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A NEW WAY TO CONTROL PARTICLE MORPHOLOGY IN HETEROPHASE POLYMERIZATIONS

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SUMMARY: The formation of microphase separated structures in the confined space of latex particles is reported. Three different systems are investigated: emulsion polymerizations started either with polymeric radicals or with persulfate in the presence of ionic chain transfer agents, aqueous dispersions of well defined polystyrene model oligomers with sulfonate end groups, and miniemulsion polymerization in the presence of large amounts of preformed polymer in the droplets. In any of these cases microphase separation leads to the formation of inhomogeneities in the particles. Electron microscopy, atomic force microscopy, and X-ray absorption microscopy show identical structures and hence prove that the inhomogeneities already exit in the dispersed state.

INTRODUCTION

Mixtures of two polymers are usually immiscible provided their concentrations are not too low and they do not strongly interact, respectively. As a result phase separation occurs leading in the case of block copolymers to a variety of different morphologies [1)]. In the case of hydrophilic – hydrophobic polymer mixtures the driving force is so strong that even in glassy mixtures which appeared after preparation homogeneous phase separation takes place admittedly over a period of weeks. Figure 1 shows an example of a poly(ethylene glycol) (PEG) - poly(methyl methacrylate) (PMMA) bulk mixture. Sample **A** was prepared by radical polymerization of methyl methacrylate initiated with 2,2'-azobisisobutyronitrile (AIBN) in the presence of PEG with a molecular weight of

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10^4 g mol^{-1}. In case of samples B and C the polymerization was started with a PEG-azo-initiator (PEGA) $^{2)}$ with a molecular weight of the PEG of $2 \cdot 10^3$ g mol^{-1} and 10^4 g mol^{-1}, respectively. The picture was taken six weeks after the polymerization where the phase separation between PMMA and non-covalently bound PEG (sample **A**) on a macroscopic scale is almost finished. It is noteworthy, that the glassy PMMA phase shows no holes or cracks but appears homogeneous. In case of covalently bound PEG (samples **B** and **C**) a phase separation on a macroscopic scale is obviously suppressed but restricted to small domains leading to a slight turbidity.

Fig. 1 : Phase separation in bulk mixtures of PEG and PMMA
Left – sample **A**; Middle – sample **B**; Right – sample **C**
(sample **A**: bulk mixture; samples **B, C**: block copolymers; for a further explanation see the text)

The aim of this contribution is to report phase separations occurring in latex particles either due to the action of hydrophilic initiator end groups or due to the presence of two different polymers by means of transmission electron microscopy (TEM), atomic force microscopy (AFM), and X-ray absorption microscopy (XAM) investigations. This is different from the case of phase separation in latex particles consisting of two hydrophobic polymers where many examples are known $^{3)}$.

EXPERIMENTAL

KPS (Aldrich) was used as received. Deionized water was taken from a REWA HQ 5 system (18 MΩ cm^{-1}) and degassed prior to use. Styrene (Aldrich) was distilled under reduced pressure to remove inhibitors and stored in a refrigerator. Prior to use the monomer was checked whether or not oligomers have been formed by instill a drop into an excess of methanol. Only oligomer free monomer was used. PEGA2.000 and PEGA10.000 initiators with a molecular weight of the PEG of $2 \cdot 10^3$ g mol^{-1} and

10^4 g mol^{-1}, respectively, were synthesized as described elsewhere [2, 4]. The polymerizations were carried out batchwise in glass reactors with a heating jacket to control the polymerization temperature. The reactors were equipped with a baffle stirrer, a reflux condenser, a nitrogen inlet, and a valve on the bottom to remove the latex. PEG-PS block copolymer particles were prepared according to a procedure described in [2]. The particles depicted in Figure 2 were prepared by reaction of 3 g of styrene with 3,7 g of PEGA2.000 in 100 g of water at 90 °C for 5 hours.

The KPS initiated surfactant-free polymerizations in the presence of chain transfer agents were carried out as described in [5].

