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Covalently closed microemulsions in presence of triblock terpolymers

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Abstract

This paper is focused on the influence of polystyrene (PS)–poly(1,4-butadiene) (PB)–poly(ethylene oxide) (PEO) triblock terpolymers on the w/o microemulsion of the pseudo-ternary system water/sodium dodecylsulfate (SDS)/xylene-pentanol. Despite the insolubility of the copolymer in water as well as in the xylene–pentanol mixture, it can be incorporated into the w/o microemulsion and interactions between the triblock terpolymer molecules and the anionic surfactant headgroups can be detected by differential scanning calorimetry (DSC) measurements. Furthermore, dynamic light scattering measurements were used to determine the aggregate diameter of the modified microemulsions. For lower polymer concentrations large aggregates between 100 and 500 nm can be observed. Surprisingly, at a higher terpolymer concentration of 5 wt%, significant smaller aggregate diameters can be identified by dynamic light scattering and Cryo-SEM. One can conclude that the copolymers are incorporated in the inverse microemulsion droplets, where the PB blocks cover the water droplets. The thermally induced radical cross-linking of the butadiene units in the presence of azobisisobutyronitrile (AIBN) leads then to covalently closed nanocapsules with an average size of 10 nm. © 2007 Elsevier Inc. All rights reserved.

Keywords: Triblock terpolymer; Microemulsion; Nanocapsules

1. Introduction

Microemulsions are thermodynamically stable, transparent mixtures of water, oil and surfactant with a multitude of mesoscopic structures. One has to distinguish between different types of microemulsions, i.e., water-in-oil, oil-in-water, or bicontinuous ones. The formation depends on the structure and stability of the surfactant film, which divides oil and water domains [1]. Microemulsions are of special interest with regard to numerous applications, e.g., as templates for the preparation of nanostructured inorganic or organic materials or as vehicles in extraction processes [2].

During the last years the influence of noncharged [3–6] and charged [7] polymers on microemulsions has been studied, with regard to polymer–surfactant–interactions and their

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influence on the stability and structure of the microemulsion. Recently, we have shown that the formation of a bicontinuous phase channel can be induced when the nonionic polymers poly(ethylene oxide) (PEO) [8] or poly(N-vinyl-2-pyrrolidone) (PVP) [9] were solubilized. The presence of polyelectrolytes in microemulsions can lead to an expansion of the inverse microemulsion phase [10,11] and influence the size and the stability of the nanodroplets. However, such polymer-modified microemulsions can be used as a new type of template for the nanoparticle formation [12,13]. Furthermore, microemulsions can be modified by amphiphilic block copolymers [14-17]. Jakobs et al. [18] reported at first about an enormous enhancement of the solubilization capacity of microemulsions by adding amphiphilic poly(ethylene-alt-propylene)poly(ethylene oxide) (PEP-PEO) block copolymers. Charged diblock copolymers can be used also for the stabilization of microemulsions in absence of a cosurfactant [19].

Due to their amphiphilic behavior block copolymers can associate into a number of microstructures depending on the type of solvent. For example, Alexandridis et al. [20] observed

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nine different phases (four cubic, two hexagonal, one lamellar lyotropic crystalline phase, and two micellar solutions) for a system consisting of poly(ethylene oxide)-poly(propylene oxide) block copolymer/water and p-xylene. The different morphologies of triblock terpolymers in solution were discussed for example in the review given by Fustin et al. [21] including coreshell-corona micelles, micelles with a mixed corona, Janus micelles and vesicles. On the basis of these morphologies triblock terpolymers are useful for the preparation of nanotubes [22], hollow nanospheres [23], and nanoporous membranes [24,25]. There are a lot of interesting applications of block copolymer micelles summarized in a review by Riess [26], e.g., for emulsion stabilization, catalytic support, and biomedical applications. Moreover, the employment of block copolymer micelles as templates for the formation of metal nanoparticles (e.g., silver, gold, and palladium) has been reported recently [27-29].

The aim of our research is first of all to incorporate block copolymers in a microemulsion, which can be cross-linked then in a second step to form nanocapsules of very small dimensions. Therefore, we incorporated polystyrene (PS)–poly(1,4-butadiene) (PB)–poly(ethylene oxide) (PEO) triblock terpolymers into the well known water/SDS/xylene-pentanol (1:1) microemulsion system [30], and characterized the resulting self-assembled systems by means of dynamic light scattering (DLS) and DSC measurements.

