

Polymerisation of Emulsions

based on the PhD work of Sebastijan Kovacic
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1. Emulsions

In food industry, petroleum production (drilling fluids), pharmaceuticals (mainly cosmetics), and environmental applications the mixing of oil and water is required and the production and use of stable emulsions had been extensively examined. Emulsions are heterogeneous dispersions in which drops of liquid are dispersed in an immiscible liquid phase of different composition. The dispersed phase is sometimes referred to as internal phase and the continuous phase as the external phase. In most cases, one of the liquid is water, while the other liquid is a hydrocarbon. One of the most important characteristic of an emulsion is its morphology (the spatial organization of matter in the emulsions). From that point of view, two types of emulsions can be distinguished in principle, depending upon which liquid forms the continuous phase:¹

- oil-in-water (O/W) for oil droplets dispersed in water
- water-in-oil (W/O) for water droplets dispersed in oil

Also double emulsion can be prepared, oil-in-water-in-oil (O/W/O) or water-in-oil-in-water (W/O/W). O/W/O denotes a double emulsion containing oil droplets dispersed in aqueous medium that are in turn dispersed in a continuous oil phase (or vice versa for W/O/W types).² Emulsions with no aqueous phase, so-called anhydrous or oil-in-oil emulsions can also be prepared. In this case, the selection of the phases depends largely on the polarity of the solvents. Non-aqueous emulsions could replace regular aqueous emulsions wherever the presence of water is undesirable; for example, in cleaning systems that are sensitive to the formation of rust.³

The type of emulsion that is preferred depends on a number of factors including temperature, electrolyte concentration, proportions of components, nature of components and surfactant structure. Simple emulsion structures are droplets of water, in case of water-in-oil (W/O) emulsions or droplets of oil, in case of oil-in-water (O/W) emulsions. The interface between phases in both emulsion types is formed with the aid of stabilizer molecules. Most meta-stable emulsions that are used in practice contain oil, water and stabilizers that are usually surfactants (relying on charge and attractive forces stabilisation) or macromolecules (relying by steric stabilisation). The surfactant is needed to make emulsion easier to form by creating a protective film around the droplets and keeping the emulsion from breaking. The liquid in which the surfactant has a higher solubility tends to be the continuous phase,

¹ Schramm, L. L. *Emulsion, foams and suspensions: Fundamentals and applications*. Weinheim, Wiley-VCH, **2005**.

² Davis, S.S., Hadgraft, J., Palin K.J.: in P.Becher (ed): *Medical and Pharmaceutical application of emulsions. Encyclopaedia of Emulsion technology*, Vol.2, Marcel Dekker, New York, **1985**.

³ Imhof, A., Pine, J., *Stability of nonaqueous emulsions*, *J. Coll. Interf. Sci.*, **1997**, 192, 368-374.

meaning that W/O emulsions persists in the presence of oil soluble surfactant and are rapidly destroyed in the presence of a water soluble surfactant. Conversely, O/W emulsions persist in the presence of water soluble surfactants. This is a model, which predicts the emulsion morphology based on surfactant affinity to the continuous phase and is named Bancroft's rule.⁴ Assumption of emulsion morphology by Bancroft's model seems to be unlikely because it leaves us with question: which properties of a surfactant determine its affinity for a particular phase. The first who has quantified the surfactants affinity for the aqueous or the oil phase of the emulsion and gave answer to the preferred emulsion morphology was Griffin by introducing the hydrophilic-lipophilic balance concept (HLB).⁵ The drawback of Griffin's method is that not for all surfactants classes a direct link between structure of the surfactant and its HLB can be established. The phase inversion temperature (PIT) concept describes emulsion as a whole and was proposed by Shinoda and Kunieda as a method for the classification of non-ionic surfactants (and to predict the correlation between emulsion morphology and temperature).⁶ In the PIT concept, the phase inversion temperature is introduced. At this temperature, the surfactant affinity for both phases in the emulsion is equal. It is to note, that the PIT concept is only valid when non- ionic surfactants are used.

Beside temperature and surfactant affinity, there are several other variables that influence the surfactant distribution at the interface and consequently the emulsion morphology:

- the salinity of the aqueous phase,
- the polarity of the oil phase,
- the HLB value of the surfactant and the co-surfactants.

Salager suggested merging all variables into one parameter, which should describe the preferred emulsions morphology.⁷ All of these factors in some way affect the interaction between surfactant molecule and each phase of the emulsion and this interaction can be thermodynamically expressed as chemical potential of the surfactant in the water or the oil phase

$$\mu_{w(o)} = \mu_{w(o)}^* + RT \ln x_{w(o)} \gamma_{w(o)} \quad \text{Equation 1}$$

where μ_i is the chemical potential, μ_i^* is the standard chemical potential, x_i the molar fraction and γ_i the activity coefficient of the surfactant in the water phase (subscript w) or oil phase (subscript o). With this equation, the surfactant affinity to the individual emulsion phase is described. A low standard chemical potential corresponds to a high affinity and vice versa.⁸

As mentioned before, the simplest emulsion structures are droplets, which are isolated and spherical if the emulsion is diluted while during concentrating, the

⁴ Bancroft, W.D., The theory of emulsification I, *J.Phys.Chem.* 16, **1912**, 177-233.

