the PIB content increases, the morphology changes and other arrangements appears. It can be observed that the conetworks with 44-60% PIB content possess a special cocontinuous (bicontinuous) morphology. In these cases, both the PIB and the PDMAAm domains form continuous phases in each other. When the PIB content reaches a certain value, the morphology changes again and shows similar picture than that in the case of low PIB content, but here the separated sphere-like phases are PDMAAm and PIB is the surrounding matrix.

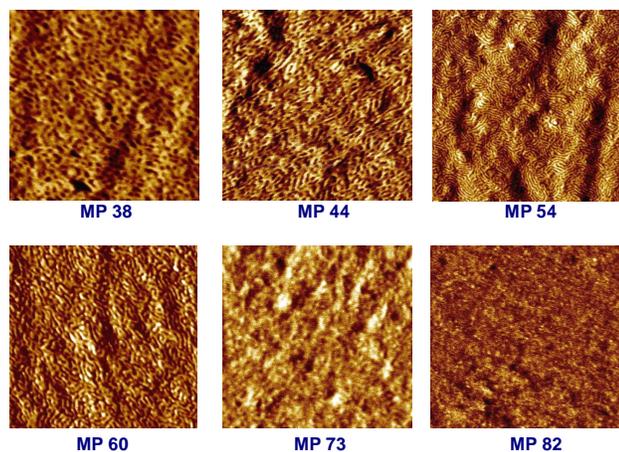


Figure 3. Phase mode AFM images of PDMAAm-*l*-PIB conetworks (500x500 nm)

It is clear from the AFM images that the sizes of the phases are in the nanometer range. We can get some further information about the structural properties from the results of small angle X-ray scattering measurements (Fig. 4). The results of the SAXS measurements for both the dry and the swollen state (in water) are shown here.

The scattering curves indicate that short range order

exists in the PDMAAm-*l*-PIB APCN's phases. The average domain periodicity can be easily calculated from the scattered maxima. These values are in the 8-13 nm range in the case of dry samples. If we measure the scattering in the swollen state in water, different type of scattering curves appear. Because only the hydrophilic phase swells in water, the periodicity of the domains change to the range of 8-18 nm (Fig. 5). It is apparent that the samples which are unable to swell in water (samples with 73 and 82% PIB content) do not show any changes in the scattering profiles.

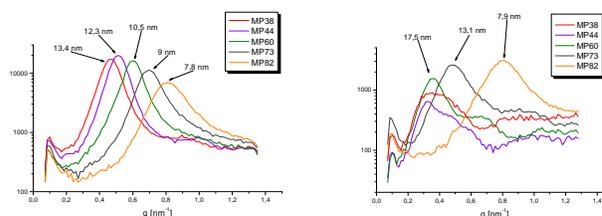


Figure 4. SAXS curves of the PDMAAm-*l*-PIB conetworks in dry (left) and swollen state in water (right).

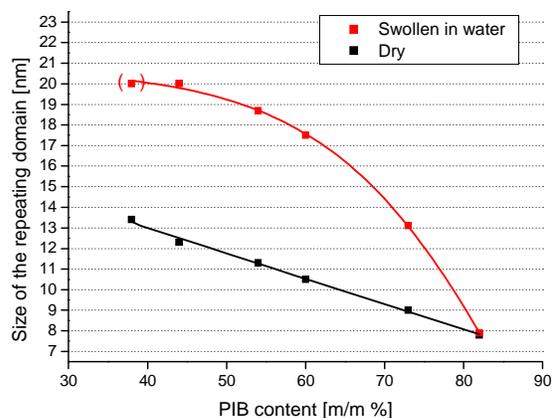


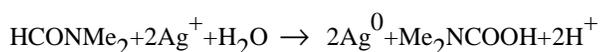
Figure 5. The average domain distances in PDMAAm-*l*-PIB APCNs in dry and swollen states.

The scattering curves change drastically in the case of those samples which are able to swell in water to high degrees (with low PIB content). The short range order increases or disappears completely (MP 38 and 44). These results indicate that the nanophase separated morphology of the PDMAAm-*l*-PIB amphiphilic conetworks remains upon swelling, and only the average domain distance increases. In other words, the swelling of one of the phases does not destroy the morphology, it only expands the domain size of the swollen phase. This observation is very important for a variety of specialty applications ranging from drug release, to biomaterial, membrane, catalysis etc. applications.

3.2 Nanoparticle synthesis

Due to the unique nanostructured morphology of the APCNs, it is possible to carry out chemical reactions inside one of the phases of the conetworks. A selected phase can load with a chemical reagent by means of swelling. In the case of water soluble components, e. g. silver nitrate, the corresponding phase will be the hydrophilic PDMAAm. A reaction with the loaded compound will take place in this nanophase by adding an appropriate reagent. Consequently, the reaction product will be formed in this nanoreactor and can be deposited there.

The chemical reaction what we have tried to utilize for the production of silver particles inside the conetworks was the following:



As already discussed, the PDMAAm-*l*-PIB APCNs possess nanophase separated morphology. As shown in Figure 6, utilizing this simple chemical reaction inside the nanophase of the conetwork results in nanosized silver particles in the hydrophilic PDMAAm phase. The concentration of the aqueous silver nitrate solution was 0.6 mol/L. After swelling the conetworks with this solution for 1 day in a dark place, the samples were placed into dimethylformamide and the reduction process occurred in the conetwork's hydrophilic phase. The reduction time was 48 hours. As we can see from the TEM image in Figure 6, the average particle size of the silver particles is ~20nm.

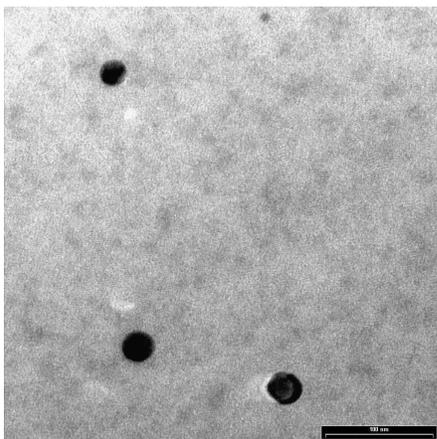


Figure 6. TEM image of MP44 sample with silver nanoparticles inside (500x500nm).

4 CONCLUSIONS

PDMAAm-*l*-PIB amphiphilic conetworks were synthesized in a wide range of composition. The conetworks were characterized by several techniques. Swelling experiments and DSC analyses were performed in

order to prove amphiphilic character and the phase separation of the conetworks, respectively. From the AFM and SAXS measurements it can be concluded that these amphiphilic conetworks possess unique nanophase separated morphology. The nanophases of the conetworks have composition dependent spatial arrangement, where the size of the phases are in the nanometer range in all cases.

We have successfully synthesized silver nanoparticles by utilizing the conetwork's hydrophilic phase as a nanoreactor. According to TEM measurements the size of the resulted silver particles is about 20 nm. These results indicate that amphiphilic conetworks have large potential to produce different type of nanohybrids with inorganic or organic nanoparticles.

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