The polybutadiene blocks are cross-linked then due to a radical reaction in the presence of azobisisobutyronitrile (AIBN), and covalently covered nanocapsules are produced, characterized by DLS and Cryo scanning electron microscopy (Cryo-SEM). The aim was to produce nanocapsules on a scale range below 20 nm, which is still a scientific challenge.

However, when a nanoparticle formation process is realized before the cross-linking, block copolymer covered nanoparticles can be obtained, finally.

2. Experimental

2.1. Materials

Pentanol (>99%), sodium dodecylsulfate (SDS) (>99%) and azobisisobutyronitrile (AIBN) (\geq 98%) are purchased from Fluka and used without further purification. Xylene (>99%), a commercial product from Roth, is used as obtained. Water is purified with a Modulab PureOne water purification system (Continental). For interfacial tension measurements, toluene (>99%), obtained by Fluka, and water are passed through a 0.2 µm filter for further purification.

A series of polystyrene (PS)–poly(1,4-butadiene) (PB)– poly(ethylene oxide) (PEO) triblock terpolymers are synthesized by living anionic polymerization. The polymerization is initiated by sec-butyllithium using benzene as the solvent, by adding sequentially styrene, butadiene and ethylene oxide, which leads to the desired 1,4-microstructure of polybutadiene. The phosphazene base t-buP₄ is added one hour after addition of the ethylene oxide, in order to enable polymerization of this third monomer in the presence of lithium counter ions. Before adding butadiene as the second monomer, a small amount of the polymerization solution is removed from the reactor to get the homopolystyrene corresponding to the PS block of the final triblock terpolymer. Molecular weights and polydispersities are determined by size exclusion chromatography (SEC) using a Waters instrument and tetrahydrofurane as solvent. PS standards are used for calibration. The composition is determined by ¹HNMR spectroscopy and from this and the molecular weight of the PS block the total molecular weight of the triblock terpolymer is determined. Details of the polymerization of these monomers are described elsewhere [31].

2.2. Sample preparation

Due to the nonsolubility of the triblock terpolymers neither in water nor in the pentanol/xylene mixture (1:1), oilcontinuous microemulsions of water/SDS/xylene–pentanol are prepared at first by mixing the three components in absence of a polymer. In a second step the appropriate amount of triblock terpolymer is added to the microemulsion. The concentrations of the triblock terpolymers are referred in relation to the total amount of oil. Finally, the samples are stirred at room temperature until complete solubilization of the polymer.

To examine whether it is possible to cross-link the PB blocks in the block copolymer-modified microemulsions, samples are prepared separately. Therefore, the radical initiator AIBN (0.1 wt%) is added to the xylene/pentanol mixture (1:1) before preparing the microemulsions. After complete solubilization of the triblock terpolymers, the AIBN-containing microemulsions are heated up to $80 \,^{\circ}$ C for 10 min. Finally, all samples are cooled down and kept at room temperature for further characterization.

3. Methods

3.1. Interfacial tension measurements

To characterize the amphiphilic behavior of the PS–PB–PEO triblock terpolymers at 20 ± 0.5 °C a spinning drop tensiometer SVT (DataPhysics) is used [32–35]. For these experiments the block copolymers are added to a toluene/pentanol (3:1) mixture. Noteworthy, the block copolymers can be completely solubilized in presence of an excess of toluene. A drop of the polymer solution, embedded in water, is deformed by high speed rotation of the cylindrical measuring tube around its axis. The used apparatus allows a rotation speed up to 10,000 rpm.

3.2. Differential scanning calorimetry (DSC)

Microdifferential scanning calorimetry, Micro-DSC III (Setaram), can be used to charaterize different types of water in inverse microemulsion droplets. Therefore, the samples are characterized in the temperature region between -20 and 80 °C. The heating and cooling rate is fixed at 0.3 K/min. Starting at 25 °C, the samples are cooled down and kept frozen for 2 h at -20 °C. The following heating curve ends with a second isotherm at 80 °C. After a second cooling and heating cycle all measurements are finished at 25 °C.

