# Nonaqueous Emulsions – A Versatile Tool for New Types of Functional Nanoparticles

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**Summary**: The preparation of functional polymer latex particles is usually carried out in aqueous heterogeneous systems, *i.e.* for example in emulsion or mini-emulsion polymerization. Due to the presence of water, moisture sensitive reactions like step growth polymerizations or metal catalyzed reactions can not be accomplished without side reactions and / or decomposition. In order to avoid these side reactions, different nonaqueous emulsion systems have been developed. According to the desired polymerization procedure, these systems consist of a nonpolar organic phase surrounded by a perfluorinated solvent or of a polar organic phase which is dispersed in a nonpolar organic solvent. Both emulsions are stabilized by amphipolar block copolymers and result in long time stable particle dispersions. The resulting dispersions yield particles with narrow size distributions and – depending on the reaction conditions – diameters down to tens of nanometers. This technique allows the formation of particles consisting of numerous different classes of polymers, *e.g.* polyurethanes, polyesters, polyolefins etc. and the formation of more complex morphologies such as core shell structures.

**Keywords:** emulsion polymerization; nanoparticles; polyolefins; polyurethanes; ROMP

## Introduction

Functional nanoparticles have wide-spread applications ranging from electronics,[1] pharmaceuticals, and photonics to cosmetics, coatings,[2] and catalysis.[3] This is due to their unique mechanical, optical, thermal, electrical, magnetic and catalytic properties[4] as well as their well-defined morphology, size, and surface. Usually, latex particles are prepared by emulsion, mini-emulsion, or suspension polymerization or other heterogeneous water-based systems in a size range from a few nanometers up to several micrometers.[5] However, these processes require water-stable reaction components to avoid side reactions, and that is why they are almost completely limited to radical polymer formations.[6] The synthesis of particles based on moisture sensitive monomers like isocyanates for the preparation of polyurethanes or metallocene catalysts for the formation of polyolefins is not achievable by these classical approaches due to the decomposition of the catalysts and other side reactions which shift the stoichiometric ratio of the monomers. Therefore, different new biphasic organic solvent systems tolerating these sensitive compounds have been developed recently. As the different aforementioned examples require either a polar (oxidative polymerizations[7] and step-growth polymerizations[8,9]) or a non-polar (olefin polymerization[10,11] dispersed phase, two different systems were designed and are presented herein. A decisive issue within the development was the synthesis of suitable emulsifying block copolymers which form stable emulsions, whilst the biphasic systems possess narrow size-distributed droplets in a tunable size range.

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## Results and Discussion

The preparation of nonaqueous emulsions requires a combination of two immiscible organic solvents. In the literature, different mixtures of methanol, ethanol or glycol in nonpolar solvents are presented;[12,13] however, these systems are not suitable for the aforementioned types of polymerization as they poison the highly sensitive catalysts and / or undergo decomposition reactions with the used monomers. Thus, exclusively solvents without reactive protic groups like hydroxyl or amino functions have been used for our approach to nonaqueous emulsions.

### Polymerization in Polar Dispersed Phase

In order to conduct polymerizations of polar monomers and to form polyurethanes or polyesters, emulsions consisting of a polar dispersed phase and a nonpolar continuous phase were created. Different solvent combinations are suitable for this approach; for example *N*,*N*-dimethyl formamide (DMF) dispersed in *n*-hexane or acetonitrile dispersed in cyclohexane. A combination of DMF and *n*-hexane was already used by Riess *et al.* although the phases have been inverted in the presented emulsion.[13] Additionally, an emulsifier (PS-PMMA) different from ours was used, which turned out not to provide long time droplet stabilization. Due to the better compatibility of polyisoprene (PI) and *n*-hexane, a different emulsifier consisting of PI and polymethyl methacrylate (PMMA) was used to disperse the polar organic solvent inside the nonpolar phase. With respect to the droplet size and stability, the optimal ratio of the block copolymer constitutes 73 mol-% PI and 27 mol-% PMMA. This emulsifier was synthesized by a sequential anionic polymerization technique described in the literature.[14,15] The PMMA block of the emulsifier acts as an anchor group inside the droplets due to its better solubility in the dispersed phase whilst the PI block functions as a stabilizing moiety because of its selective solubility in the continuous phase.