The miniemulsion polymerization were performed at 70 °C according to a general procedure described in [6]. An overall recipe comprises 112 g of water, 0,323 g of sodium lauryl sulfate (SLS) (Aldrich), 0,814 g of cetyl alcohol (Aldrich), 0,0412 g of KPS, 0,0126 g of sodium hydrogencarbonate, and 28,28 g of styrene. Deviating from that procedure the PEG was dissolved in styrene prior the emulsification. Ultrafiltration was carried out through a Ultran RC/100 membrane (Schleicher & Schuell) with a SLS solution with a concentration above the critical micelle concentration.

The preparation of the polystyrene model oligomers is described elsewhere [5].

TEM was performed either on a TESLA BS 500 transmission electron microscope with an acceleration voltage of 60 kV or on a Zeiss EM 912 Omega. The samples were prepared according to standard procedures [4]. Particles size distribution (PSD) and average particle diameters were estimated by enumerating at least 700 particles.

FT-IR spectra were recorded with an Impact 400 spectrometer (Nicolet) where the samples were embedded in potassium bromide pellets.

The atomic force measurements (AFM) were performed with a Nanoscope IIIa Multi-Mode^{TM} Scanning Probe Microscope (Digital Instruments, Inc., Santa Barbara, CA, USA) as described in [5].

X-ray absorption microscopy studies were carried out at the synchrotron BESSY in Berlin, Germany, using a special device developed in at the university of Göttingen, Germany. The procedure is described in detail elsewhere [7].

RESULTS AND DISCUSSION

The use of PEGA in a styrene polymerization leads to the formation of triblock copolymers with a PEG block at each end [2, 4]. The morphology of such block copolymer particles is very special and varies in dependence on the particular conditions in such a way that in most of the cases multiple morphologies are observed comprising hollow as well as hairy particles [4, 8]. These morphologies are non-equilibrium structures as the polystyrene (PS) blocks are at a polymerization temperature of 90 °C not yet in a molten state. Figure 2 shows typical phase separated morphologies of PEG-PS-PEG block copolymer particles.

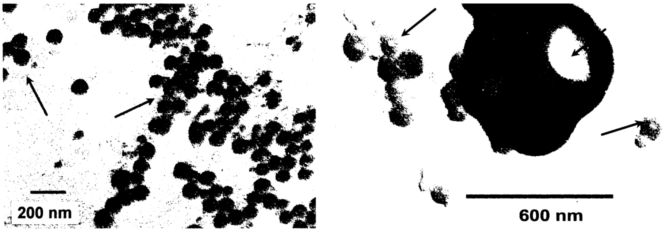

Fig. 2: TEM pictures of phase separation in PEG-*b*-polystyrene block copolymer particles (the arrows indicate particles with less electron dense regions)

The phenomena of phase separation is not restricted to block copolymer particles alone. Also in ordinary emulsion polymerizations started with KPS particles with an anomalous morphology have been occasionally observed on TEM pictures [5, 9, 10]. The formation of these anomalous morphologies can also be explained by a phase separation where the driving force is the competition between repulsion of the ionic end groups and attraction of the hydrophobic chains provided that in the swollen particles the chain mobility is in a certain range [5]. Figure 3 illustrates these anomalous structures by means of particles prepared in a surfactant-free emulsion polymerization of styrene started with KPS. A detailed characterization of these particles (Fig. 3a) is as follows: sampling time 90 minutes, conversion 7 %, number average particle size 204,4 nm, weight average particle size 205,6 nm, number average molecular weight (M_N) $1{,}02 \cdot 10^4$ g mol^{-1}, weight average molecular weight $2{,}09 \cdot 10^4$ g mol^{-1}. These chestnut-like particles are formed only in a certain conversion range but they disappear again at higher conversions. A further support for the thesis about the formation of these structures comes from the fact that their formation can be induced if the polymerization is carried out in the presence of an ionic chain transfer agent like thiomalic acid [5]. Fig. 3b shows the morphology of such particles. In both cases the particles show less electron dense regions and indentations leading to an increase in the particle surface.