3.3. Dynamic light scattering

To determine the size and the size distribution of the droplets and aggregates of the triblock terpolymer-modified microemulsions, dynamic light scattering measurements are carried out at 25 °C, at a fixed angle of 173° using the Nano Zetasizer (Malvern), equipped with a He–Ne laser (4 mW) and a digital autocorrelator. The apparatus allows to carry out measurements up to 80 °C, without any additional thermostat. The solvent viscosities and densities were adapted to the respective measuring temperature. Noteworthy, the contrast in the nonmodified microemulsion system is not strong enough for dynamic light scattering.

3.4. Cryo scanning electron microscopy (Cryo-SEM)

The structure of the block copolymer-modified microemulsion was examined by Cryo-high resolution scanning electron microscopy (S-4800, Hitachi, equipped with a field emmision gun). Each sample is cooled by plunging into nitrogen slush at atmospheric pressure. Afterwards, the samples are freezefractured at -180 °C, etched for 60 s at -98 °C and sputtered with Platinum in the GATAN Alto 2500 Cryo-preparation chamber and then transfered into the Cryo-SEM.

4. Results and discussion

4.1. Characterization of the triblock terpolymers and the inverse microemulsion

4.1.1. Composition and molecular weights of the triblock terpolymers

The molecular weights, the compositions and the short names of the triblock terpolymers are given in Table 1.

Table 1

| Composition | and features | of the pol | lystyrene | (PS)–block- | -polybutadiene | (PB)- |
|--------------|---------------|-------------|-------------|-------------|----------------|-------|
| block-poly(e | thylene oxide | e) (PEO) ta | riblock ter | polymers | | |

| Block copolymer | $M_{\rm w}{}^{\rm a}$ (g/mol) | Composition ^b (wt%) PS-PB-PEO | γ ^c (mN/m) (average value) |
|---|-------------------------------|---|--|
| S ₁₄ B ₄₆ EO ₄₀ ¹⁰² | 102,000 | 14-46-40 | 8.4 ± 0.5 |
| S ₁₈ B ₃₆ EO ⁶⁰ ₄₆ | 60,000 | 18–36–46 | 7.8 ± 0.2 |
| $S_{43}B_{21}EO_{36}^{111}$ | 111,000 | 43-21-36 | 7.1 ± 0.1 |

^a Molecular weight determined by SEC.

^b Composition of the triblock terpolymers determined by NMR.

^c Interfacial tension measured at a water/toluene–pentanol (3:1) system in presence of 1 wt% of the triblock terpolymers.

4.1.2. Interfacial tension measurements

The amphiphilic behavior of the PS–PB–PEO triblock terpolymers, which is caused by the hydrophilic ethylene oxide block and the hydrophobic styrene and butadiene blocks, can be checked by interfacial tension measurements. Therefore, the interfacial tension of a water/toluene–pentanol (3:1) droplet is determined as a function of the rotation speed between 2000 and 4500 rpm, while 30 to 40 single measurements are done for each rotation speed. Since one measurement per second is performed, the measuring time for each sample is between 4 and 5 min. Further experiments have shown, that the droplets are less stable after a longer period of time (>10 min) and a slight diffusion of pentanol from the droplet into the aqueous phase can be observed.

Fig. 1 shows an increase of the interfacial tension with increasing rotation speed in absence of the polymers. An increase of the rotation speed from 2000 to 4500 rpm leads to an increase of the interfacial tension from 12.9 ± 0.4 to 16.7 ± 0.3 mN/min. However, the error range of the single measurements is broad, in particular for lower rotation speeds.

In contrast to these results only a very slight increase of the interfacial tension and a more narrow distribution of the sin-



Fig. 1. Interfacial tension of a water/toluene-pentanol (3:1) interface as a function of the rotation speed.

gle measurements can be observed in the presence of 1 wt% of the triblock terpolymers. Moreover, the presence of the block copolymers leads to a clear decrease of the interfacial tension and an average value between 7 and 9 mN/m can be observed. $S_{43}B_{21}EO_{36}^{111}$ shows the strongest decrease to 7.1 mN/m, while $S_{14}B_{46}EO_{40}^{102}$ decreases the interfacial tension to 8.4 mN/m (Table 1). The differences in the interfacial behavior of the triblock terpolymers can be related to their structural differences. When the polystyrene block length is increased from $S_{14}B_{46}EO_{40}^{102}$ to $S_{43}B_{21}EO_{36}^{111}$, the interfacial tension is decreased. That means, especially the hydrophobic polystyrene block is responsible for a pronounced amphiphilic behavior.