The synthesis of particles in these solvent mixtures can usually be considered as an emulsion polymerization based on a diffusion controlled process. Hitherto, there are also approaches available using compounds which are completely insoluble in the continuous phase. Thus, there is no diffusion control but only ''nano-vessels'' present which is known as a mini-emulsion process. The synthesis of particles by the emulsion polymerization mechanism is schematically presented in Figure 1. The emulsifier (PI-*b*-PMMA) is dispersed homogeneously inside the continuous phase and, finally, micelle formation occurs. The addition of the polar phase containing compound A (*e.g.* a diol for the formation of polyurethanes or polyesters) and several minutes of ultrasonification then lead to a stable emulsion. By dropwise addition of compound B (*e.g.* a diisocyanate for polyurethanes, a diacid dichloride for polyesters or a catalyst for ROMP) to the continuous phase and diffusion of B into the droplets initiates the reaction. Since component A is barely soluble in the continuous phase, the reaction takes place exclusively inside the droplets. This is in particular presented for different types of reactions such as polyadditions, polycondensations and catalytic reactions.

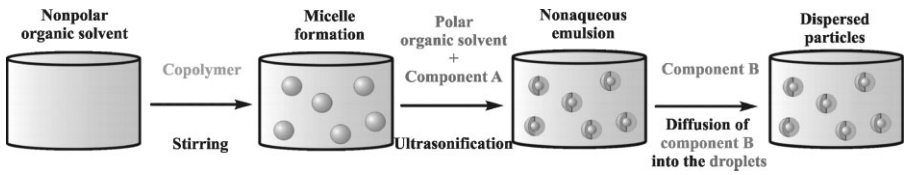


***Figure 1.***
Schematic description of the polymerization in nonaqueous emulsion.

 

*Polyaddition*

The use of this nonaqueous emulsion systems opens access to versatile polymerization procedures and, therefore, different materials for the preparation of nanoparticles. One important example is the polyaddition reaction which, for example, is used to form polyurethane particles. In order to accomplish such a synthesis, compound A was chosen to be a diol (*e.g.* 1,4-bis(hydroxymethyl)cyclohexane) and compound B a diisocyanate (*e.g.* 4,4′-methylenebis(cyclohexyl isocyanate)). Additionally, a catalyst was employed (*e.g.* dibutyltin diacetate) which was added to the polar organic phase. In most cases this polar phase was DMF, dispersed in *n*-hexane. However, acetonitrile dispersed in cyclohexane or NMP in tetradecane were also used and the type of monomer was varied as well (*e.g.* ethylene glycol and 4,4′-methylenebis(phenyl isocyanate)).

It is possible to prepare polymer particles with molecular weights as high as $M_n = 40{,}000\,g\,mol^{-1}$ (PDI = 2.0) which equals – in regards to the Carothers equation – a conversion higher than 99%. It is assumed that two main factors are responsible for the high molecular weights and conversions: (i) the absence of water during the reaction, which diminishes the amount of side reactions of the isocyanates and water forming urea derivatives and thus results in an unbalanced stoichiometry; (ii) Schotten-Baumann conditions, which means that the 1:1 stoichiometry which is necessary for the polyaddition at the interface is controlled by the diffusion of the monomers at the interface of the continuous and the dispersed phase. As the diols are predominantly soluble in the dispersed droplets, the stoichiometry of the reaction is controlled by the diffusion of the diisocyanate component into the micelles.[9]

As shown in Figure 2, PU particles which are prepared by this method possess a very narrow size distribution and a diameter of approximately 20 to 70 nm. The particles have a well defined spherical morphology and do not agglomerate (monomodal distribution according to DLS measurement). The slight aggregation visible in the SEM image is caused by the sample preparation during solvent evaporation.