⁵ (a) Griffin, W.C., Classification of Surface-active Agents by "HLB", *J. Soc. Cosmet. Chem.* **1949**, 1, 311-326; (b) Griffin, W.C., Calculation of HLB values of nonionic surfactants, *J. Soc. Cosmet. Chem.* **1954**, 5, 249-256.

⁶ Shinoda, K., Kunieda, H. in P. Becher, (ed.): *Encyclopedia of Emulsion technology*, Volume 1, Marcel Dekker, New York, chapter 5, **1983**.

⁷ Salager J.L., Phase behavior of amphiphile-oil-water systems related to the butterfly catastrophe, *J. Coll. Interf. Sci.*, **1985**, 105, 21-26.

⁸ Salager J.L. in P. Becher (ed): *Encyclopedia of Emulsion technology*, Volume 3. Marcel Deckker, New York, chapter 3, **1988**.

emulsion drops become packed as dense as possible and changing their spherical shape into the rhombic dodecahedral shapes.⁹

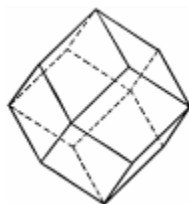


Figure 1. Rhombic dodecahedron shape

Emulsions exhibit a classical “milky” look with which they are usually associated after preparation. All kinds of appearances are possible, depending upon droplet size and the difference in refractive index between phases. An emulsion can be transparent if either the refractive index of both phases is the same, or if the dispersed phase is made up of droplets that are sufficiently small compared to the wavelength of the light. Emulsions that overcome emulsification treatments may be stable for days, weeks or even months if prepared with appropriate combination of variables needed for this kinetic stability.

1.1 Surface active agents (surfactants)

Surfactants are amphiphilic molecules, which exhibit a polar/unpolar duality. A typical amphiphilic molecule contains a polar group which contains hetero atoms such as O, S, P or N included in different functional groups and on the other hand a nonpolar group which is usually hydrocarbon chain of alkyl or alkylbenzene type (Figure 2).

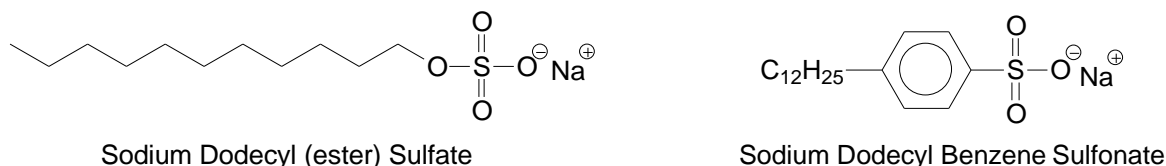


Figure 2. Amphiphilic molecules

A surfactant must satisfy certain conditions to act as an emulsifier. It has to show good surface activity and produce a low interfacial tension at interface. In other words, the surfactant must have the tendency to migrate into the interface rather than stay dissolved in either one of the bulk phases. Another required feature is the ability to form an as highly as possible condensed interfacial film, either by itself or incorporating other adsorbed molecules that are present in the film. Theoretically, the most condensed interfacial film between oil and water is formed when a maximum number of surfactant molecules is packed and are oriented vertically.¹⁰ Surfactant concentration at the interface depends upon the surfactants structure and the chemistry of the two phases that meet at the interface. Surfactants must migrate to the interface at a rate that interfacial tension is reduced to a level of stability during the emulsion preparation. The rate of migration depends on whether the surfactant is soluble in the oil or the water phase. The surfactant simultaneously serves three

⁹ Neil C.R., Sherrington D.C., High internal phase emulsions (HIPEs)-structure, properties and use in polymer preparation, *Adv. in Polym. Sci.*, **1996**, 124, 163-214.

¹⁰ Israelachvili J., The science and applications of emulsions - an overview, *Coll. and Surf. A*, **1994**, 91, 1-8.

functions in stabilizing an emulsion. It plays an essential role in determining whether oil or water is the continuous phase. It controls many of the attractive and repulsive forces between droplets. These forces govern flocculation and coagulation processes. Surfactants determine the mechanical properties of the interfacial films, which, in turn, control the coalescence rates.