4.1.3. Phase behavior of the nonmodified microemulsion

At room temperature (25 °C) the partial phase diagram of the pseudo-ternary system water/SDS/xylene-pentanol (at a constant ratio pentanol/xylene = 1) shows an optically clear area at the oil corner, i.e., a w/o microemulsion or so-called L2 phase, as to be seen in Fig. 2. Furthermore, the phase behavior of the system was investigated at 80 °C, that means the temperature range of the radical reaction initiated by AIBN. A significant enlargement of the isotropic phase range in direction to the water and the surfactant corner can be observed. Temperature sensitivity of microemulsions was mostly described for nonionic microemulsions [36-38] and arises from the influence of the temperature on the spontaneous curvature of the surfactant monolayer. However, a slight widening of the L2 phase of the ionic system SDS/toluene-pentanol/water can be observed when the temperature is increased to 40 °C, as already reported in [39]. For ionic microemulsions, this increase of the water solubilization capacity can be also related to changes in the curvature of the surfactant film [40,41].

4.2. Triblock terpolymer-modified inverse microemulsions at room temperature

4.2.1. Phase behavior

Because of a limitation in the amount of the triblock terpolymers only at the marked points A, B, and C (compare Fig. 2) the phase behavior was checked in more detail.

At a polymer concentration of 1 wt% the microemulsions become cloudy, but the resulting opaque solutions are stable and do not precipitate. By increasing the polymer concentration to 5 wt% the microemulsions become surprisingly optically clearer, and only a slightly turbid solution is observed. Noteworthy, the best transparent mixtures were observed in presence of the $S_{18}B_{36}EO_{46}^{60}$ terpolymer, that means the polymer with the lowest molar mass. However, the most efficient incorporation was observed in presence of polymer $S_{43}B_{21}EO_{36}^{111}$ showing the strongest surface tension decrease effect.

4.2.2. Differential scanning calorimetry (DSC)

It is widely known that DSC measurements are very useful to describe the melting behavior of water in confined spaces and in the presence of adjacent surfactants. Furthermore, different types of microemulsions (e.g., w/o or bicontinuous microemulsion) can be identified by DSC measurements.



Fig. 2. Partial phase diagram of the quasi-ternary system water/SDS/pentanolxylene (1:1) (marked compositions A, B, and C).

Micro-DSC measurements of microemulsions containing 1 wt% of $S_{14}B_{46}EO_{40}^{102}$, $S_{18}B_{36}EO_{46}^{60}$, and $S_{43}B_{21}EO_{36}^{111}$ are realized at point B in comparison to the unmodified microemulsion. At point A, that means at the lowest water content, no DSC peak can be obtained, in agreement to other polymer-modified microemulsion systems [10]. Fig. 3 shows the heating curves of the different systems. In the case of the unmodified microemulsion a large bulk water peak at about 0 °C, and two smaller ones with a peak top at -7.1 and -10.2 °C can be observed. According to Senatra et al. [42] these last mentioned two peaks can be related to 'interphasal' and 'bound' water. The presence of the triblock terpolymers leads to a significant decrease of the bulk water peak and a slight shift of the peak top to lower temperatures. Moreover, a disappearance of the interphasal water peak can be observed and just a weak shoulder at about $-5 \,^{\circ}\text{C}$ remains. However, the peak at about -10 °C is not strongly changed due to the presence of the block copolymers. These results show that the triblock terpolymers directly influence the solubilization of the surfactant headgroups.

One can conclude that the polymers are partly fixed nearby the surfactant head groups, that means the PEO blocks are inside the water droplets. Significant differences between the three terpolymers $S_{14}B_{46}EO_{40}^{102}$, $S_{18}B_{36}EO_{46}^{60}$, and $S_{43}B_{21}EO_{36}^{111}$ cannot be observed.