Besides the synthesis of particles consisting solely of non-porous PU, more complex morphologies such as core-shell or porous structures can be achieved by this type of emulsions. For instance the preparation of porous particles by the slow and controlled addition of a well defined amount of water is possible. Hereby, some of the isocyanate groups undergo side reactions with water, forming urea derivatives. Simultaneously, carbon dioxide is

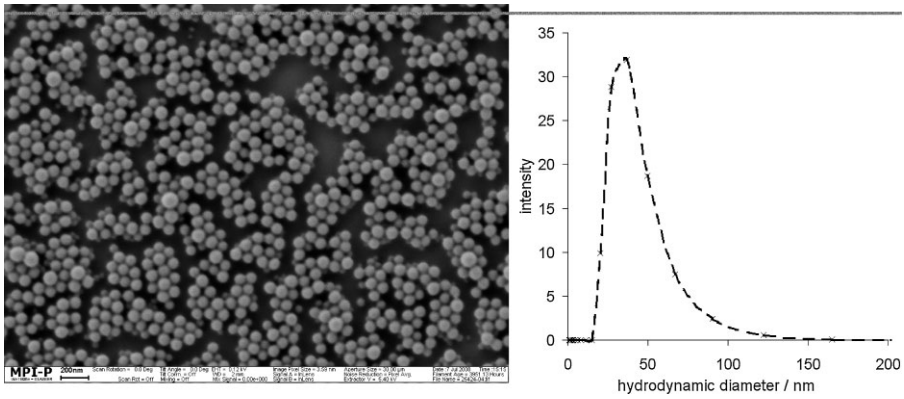


***Figure 2.***
left) SEM image of PU particles drop casted on Si waver @ 120 V; right) DLS curve from diluted primary PU particle dispersion at 90 ° scattering angle.

 

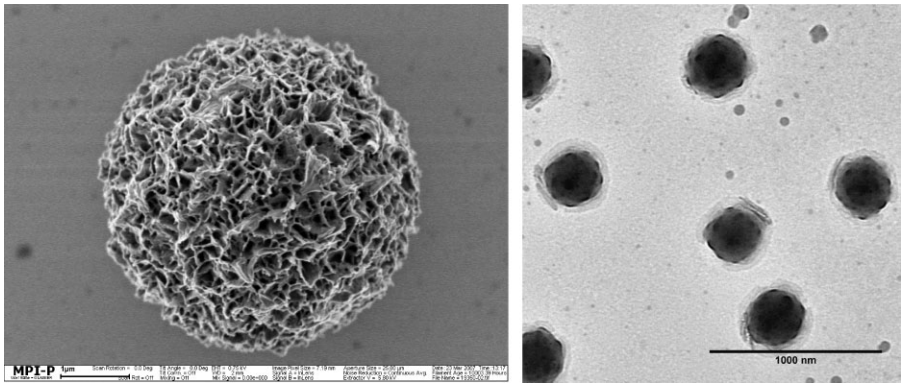


***Figure 3.***
left) SEM image of porous PU particles drop casted on Cu grid @ 750 V; right) TEM image of PU-core PMMA-shell particles drop casted dispersion at 200 kV.

released forming pores inside the viscous polymeric material. These particles with diameters from several hundreds of nanometers up to several micrometers have pore sizes in the range from 30 to 500 nm. Further investigations concerning the gas absorption and the application as an impact modifier are ongoing. Also, experiments concerning the use of porous PU particles as a support for the metallocene polymerization have been accomplished. Another possible morphology for these PU particles is the preparation of core-shell particles. It is possible to create a polymeric shell from different methacrylate monomers by free radical polymerization around the existing PU core.[16] These particles were prepared with small diameters of about 100 to 300 nm and high molecular weights. Figure 3 shows a SEM image of one of the mentioned porous PU particles and a TEM image of some PU-core PMMA-shell particles.

*Ring Opening Metathesis Polymerization (ROMP)*
The possibility to use moisture sensitive monomers in nonaqueous emulsions is an important advantage of these emulsion systems. Another possibility is the use of fragile catalysts to perform such tasks as metathesis reactions or polymerization oxidative coupling. The use of different norbornene derivatives and Grubbs 2$^{nd}$ generation catalyst leads for example to well defined polymer nanoparticles. Hereby, a polar modified norbornene acts as compound A and is situated predominantly inside the droplets. By addition of the catalyst (compound B) - solved in a few drops of the continuous phase – and its diffusion into the droplets the polymerization is started. Within a few minutes the monomer is completely converted and the number averaged molecular weight of the resulting polymer can be as high as $200{,}000\,g\,mol^{-1}$ (PDI = 1.9). Monomers which can be used for these reactions are different 5-norbornene derivates, for example dimethyl 5-norbornene-2,3-dicarboxylate. More nonpolar norbornene derivatives were polymerized in the system using a nonpolar dispersed phase as described below .