Two other general guidelines have to be taken into account for the selection of surfactants. Surfactants that are preferentially oil soluble form W/O emulsions and those, which are water soluble form O/W emulsions. A mixture of oil soluble and water soluble surfactants often produce better and more stable emulsions than an individual surfactant.¹¹

A frequently used method for the selection of appropriate surfactant is known as the HLB (hydrophobic-lipophobic balance) method. It is a rule-of-thumb to predict a preferred emulsion type produced by a certain surfactant. In this method, a number (0-40) is related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the molecule and has been assigned to many commercial surfactants. When a combination of surfactant with different HLB values is used, the HLB number of the mixture is calculated as the weight average of the individual HLB numbers:¹³

$$HLB_{\text{mix}} = \sum x_i \cdot HLB \quad \text{Equation 2}$$

Typical W/O surfactants have an HLB number in the range of 4-8, O/W surfactants fall in the range of 12-16.

1.2 Stability of the emulsions

Emulsions are heterogeneous systems, which will eventually phase separate into two homogeneous layers. Liquid/liquid immiscibility creates an interfacial tension at the contact area between the two liquids, which disturbs the emulsion stability. As a consequence emulsions are thermodynamically unstable systems which mean that the increase of interfacial contact area is accompanied by the increase of chemical potential which causes the free energy penalty (increasing of ΔG), meaning phase separation. The free energy penalty of emulsion formation can be reduced through the surfactant addition, which sufficiently reduce the interfacial tension.

From thermodynamics it is known that spontaneous processes occur in the direction of decreasing Gibbs free energy ($\Delta G < 0$). In the case of emulsions, the spontaneous trend leads towards diminishing of interfacial area between the dispersed phase and the dispersed medium. For the dispersed systems, such as emulsions, the degree of kinetic stability is very important. Minimizing the interfacial area is reached mainly by two mechanisms, coalescence and Ostwald ripening (the most studied mechanism).^{12,13} The former is the process by which larger droplets grow at the expense of the higher solubility of smaller ones in the continuous phase. There is no fusion of droplets involved. Ostwald ripening can be minimized by decreasing the solubility of the dispersed phase in the continuous phase by decreasing the interfacial tension between the two phases.

¹¹ Atwood, D., Florence, A.T. *Surfactant systems*. New York: Chapman and Hall, **1985**.

¹² De Smet, Y., Deriemaeker, L., Finsy R., Ostwald ripening of alkane emulsions in the presence of surfactant micelles, *Langmuir*, **1999**, 15, 6745-6754.

¹³ Bhakta, A.; Ruckenstein, E., Ostwald ripening: A stochastic approach, *J. Chem. Phys.* **1995**, 103, 7120-7136.

Kinetic stability. Emulsion stability is a kinetic concept. A freshly prepared emulsion changes its properties with time due to series of processes that occur at the microscopic level. Emulsion will always spontaneously change into a smaller number of larger droplets. A complete characterisation of emulsion stability requires consideration of the different processes through which dispersed droplets can encounter each other. The four main ways in which an emulsion may become unstable are creaming (or sedimentation), aggregation (flocculation), coalescence and Ostwald ripening (Figure 3).

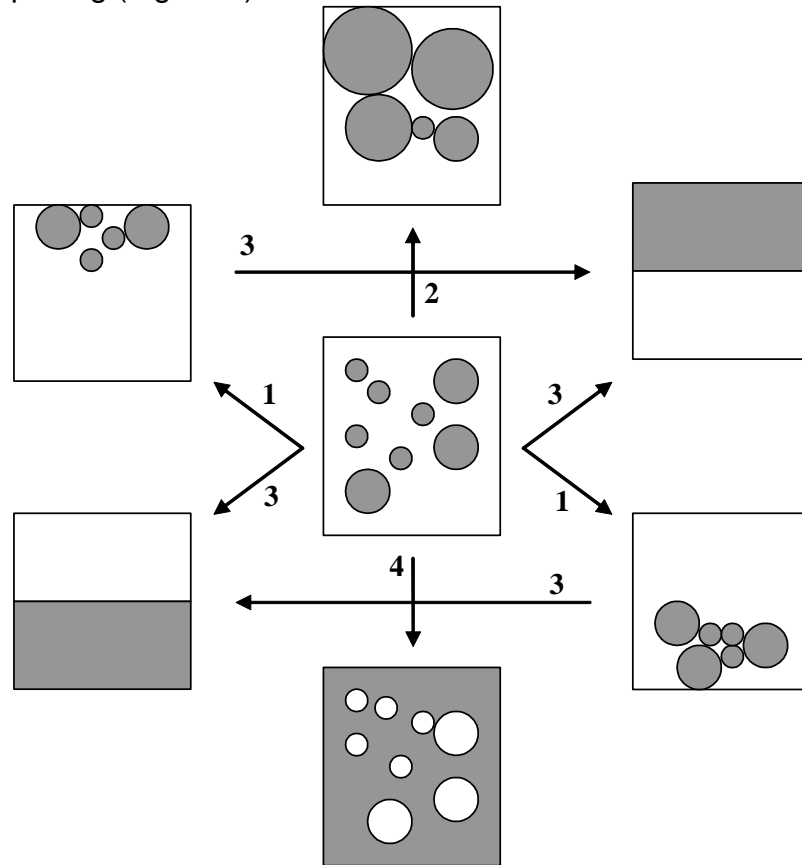


Figure 3. Degradation of emulsion: 1 phase separation (creaming, sedimentation); 2 Ostwald ripening; 3 aggregation processes (flocculation, coagulation, coalescence); 4 phase inversion