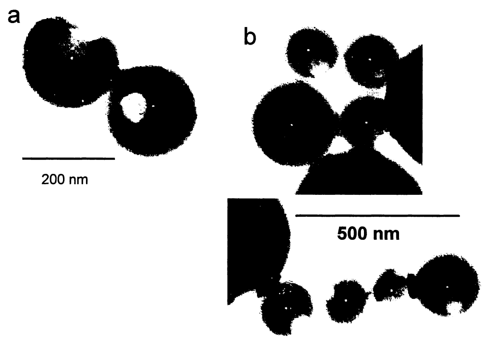

Fig. 3: TEM pictures of phase separated structures (chestnut-like particles) formed during a surfactant-free emulsion polymerization of styrene initiated with KPS (a) and in the presence of thiomalic acid (1 mol-% relative to styrene) as chain transfer agent (b)

The structure of these particles has been proved also by AFM investigations. Fig. 4 shows an AFM topographic image where the indentations are visible as a dark spot. The corresponding depth profile reveals that the indentation has a depth of almost 150 nm.

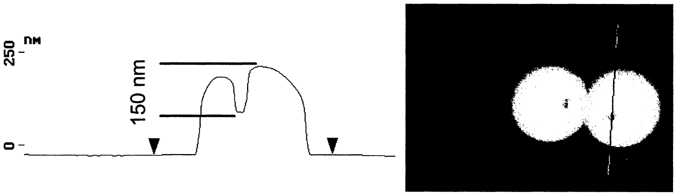

Fig. 4: AFM images and depth profile of chestnut-like polystyrene particles

In order to have better defined conditions with respect to molecular weight and chemical homogeneity polystyrene model oligomers prepared by anionic polymerization with average styrene chain lengths of 2, 5 and 12 (st02, st05, and st12) have been included in the investigations. These oligomers have a perfect structure (cf. Fig. 5) proved by end group analysis with mass spectroscopy [5].

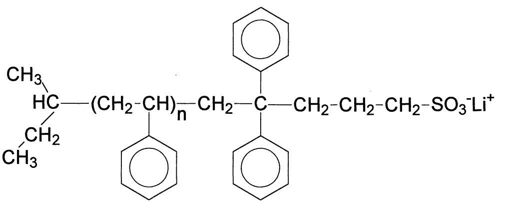

Fig. 5: Structure of the polystyrene model oligomers n:2, 5, 12

Upon contact with water all of these oligomers do not dissolve but form despite of the chain length dispersions. The particles of these dispersions have a very special morphology as documented in Fig. 6. The photographs resemble much more broken structures than latex particles. Furthermore, these particles possess an internal inhomogeneous morphology which reflects the structure inside the bulky solid samples. Upon swelling with an organic solvent the morphology changes considerably in dependence on the oligomer chain length (cf. Fig. 7).

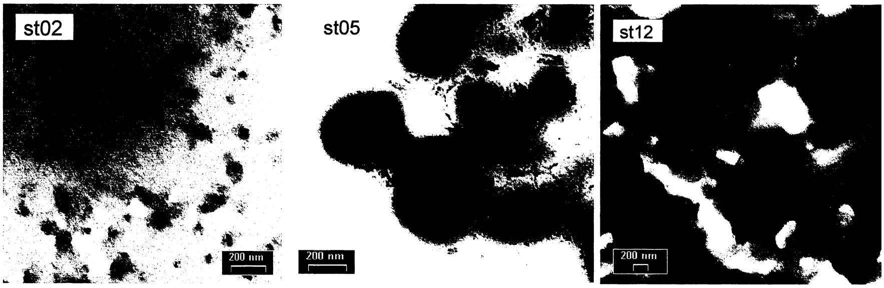

Fig. 6: TEM photographs of the model oligomers dispersed in pure water

The model oligomer polystyrene dispersion of st12 resembles now ordinary latex particles with an almost spherical shape. Whereas, st05 and st02 show completely different morphologies which resemble hollow particles for st05 and very loose aggregates (highly swollen due to the low degree of polymerization) for st02. The particles marked with white circles (right hand site of Fig. 7) show a very special morphology. The upper particle shows spatial electron density inhomogeneities whereas the lower particle additionally has a very pronounced die-shape.