## Polymerization in Nonpolar Dispersed Phase – Perfluorinated Systems

The aforementioned nonaqueous emulsions provide access to particles formed in step growth polymerizations or in metal catalyzed metathesis. Unfortunately, these solvent mixtures cannot be applied for the polyolefin synthesis by highly sensitive metallocene catalysts because the dispersed acetonitrile or DMF will complex with the active metal species and thus enormously decrease polymerization activity.

Therefore, nonaqueous systems based on a perfluorinated solvent (e.g. perfluor-

 

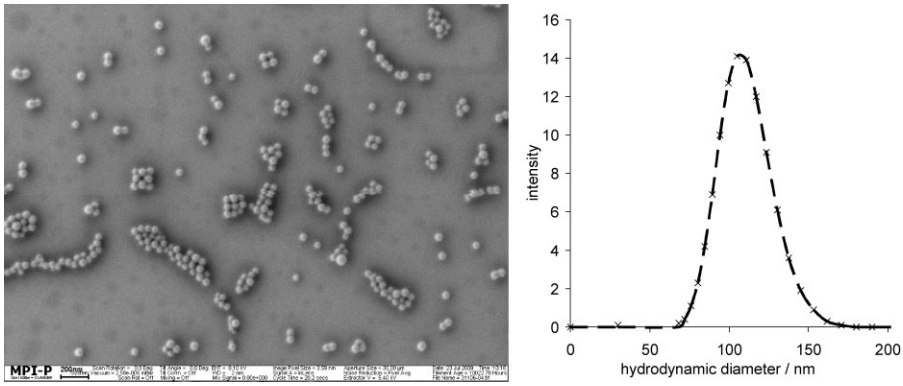


***Figure 4.***
left) SEM image of PNorb-Derv particles drop casted on Si waver at 100 V; right) DLS curve from diluted primary PNorb-Derv particle dispersion @ 90 ° scattering angle.

omethyl-cyclohexane (PFMCH)) as the continuous phase and a hydrocarbon (e.g. toluene) as the dispersed phase were designed.[10,17,18] High molecular weight block copolymer emulsifiers which are synthesized in a nitroxide mediated controlled polymerization of styrene and pentafluorostyrene turned out to be most suitable for the stabilization of these emulsions (Figure 5). Light scattering investigations indicated the formation of stable droplets, and the classical dependence on the amount of emulsifier was observed, while there is no change in droplet size over a broad temperature range – even above the boiling point of PFMCH. The droplet size can be decreased to a few tens of nanometers with 10 wt.-% emulsifier concerning the dispersed phase.

The fluorous oil-in-oil emulsions were successfully exploited for the synthesis of polyolefin particles by metallocene catalysis from gaseous ethene or propene (Activity: 400 kg PP (mol Zr hr bar)$^{-1}$ at 1 bar and 60 °C with MBI catalyst; Figure 5). After formation of the micelles and ultrasonification treatment, the hydrocarbon and the activator (methylaluminoxane) are added and the emulsion is saturated with the gaseous monomer. Subsequent addition of the metallocene-based precatalyst initiates the polymerization. As all

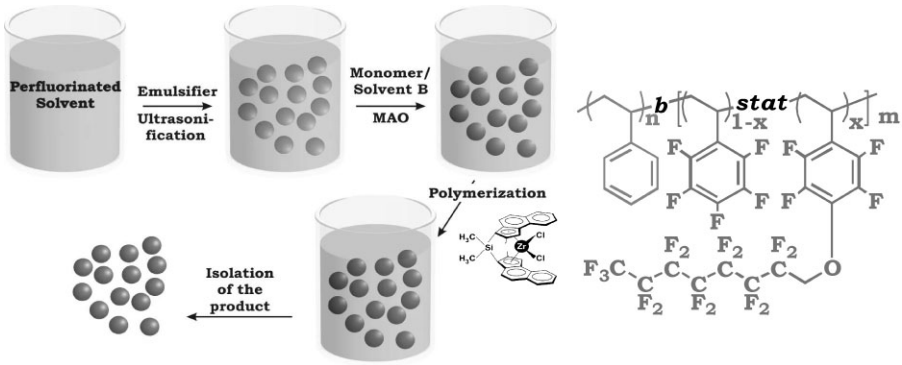


***Figure 5.***
Schematic description of the polyolefin synthesis in a perfluorinated emulsions (with MBI catalyst) and applied block copolymer emulsifier.