Coalescence is the formation of larger droplets by merging of smaller ones where small droplets come into the contact by thinning and finally dissolution of the liquid surfactant film that covers them. Aggregation is a process in which smaller droplets clump together like a grape and form bigger aggregates. The major difference between aggregation and coalescence is that aggregation process does not form new bigger droplets. For that reason, there is no reduction of the total surface area in the case of aggregation, while in the case of coalescence the total surface area is reduced. The emulsion that is stable against coalescence and aggregation is called kinetically stable emulsion.

In this case, the word “stable” describes the extent to which smaller droplets can remain uniformly distributed in emulsion. Furthermore, kinetically unstable emulsions can be described as dynamically stable when agitation is applied. In this case, droplets formation counteracts coalescence. Emulsion instability can also be described by other processes, which encounter the changing of emulsion properties. Creaming results from the density difference between the dispersed and continuous phase and produces two separate layers. In other words creaming is the process by

which emulsion droplets tend to rise to the top of a container. The sedimentation is the same process as creaming, but in the opposite direction. If one of the layers (upper or lower) will contain an enhanced concentration of dispersed phase, this may promote aggregation. In aggregation, droplets retain their identity but lose their kinetic independence since the aggregate moves as a single unit. Therefore, kinetic stability could thus have different starting points. However, a system can be kinetically stable with respect, for example to the coalescence, and is unstable with respect to the aggregation. Alternatively, a system could be kinetically stable with respect to aggregation, but unstable with respect to sedimentation.¹⁴

Emulsion stability is not necessarily a function of dispersed droplets size, although there may be an optimum size for an individual emulsion type. Most emulsions contain droplets, which are polydisperse. Stirring and vigorous mixing tend to produce an uncontrolled and wide droplet size distribution. Several methods for the preparation of monodisperse emulsions exist, of which the simplest is extrusion of a dispersed phase through a pipette into a continuous phase. The size distribution has an important influence on the viscosity. The viscosity of all emulsions will tend to be higher when the dispersed droplets sizes are relatively homogeneous.

1.3 Microemulsions, macroemulsions and high internal phase emulsions (HIPE)

From a thermodynamical point of view, we can distinguish between two emulsion types. Thermodynamically stable systems are known as microemulsions, while thermodynamically unstable (potentially metastable) systems are known as macroemulsions. High internal phase emulsions or HIPEs are a subset of macroemulsions. The different emulsions feature different feature sizes. While microemulsions are typically characterized by droplet diameters below 100 nm, macroemulsions (and high internal phase emulsions) feature droplet diameters of 100 nm up to 10 μm .

Microemulsions are thermodynamically stable liquid dispersions of an oil or a water phase. The dispersed phase is included in aggregates of surface active agents. The concentration of the latter is generally much higher compared to macroemulsions.^{15,16} Droplets involved in microemulsions are in a size range of 5 nm - 100 nm, and have a very low oil/water interfacial tension. Because the droplets sizes are smaller than the wavelength of visible light, microemulsions exhibit a transparent appearance. Formation of microemulsions occurs readily (sometimes even spontaneously) and generally without high energy input. The formation of microemulsions cause a decrease of the Gibbs free energy ($\Delta G < 0$). Small droplet sizes increase the specific surface area (which increases the surface tension) and increase the Gibbs free energy according to equation 3,

$$dG = \gamma \cdot dA \quad \text{Equation 3}$$

where γ is surface tension and A is the surface area. The excess free energy per unit area that exists in the surface molecule is defined as the surface tension (γ). Surface

¹⁴ Tadros, T.F., Vincent, B.: *Emulsion stability*, in P. Becher (ed): *Encyclopedia of Emulsion technology*, Volume 1. Marcel Decker, New York, 129-285, **1983**.

¹⁵ Ruckenstein, E., The Thermodynamics of Microemulsions revisited, *Langmuir* **1994**, 10, 1777-1779.

¹⁶ Ruckenstein, E., *In Progress in Microemulsions*; Martelluci, S., Chester, A. N., (Eds.), Plenum Press, New York, p.3, **1989**.

tension is a thermodynamic property and can be measured under constant T and p and its value represents the amount of minimum work required per unit area to create a greater surface area.