4.2.3. Dynamic light scattering

A characterization of the polymer-modified microemulsions by dynamic light scattering gives information about the aggregate or droplet sizes of the microemulsion. Therefore, samples with a polymer concentration between 1 and 5 wt% were prepared for each terpolymer. The aggregate diameters (d) observed by DLS are summarized in Table 2, as a function of the polymer concentration.

Generally, a significant increase of the aggregate diameters up to 600 nm can be observed with increasing concentration of the triblock terpolymers. In more detail, the results show that in the presence of $S_{18}B_{36}EO_{46}^{60}$ the smallest aggregate diameter between 100 and 250 nm can be found. Furthermore, it is noticeable that a second fraction of significant smaller aggre-



Fig. 3. DSC heating curves of the original and copolymer-modified microemulsions at point B of the phase diagram.



Fig. 4. Photograph of copolymer-modified (a) (1 wt% $S_{18}B_{36}EO_{46}^{60}$) and (b) (5 wt% $S_{18}B_{36}EO_{46}^{60}$) microemulsion at point A, after heating in the presence of AIBN.

gates ($d \le 50$ nm) can be observed at higher concentrations of $S_{18}B_{36}EO_{46}^{60}$. Based on these results we restricted the following experiments on $S_{18}B_{36}EO_{46}^{60}$.

4.3. Triblock terpolymer-modified microemulsions after heating in the presence of AIBN

4.3.1. Phase behavior

When the microemulsion in presence of 1 wt% $S_{18}B_{36}EO_{46}^{60}$ and AIBN is heated up to 80 °C the opaque solution be-

comes more turbid (Fig. 4a). In contrast to this observation, the slightly turbid microemulsion at a polymer concentration of 5 wt% becomes completely transparent after heating up to $80 \degree C$ (Fig. 4b).

4.3.2. Dynamic light scattering

The influence of the heating process in presence of AIBN, to the aggregate diameter of the polymer-modified microemulsions, is examined as a function of the concentration of $S_{18}B_{36}EO_{46}^{60}$. The results obtained by automatic peak analysis



Fig. 5. Size distribution of the polymer-modified (a) (1 wt% $S_{18}B_{36}EO_{46}^{60}$) and (b) (5 wt% $S_{18}B_{36}EO_{46}^{60}$) microemulsion at point A, during the heating in presence of AIBN, determined by dynamic light scattering (automatic peak analysis by volume).

| Table 2 |
|--|
| Aggregate diameter of the polymer-modified microemulsions (point A) deter- |
| mined by dynamic light scattering |

| Sample | Size distribution ^a | | |
|---|--------------------------------|-----------------------------|--|
| | 1 wt% | 5 wt% | |
| S ₁₄ B ₄₆ EO ₄₀ ¹⁰² | 214 nm (100%) | 527 nm (100%) | |
| S ₁₈ B ₃₆ EO ₄₆ ⁶⁰ | 127 nm (93%) | 233 nm (65%) 30 nm (13%) | |
| S ₄₃ B ₂₁ EO ₃₆ ¹¹¹ | 295 nm (100%) | 600 nm (100%) | |

^a Obtained by automatic peak analysis by intensity.

Table 3 Aggregate diameter of the polymer-modified microemulsions (point A) after

| heating in the presence of AIBN, determined by dynamic light scattering | | | | |
|---|--------------------------------|---------------------|--|--|
| Sample | Size distribution | | | |
| | Intensity ^a | Number ^b | | |
| 1 wt% S ₁₈ B ₃₆ EO ⁶⁰ ₄₆ | >1000 nm (70%) 130 nm (30%) | 120 nm (99%) | | |
| $5 \text{ wt\% } S_{18}B_{36}EO^{60}_{46}$ | 190 nm (60%) 10 nm (21%) | 10 nm (100%) | | |

^a Obtained by automatic peak analysis by intensity.