 

reactants are barely soluble in PFMCH, the reaction takes place in the confined geometry of the dispersed hydrocarbon droplets, which can be considered as ''nanovessels''. The nonaqueous fluorous emulsions yield high molecular weight polyolefin particles ($e.g.\ M_{n,PE} = 450{,}000\ g\ mol^{-1}$, PDI = 3.1), and the diameters are controlled by parameters like polymerization time as well as pressure. Thus, a decrease of the particle diameters is accomplished by decreasing both parameters, which is typical for a classic emulsion and also consistent with a diffusion controlled polymerization process. Unfortunately, the diffusion of the monomer from the gas phase into des dispersed hydrocarbon droplets results in low activities (*vide infra*). Besides these characteristics of an emulsion process, it should be noted that initiation takes place in the droplets – a characteristic of a miniemulsions or suspension process. In these new emulsions, metallocene catalysts are applied under pseudo-homogeneous conditions and, therefore, no tedious immobilization process is needed before, which is usually necessary in order to avoid reactor fouling – caused by local overheating – and to gain control over the product morphology .

In order to overcome the limitation of the diffusion of the gaseous monomer through the perfluorocarbon into the dispersed organic phase, metallocene catalyzed polymerization of liquified propene in a perfluorinated solvent was developed.[11] By switching completely to mini-emulsion conditions, the activities are increased significantly (3500 kg PP (mol Zr hr)$^{-1}$ at 25 bar and 60 °C with MBI catalyst). With this new method, monomer diffusion through the continuous phase is avoided whilst additional organic solvents can be omitted. Due to the surrounding perfluorinated solvent, heat transfer is guaranteed from this highly exothermic process, and therefore no reactor fouling is observed, which is caused by molten polymer under homogeneous conditions. Furthermore, the obtained molecular weights are much higher than those which are achieved in aqueous biphasic systems.

## Conclusion

Two novel emulsion systems, stabilized by PI-*b*-PMMA and PS-*b*-PFS, respectively, are presented and the versatile fabrication of various polymer nanoparticles is described. One of the particularly important advantages of the developed procedures is the use of aprotic solvents thus facilitating moisture sensitive catalytic polymerization and step-growth reactions. These systems enable the formation of nanoscale particles from versatile materials and morphologies which can be used to

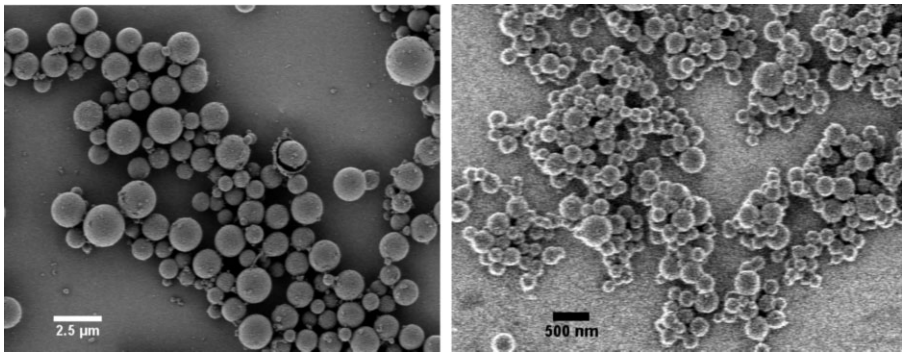


***Figure 6.***
SEM micrograph of (left) PE particles after 30 min at 60 °C and 40 bar and (right) PP particles after 10 min at 60 °C and 2 bar with MBI zirconocene catalyst (see Figure 5).

 

form nanocomposites and novel particle architectures such as core-shell structures based on different monomers and polymerization procedures which cannot be obtained by aqueous systems.

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