Furthermore, the Young-Laplace equation predicts an inverse relationship between pressure and droplets radius which means the smaller the droplets radius the higher the surface tension, which again consecutively increase Gibbs free energy by the equation,

$$\Delta p = \gamma \cdot (1/R_1 + 1/R_2) \quad \text{Equation 4}$$

for spherical objects $R_1=R_2= R_s$, and

$$\Delta p = 2\gamma/R_s \quad \text{Equation 5}$$

where Δp is pressure difference inside and outside of the curvature drop's surface, γ is the surface tension and R stands for the droplet radii.¹⁷ Arguments which are in accordance with Young-Laplace predictions (eq. 3) and surface Gibbs free energy (eq. 1), predict a coalescence of the droplets and for that reason there is no prove about thermodynamically stable system.

However, microemulsion formation can be considered to depend on the extent to which surfactant lowers the surface tension of the oil–water interface or depend on the change of entropy of the system by equation 6,

$$dG = \gamma dA - T dS \quad \text{Equation 6}$$

where dG is the Gibbs free energy of formation, γ is the surface tension of the oil–water interface, dA is the change in interfacial area, dS is the change in entropy of the system, and T is the temperature. When a microemulsion is formed, the change in dA is very large due to the large number of very small droplets formed. The work done by lowering the interfacial tension is for that reason based on system's entropy (ΔS) due to a creation of a large number of nano-sized droplets. Thus, a negative free energy of formation is achieved through large reductions in surface area, which is accompanied by significant favourable entropic change. Microemulsions form only spontaneously when the interfacial tension is small (in the order of 10^{-3} mN/m).^{18,19}

Macroemulsions tend to coalesce and are for that reason thermodynamically unstable systems. Their fate is pretty much clear: they will eventually phase-separate in order to minimize the interfacial area into two (or more distinct) equilibrium phases. Macroemulsions are usually cloudy because droplets are large enough to scatter light. Droplets involved are in a size range of $0.5 \mu\text{m} - 10 \mu\text{m}$. The general goal in macroemulsions preparation is the formation of a metastable state where droplets have to stay intact as long as possible. There is always competition between two processes: migration of the emulsifier to the droplet's surface to stabilize it versus coalescence with another droplet to destroy it.²⁰

¹⁷ Hiemenz P. C., Rajagopalan R., *Principles of colloids and surfaces chemistry*, 3rd Ed., Marcel Dekker, New York, **1997**.

¹⁸ Ruckenstein, E., Chi, J. C., Stability of microemulsions, *Faraday Trans. II*, **1975**, 71, 1690-1707.

¹⁹ Ruckenstein, E., Microemulsions, macroemulsions, and the Bancroft rule, *Langmuir*, **1996**, 12, 6351-6353.

²⁰ Stokes R. J., Evans D. F.: *Fundamentals of interfacial engineering*, Wiley-VCH, New York, chapter 5, 240-247, **1997**.

The distinction between a stable and an unstable emulsion depends mostly on the time scale. A number of effects contribute to the stabilization of an emulsion and addition of surfactant is the most commonly used strategy. Production of macroemulsions with higher volume fractions of internal phase, up to 0.99, will require more surfactant than usually required for the preparation of macroemulsions. Such emulsions are called high internal phase emulsions. At such high volume fraction of internal phase, the droplets size distribution is usually polydisperse. Due to the high concentration of high internal phase the droplets deform into non-spherical shapes and only a thin film of continuous phase remains between them.

High internal phase emulsions (HIPE). Despite the large amount of work devoted to this issue, emulsions lifetime still raise challenging questions, especially in concentrated emulsions. High internal phase emulsions are very concentrated dispersed systems in which the dispersed phase occupies more than 74.05% of whole volume fraction.²¹ The maximum volume packing fraction where droplets retain non deformable and spherical is in the region of 71% - 75% of the whole emulsion volume. Maximal packing density while spherical objects maintain their spherical shape was first stated by mathematician Johannes Kepler and is known as Kepler's conjecture.²² The average density of maximal packing by Kepler's conjecture is:

$$\pi / \sqrt{18} \approx 0.74048$$

Equation 7

High internal phase emulsion system exceeds this maximum packing and for that reason deformation of spherical droplets takes place via compression. This results in transformation from spherical droplets into tightly packed polyhedral drops (Figure 1) which are separated by the oil (or water) surfactant solution or so-called continuous phase.^{7,23}

HIPEs are a typical example of non-equilibrium systems because the interfacial free energy associated with the large interfacial area is maximized.²⁴ The system is not at its minimum total free energy and is thus not in equilibrium.

Like ordinary non-concentrated emulsions, HIPEs can be prepared either from water-in-oil (W/O) or oil-in-water (O/W) types. Also non-aqueous high internal phase emulsions (HIPEs), where petroleum ether was dispersed in different polar organic solvents, can be obtained.²⁵ High internal phase emulsions tend to be viscous, which is mainly caused by the surfactant properties.²⁶ Viscosity can be influenced by

²¹ Lissant, K. J., *Emulsions and Emulsion Technology Part1*, Marcel Dekker Inc, New York, **1974**.