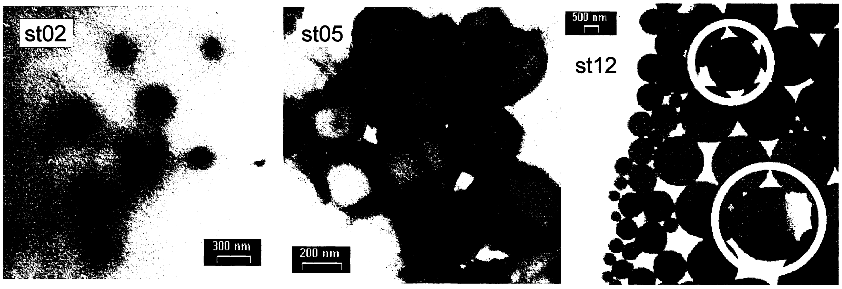

Fig. 7: TEM pictures of the model oligomer dispersions swollen with tetrahydrofuran

Another kind of phase separation based on the incompatibility of two free but different polymers in a latex particle may occur if a miniemulsion polymerization is carried out in the presence of a polymer which is dissolved in the monomer phase. In 1994 MILLER et al. reported for the first time that small amounts (up to 2 % based on styrene weight) of polystyrene added to the styrene phase lead to a substantial increase of both the rate of polymerization and the final particle concentration [11,12]. Another interesting approach was reported by WANG et al. which is the miniemulsion polymerization of acrylic monomers in the presence of an alkyd resin with up to 100 % based on total monomer weight [13]. In both cases phase separation was not reported as either the polymers are chemically identical or the alkyd resin is incorporated to a larger extend by grafting and hence compatibility is achieved.

However, the situation is changed when a chemically different and non-reactive polymer is used as for instance PEG. Although there is reported some chain transfer to PEG in a radical polymerization [14] one may consider it as much less reactive compared with alkyd resins. PEG has a very bizarre solubility pattern [15] as it is soluble in both water and styrene. At higher temperatures PEG is more soluble in organic solvents and at lower temperatures it shows enhanced solubility in water. Consequently, during the polymerization the PEG is driven into the monomer phase but will redistribute again at the end of the polymerization into the aqueous phase. At least with respect to the particle concentration the effect of large amounts of added PEG (up to 100 % based on styrene weight) is the same as in case of added polystyrene: the particle number increases. Fig.4 compares PSD of latexes prepared in the presence of different amounts of PEG. In the presence of PEG the particles are always smaller compared with the PEG-free system. This indicates at least the conversion of an enhanced number of miniemulsion droplets into particles.

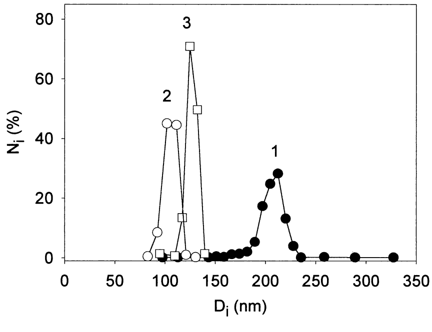

Fig. 8: PSD of latexes prepared by miniemulsion polymerization with varying amounts of PEG; 1 – without PEG; 2 – 50 % PEG based on monomer weight; 3 – 100 % PEG based on monomer weight

How the PEG is distributed between particles and water is illustrated by the FT-IR spectra depicted in Figure 9. Spectra 1 corresponds to the original sample obtained by drying up a part of the latex, spectra 2 represents isolated particles obtained by coagulating a part of the latex with NaCl and subsequent washing with water, and spectra 3 corresponds to the sample after ultrafiltration. The ratio of the band intensities at about 1100 cm^{-1} (PEG) and at about 700 cm^{-1} (polystyrene) shows that the original sample contains more PEG than the particles alone indicating that PEG is indeed distributed between particles and water. Furthermore, as there is almost no PEG absorption in spectra 3 ultrafiltration was successful in removing PEG even from inside the particles.

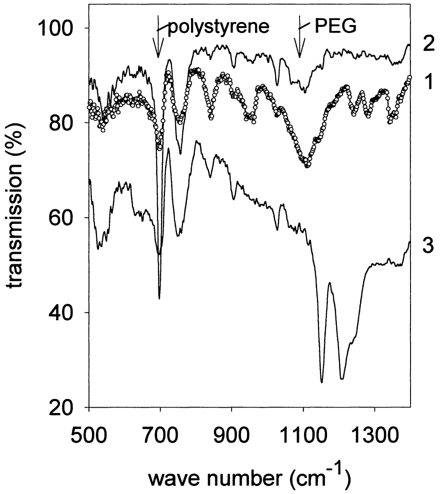

Fig. 9: FT-IR spectra of the products formed during a miniemulsion polymerization of styrene in the presence of PEG; 1 – original sample; 2 – particles; 3 – dialyzed sample