^b Obtained by automatic peak analysis by number.

by intensity and number are given in Table 3. In agreement with the results discussed above, a second fraction of smaller aggregates can be observed when the concentration of $S_{18}B_{36}EO_{46}^{60}$ is increased up to 5 wt%. However, the effect seems to be inten-

sified by heating the microemulsions in the presence of AIBN. Surprisingly, a 10 nm aggregate fraction became dominant by dynamic light scattering (peak analysis by number). In a second experiment the heating process was carried out directly in the Nano Zetasizer. Therefore, the polymer-modified microemulsions are prepared at room temperature as described in Section 2.2. and placed in the measuring cell, which is already heated up to 80 °C. With regard to the samples heated up in the oil bath, the samples stay in the measuring cell for 10 min and several measurements are performed during that period of time. Afterwards the samples are cooled down to 25 °C and again examined by DLS. Figs. 5a and 5b show the size distributions during the heating of the block copolymer-modified microemulsions in presence of 1 and 5 wt% S₁₈B₃₆EO₄₆⁶⁰.

At 1 wt% block copolymer, a broad peak between 1000 and 3000 nm can be observed when the sample is heated for only 2 min. This peak becomes more narrow during the heating process and is slightly shifted to larger and then to smaller diameters within the range of 1000 to 2000 nm. Furthermore, a small peak at about 40 to 50 nm appears after 6 min, which is enlarged by the running process. However, this fraction of smaller aggregates is not stable, since it disappears when the sample is cooled to 25 °C. In that case, a main fraction between 1000 and 2000 nm and a very small peak at about 120 nm can be observed.

In contrast, at the higher copolymer concentration (5 wt%) only one peak of small aggregates (d < 50 nm) can be detected for nearly all measurements. Just at the beginning of the heating process, a very small peak of aggregates with d between 500 and 1000 nm appears. The diameter of the main fraction is decreased with increasing measuring time from nearly 30 to 10 nm. No significant changes can be obtained when the sample is cooled to 25 °C and only one fraction with an aggregate diameter of about 10 nm can be observed.

When the same experiments were realized in absence of AIBN no effect on the particle dimensions is observed. That means, the decrease of the particle size by heating in presence of AIBN can be related to a cross-linking of the nanocapsules, and not to a better solubilization of the polymer.

Increasing the time of heating to 30–60 min, in general the system becomes more turbid, which is in full agreement with an increase of the particle dimensions detected by DLS. One can conclude that a longer heat treatment leads to a droplet–droplet cross-linking.

4.3.3. Cryo-SEM

Cryo scanning electron microscopy is used to characterize the structural changes of the microemulsion due to the presence of $S_{18}B_{36}EO_{46}^{60}$ and the heating process. Therefore, first of all a sample of the unmodified, w/o microemulsion is examined (Fig. 6). Typically, these inverse microemulsions are characterized by a more or less regular distribution of small water droplets in a continuous oil phase. The w/o microemulsion of the system water/SDS/xylene-pentanol (1:1) is characterized by a droplet size between 40 and 100 nm, with a main fraction of about 70 nm.

After modification by $S_{18}B_{36}EO_{46}^{60}$ and heating, the structure of the microemulsions observed by Cryo-SEM show significant changes.



Fig. 6. Cryo-SEM of the unmodified microemulsion at point A (10 wt% water/10 wt% SDS/80 wt% pentanol-xylene (1:1)).



Fig. 7. Cryo-SEM of the polymer-modified (1 wt% $S_{18}B_{36}EO_{46}^{60}$) microemulsion at point A, after heating in the presence of AIBN.



Fig. 8. Cryo-SEM of the polymer-modified (5 wt% $S_{18}B_{36}EO_{46}^{60}$) microemulsion at point A, after heating in the presence of AIBN.

In presence of 1 wt% of $S_{18}B_{36}EO_{46}^{60}$ larger aggregates are formed, as to be seen in Fig. 7. These irregular shaped aggregates are between 100 and 500 nanometers in size. A more detailed view shows smaller, droplet-like structures at the surface of the aggregates.

Fig. 8 shows the Cryo-SEM micrograph of the sample containing 5 wt% of $S_{18}B_{36}EO_{46}^{60}$. In contrast to Fig. 7, holes and



Fig. 9. Model of the concentration-dependent behavior of $S_{18}B_{36}EO_{46}^{60}$ in the w/o microemulsion.

needle-like structures with diameters below 20 nm can be obtained. The holes can be related to small droplets, which were removed during the freezing process, and the needles to droplet associates.

Beside the structures described above, droplets of 70 nm, comparable to those for the unmodified microemulsion, can be found for both samples.