²² Hales T. C., An overview of the Kepler conjecture, *Metric geometry*, **2002**, math.MG/9811078.

²³ Pal, R., Yield stress and viscoelastic properties of high internal phase ratio emulsions, *Coll. Polym. Sci.* **1999**, 277, 583-588.

²⁴ Lissant, K. J., The geometry of high internal phase ratio emulsions, *J. Colloid. Interface. Sci.*, **1966**, 22, 462-468.

²⁵ Cameron N. R., Sherrington D. C., Non-aqueous high internal phase emulsions. Preparation and stability, *J. Chem. Soc., Faraday Trans.*, **1996**, 92, 1543-1547.

²⁶ Prince, H.M., Rheology of foams and highly concentrated emulsions: I. Elastic properties and yield stress of a cylindrical model system, *J. Colloid Interface Sci.*, **1983**, 91, 160-175.

increasing the concentration of internal phase and vigorous mixing,²⁷ by surfactant proportion²⁸ and by droplets size or the temperature.²⁹ To prepare stable HIPEs a surfactant, which should be insoluble in droplet phase, is needed to prevent emulsion inversion at higher droplet concentration. Increasing the concentration of the surfactant leads to an increased viscosity of the continuous phase which resulting in the obstruction of Brownian motion.³⁰ Brownian motion enables droplets to come into contact with each other (and this can lead to the emulsion instability mentioned earlier by one of the four mechanisms). Another positive effect of increased surfactant concentration in the continuous phase of the HIPE is the provision of a barrier disturbing the van der Waals interactions between droplets.³¹ On the other hand, increasing the viscosity of continuous phase with the excessive surfactant addition could lead to inadequate mixing of the phases, which consecutively could lower the amount of distributed droplets in the HIPE.³² Besides the increased concentration of surfactant during HIPE preparation, the stability of HIPE can be influenced by the addition of an electrolyte to the aqueous phase, which causes inhibition of Ostwald ripening process.³³ Mixtures of co-surfactants usually yield more stable emulsions than single surfactant.³⁴

High internal phase emulsions have a number of actual and potential applications in different fields of industry such as food industry (mayonnaise), cosmetic industry (gels and creams), petroleum industry and in agriculture as sprays with pesticide properties.

2 Porous materials

One of the most useful and widely used applications of high internal phase emulsions is as template for the preparation of macroporous materials, so-called polyHIPEs.^{35,36}

²⁷ Ford, R. E., Furmidge, C. G. L., Physico-chemical studies on agricultural sprays VII.- Viscosity and spray drop size of water-in-oil emulsions, *J. Sci. Food Agric.*, **1967**, 18, 419-428.

²⁸ Welch, C. F., Rose, G. D., Malotky, D., Eckersley, S. T., Rheology of high internal phase emulsions, *Langmuir*, **2006**, 22, 1544-1550.

²⁹ Das, A.K., Mukesh, D., Swayambunathan, V., Kotkar, D.D., Ghosh, P.K., Concentrated emulsions. 3. Studies on the influence of continuous phase viscosity, volume fraction, droplets size, and temperature on emulsion viscosity, *Langmuir*, **1992**, 8, 2427-2436.

³⁰ Carnachan R. J., Bokhari, M., Prozyborski, S. A., Cameron, R. N., Tailoring the Morphology of Emulsion-templated Porous polymers, *Soft Matter*, **2006**, 2, 608-616.

³¹ Carnachan R. J., Emulsion-derived (PolyHIPE) Foams for Structural Materials Applications, PhD Thesis, University of Durham, **2004**, p.9-11.

³² Chen, H. H., Ruckenstein, E., Effect of the nature of the hydrophobic oil phase and surfactant in the formation of concentrated emulsions, *J. Colloid. Interacef. Sci.*, **1991**, 145, 260-269.

³³ Kizling J., Kronberg B., On the formation and stability of concentrated water-in-oil emulsions, *Colloid. Surf.*, **1990**, 50, 131-140.

³⁴ Atwood, D, Florence, A.T. Surfactant systems. New York: Chapman and Hall, chapter 8, p. 473, **1985**.

³⁵ Barby D., Haq Z., U.S. Patent 4522953, Low density porous crosslinked polymeric materials and their preparation and use as carriers for included liquids, **1985**.

PolyHIPE monoliths. Characteristic polyHIPE monoliths incurred as a result of continuous phase polymerisation. The procedure for polyHIPE materials preparation consists of slow addition of the droplet phase to the monomeric continuous phase mixture during constant stirring to form uniform W/O or O/W HIPE.³⁷ Mixing is followed by polymerisation of continuous phase, which depends upon the initiation system used; thermal, redox, catalytic, UV, or microwave induced initiation. Typically, polymerised monoliths are then purified by Soxhlet extraction.