As there remains after the polymerization some PEG inside the particles which is incompatible with polystyrene the question arises concerning the particle morphology. To minimize the contact with polystyrene PEG may either go into the aqueous phase or phase separate inside the particles. Compared with the particles prepared in the absence of PEG (Figure 10a) which resemble homogeneous particles the particles in Figure 10b show a quiet different morphology indicating a phase separation where the PEG forms the darker core. Note, not all particles possess this morphology as it is to see in the lower part of Figure 10b. Consequently, PEG uses both possibilities to minimize the contact with polystyrene. Most of the PEG molecules go into the aqueous phase and only a minor part stays inside the particles which is in accordance with probability considerations.

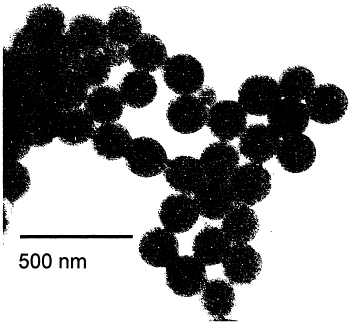

Fig. 10a: TEM picture of particles Prepared by miniemulsion polymerization in the absence of PEG

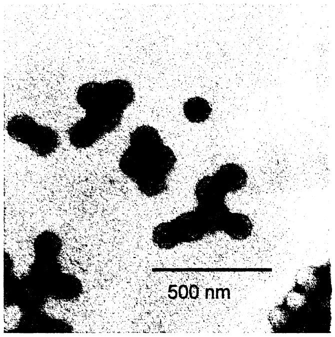

Fig. 10a: TEM picture of particles prepared by miniemulsion polymerization in the presence of PEG

If a PEGA10.000 initiator (100 % based on styrene weight) is used instead of KPS and the PEG also stable latexes result. Although the PSD is much broader compared with the PEG/KPS systems the particle morphology looks very similar.

The question whether the morphologies observed by TEM and AFM are formed during the sample preparation or already exist in the dispersed state is still unanswered. XAM is a method that allows the reproduction of objects dispersed in the aqueous phase. X-rays with a wavelength between 2,4 nm and 4,4 nm are absorbed an order of magnitude less by water than by organic molecules. This allows the reproduction of objects undisturbed in their original aqueous environment.

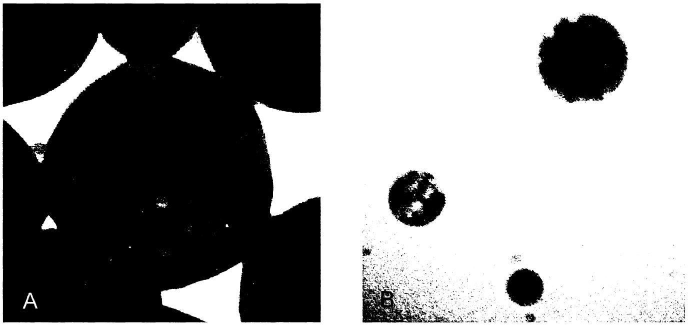

Fig. 11 TEM picture (A) and XAM picture (B) of the model oligomer dispersion (st12) swollen with tetrahydrofuran (largest particles have a size of approximately 1,2 µm)

Figure 11 shows very clearly in the case of a st12 dispersion swollen with tetrahydrofuran that the phase separated structures already exist in the dispersion. This means that these particles are not only swollen with tetrahydrofuran but also contain water inside the channels which offers interesting applications in separation techniques.

In conclusion, mixtures of two homopolymers as well as block copolymers in nm-sized latexes do phase separation. In most of the cases multiple morphologies are formed ranging from hollow particles over core shell structures up to hairy particles. Also in the case of hydrophobic homopolymers with hydrophilic end groups phase separation may occur if the chain mobility is high enough to allow the formation of thermodynamic equilibrium structures. This is fulfilled if the molecular weight is not too high and the particles are either swollen or the polymer has a glass transition temperature lower than the actual temperature of the environment. An important result is the proof that the phase separated structures already exist in the aqueous phase.

Acknowledgments

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