Based on these results one can propose a model to explain the behavior of $S_{18}B_{36}EO_{46}^{60}$ in the w/o microemulsion in dependence on the polymer concentration and the temperature program used. Because of the insolubility of the hydrophobic polystyrene in the xylene-pentanol mixture these blocks can aggregate in the continuous oil phase to microdomains (tadpole formation). One can assume that at lower triblock terpolymer concentration the PS microdomains aggregate to macrodomains surrounded by partly PEO-swollen microemulsion droplets (model A in Fig. 9). In that case the heating leads to the formation of significant larger aggregates due to the cross-linking of the polybutadiene blocks, and a more turbid system is observed.

When the block copolymer concentration is increased, more PEO chains has to be incorporated into the water droplets, and in consequence a mixed polymer-surfactant w/o microemulsion is formed surrounded by microdomains of the partly collapsed hydrophobic tails (model B in Fig. 9). However, these mixed polymer-surfactant water droplets seems to be more stable, and an aggregation to macrodomains is not observed.

Consequently, much smaller particle dimensions are obtained by dynamic light scattering and the solution becomes optically clear. Noteworthy, only in this case, when enough polybutadiene blocks are located around the droplets, the heating in the presence of AIBN, leads to covalently closed nanocapsules with dimensions of 10 nm in size, schematized in Fig. 10 [43].

Additional experiments show that for example the gold nanoparticle formation in such covalently closed microemulsions (nanocapsules) is suppressed. That means no color change is observed by mixing a HAuCl₄ containing microemulsion with another one containing a reducing agent (e.g., NaBH₄), when the microemulsions are heated before. However, when the same experiment is realized without a former heating process, that means in a "classical" microemulsion, a color change to red is observed, indicating the formation of gold nanoparti-



Fig. 10. Scheme of a covalently closed nanocapsule.



Fig. 11. UV–vis absorption spectra after mixing a HAuCl₄—with a NaBH₄containing copolymer-modified microemulsion ($1\% S_{43}B_{21}EO_{36}^{111}$ in presence of AIBN) without heating (filled line), and after heating (dashed line).

cles. The UV–vis spectra for both cases are given in Fig. 11. However, the hindrance of the reduction process is an experimental hint for the cross-linking of the nanocapsules. That means, the covalently closed nanocapsules, cannot longer realize the fast exchange processes, typically observed in microemulsions.

5. Conclusion

The results presented here show that different polystyreneblock-polybutadiene-block-poly(ethylene oxide) triblock terpolymers, can be incorporated into the inverse w/o microemulsion of the quasiternary system water/SDS/xylene-pentanol (1:1) without macroscopic phase separation. From DSC measurements the incorporation of the PEO blocks inside the water droplets can be concluded due to a change of the solubilization state of the surfactant headgroups. At lower triblock terpolymer concentration large aggregates (d = 100-500 nm) can be identified by dynamic light scattering measurements. An increase of the polymer concentration from 1 to 5% leads surprisingly to significant smaller aggregate diameters below 50 nm. The change to a more transparent solution can be related to the formation of mixed polymer–surfactant w/o microemulsion droplets of significant smaller dimensions.

In the second part we reported about the possibility to crosslink the polybutadiene blocks by a thermally induced radical reaction. At 1 wt% of the block copolymer the cross-linking leads to larger aggregates, and the system becomes more turbid. Based on the SEM micrographs one can conclude the formation of hydrophobic macrodomains surrounded by microemulsion droplets.

At 5 wt% of the added terpolymer, the system becomes optically clear. That means the PB blocks located around the water droplets can be cross-linked, and covalently closed nanocapsules with diameter of about 10 nm are formed (compare Fig. 9).

Additional experiments will now be focused on the formation of nanoparticles inside the block copolymer modified microemulsions in a first step, followed by a cross-linking of the template, which leads to nanoparticle filled covalently closed nanocapsules.

First experiments already show that the PEO chains inside the water droplets at a higher polymer concentration can reduce a gold chloride solution without the need of an additional reducing agent, like NaBH₄. Therefore, gold nanoparticle filled nanocapsules can be obtained.

Synthesis activities will be focused on the preparation of block copolymers of varying block lengths, for producing nanocapsules of defined sizes.

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