Resulting polyHIPE materials (Figure 4) possess an open pore system. This means that bigger pores (so-called cavities) which arise as a result of extraction of the dispersed phase after the polymerisation of the continuous phase are connected with smaller interconnecting pores (Figure 5). In some cases, a closed and isolated pore system, which is largely depended on the amount of added surfactant during HIPE formation, is obtained. The most probable theory explaining the formation of the typical open cellular architecture states that the amount of surfactant should exceed 7 vol. % (according to the monomer mixture). Increasing the proportion of the surfactant causes a thinning of the oil (monomer) layer between the droplets and at a critical point of surfactant loading, the monomer layer becomes very thin. Subsequently, the polymer film, which forms during the polymerisation of the continuous phase, shrinks slightly and eventually breaks forming interconnecting pores.³⁸ Another explanation is that interconnecting pores formation is a post polymerisation process. As a result of extraction and drying in vacuum the interconnecting pores form.³⁹

A low dry bulk density (typically less than 0.1 g cm^{-3} - or even lower, e.g. 0.01 g cm^{-3}) characterizes the open-cell structured monolithic polymers.⁴⁰ PolyHIPE materials possess pore volumes up to $10 \text{ cm}^3/\text{g}$ and cavities size range from 5 to $100 \mu\text{m}$. In spite of the high porosity, the specific surface area of non-modified polyHIPE materials is relatively small, between $3\text{-}20 \text{ m}^2/\text{g}$. Increasing of the polyHIPEs surface area is possible e.g. by the addition of porogenic solvents to the continuous phase of the HIPE. Introducing porogenic solvents during the synthesis of polyHIPE materials might also affect the formation of secondary pores in polymer matrix due to the phase separation and can yield materials with up to $720 \text{ m}^2/\text{g}$.⁴¹ Even extremely high surface areas can be achieved through hyper-crosslinking of the material, which is a

³⁶ Cameron N.R., In: Svec F., Tenikova T. B., Deyl Z., Editors. *Monolithic materials: preparation, properties, application*. Amsterdam: Elsevier, chapter 12, **2003**.

³⁷ For preparation procedure see: Štefanec D., Porous polymer supports from O/W high internal phase emulsions, PhD Thesis, University of Maribor, **2007**, p. 23, scheme 1.11.

³⁸ (a) Cameron, N. R., Sherrington, D. C., Albiston, L., Gregory, D. P., Study of the formation of the open cellular morphology of poly(styrene/divinylbenzen) PolyHIPE materials by cryoSEM, *Colloid Polym. Sci.*, **1996**, 274, 592-595. (b) Cameron, R. N., High internal phase emulsion templating as a route to well-defined porous polymers, *Polymer*, **2005**, 45, 1439-1449.

³⁹ Menner, A., Bismarck, A., New evidence for the mechanism of the pore formation in polymerizing High Internal Phase Emulsions or why polyHIPEs have an interconnected pore network structure, *Macromol. Symp.*, **2006**, 242, 19-24.

⁴⁰ Richez, A., Deleuze, H., Vedrenne, P., Collier, R., Preparation of ultra-low-density microcellular materials, *J. Applied Polym. Sci.*, **2005**, 96, 2053-2063.

⁴¹ Jerábek K., Pulko I., Soukupova K., Štefanec D., Krajnc P., Porogenic solvents influence on morphology of 4-vinylbenzyl chloride based PolyHIPEs *Macromolecules*, **2008**, 41, 3543-3546.

post-polymerisation process and results in materials with surface area up to 1100 m²/g.⁴²

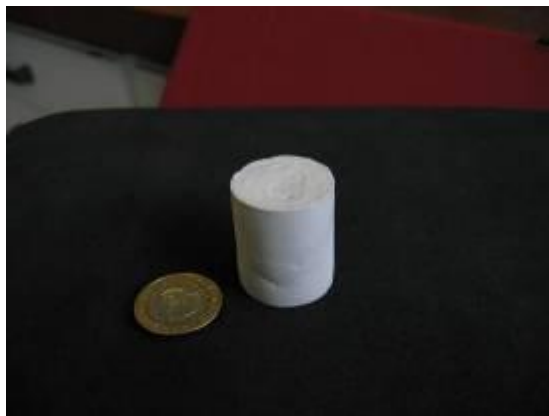


Figure 4. Photograph image of polyHIPE monolith

Various of chemistries can be used to prepare either W/O or O/W polyHIPEs monolithic materials. Styrene/DVB polyHIPE materials are very well established and have been used in many applications. While W/O HIPE morphologies and related chemistries are well researched, also O/W HIPEs were used to prepare monolithic polyHIPE materials with various chemistries including 2-hydroxyethyl methacrylate (HEMA),⁴³ or *N*-isopropyl acrylamide (NIPAM).⁴⁴

Amongst the different kind of chemistries used for polyHIPE preparation, also surface functionalization is used to further process the porous materials. The system which is very well known and has been extensively studied involves styrene/DVB chemistry and subsequent functionalization with e.g. sulfonic acid groups,⁴⁵ nitro groups or

⁴² Pulko I., Wall J., Krajnc P., Cameron N. R. Ultra-High surface area functional porous polymers by emulsion templating and hypercrosslinking: efficient nucleophilic catalyst supports, *Chem. Eur. J.* **2010**, 16, 2350 – 2354.

⁴³ (a) Kovačič, S.; Štefanec, D.; Krajnc, P., Highly Porous Open-Cellular Monoliths from 2-Hydroxyethyl Methacrylate Based High Internal Phase Emulsions (HIPEs): Preparation and Void Size Tuning, *Macromolecules*, **2007**, 40, 8056–8060. (b) Kulygin, O. Silverstein, M. S., Porous poly(2-hydroxyethyl methacrylate) hydrogels synthesized within high internal phase emulsions, *Soft Matter* **2007**, 3, 1525-1529.

⁴⁴ (a) Zhang, H. F. Cooper, A. I. Thermoresponsive “Particle Pumps”: activated release of organic nanoparticles from open-cell macroporous polymers, *Adv. Mater.*, **2007**, 19, 2439-2444. (b) Grant, N. C., Cooper, A. I., Zhang, H., Uploading and temperature-controlled release of polymeric colloids via hydrophilic emulsion-templated porous polymers, *Applied Materials and Interfaces*, **2010**, 2, 1400-1406.

⁴⁵ (a) M. Ottens, G. Leene, A. A. C. M. Beenackers, N. Cameron and D. C. Sherrington, PolyHipe: A new polymeric support for heterogeneous catalytic reactions: kinetics of hydration of cyclohexene in two- and three-phase systems over a strongly acidic sulfonated PolyHipe, *Ind. Eng. Chem. Res.*, **2000**, 39, 259–266. (b) Wakeman R. J., Bhumgara Z. G., Akay G., Ion exchange modules formed from polyHIPE foam precursors, *Chem. Eng. J.*, **1998**, 70, 133–141.

halogens.⁴⁶ Such materials are then used in applications like supports for reactions in batch-mode or flow-through set-ups,⁴⁷ as filtration media,⁴⁸ supports for peptide synthesis,⁴⁹ as absorbents in aqueous media,⁵⁰ as matrixes for tissue engineering,⁵¹ or as microbioreactors in flow-through mode.⁵²

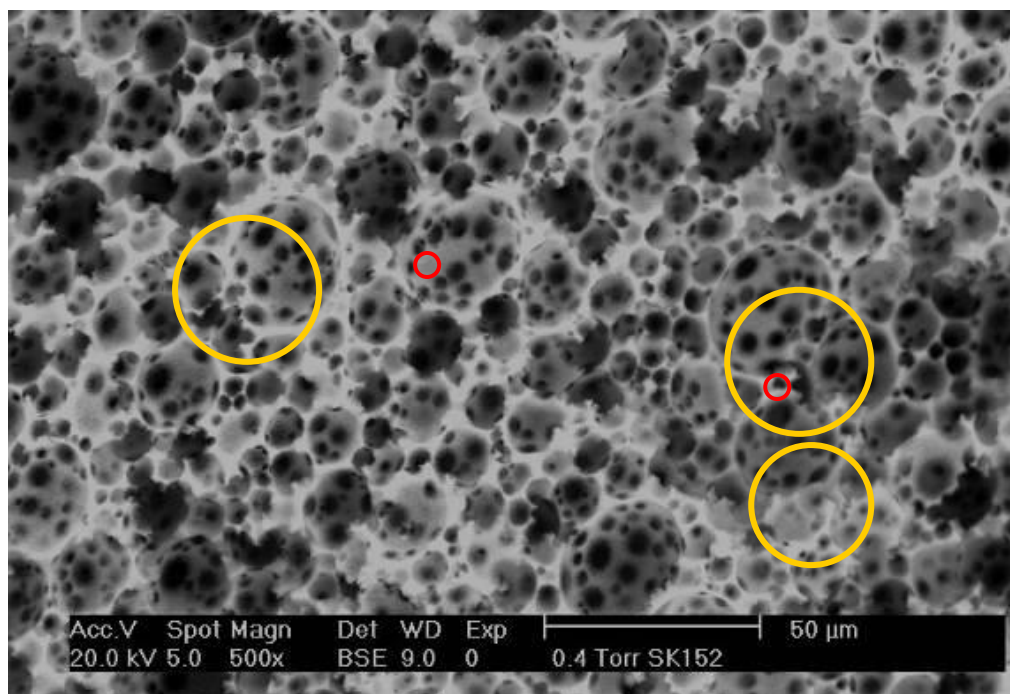


Figure 5. SEM image of acrylamide polyHIPE material with typical cavities (yellow circles)-interconnecting pores (red circles) architecture

⁴⁶ Cameron N. R., Sherrington D. C., Ando I., Kurosu H. Chemical modification of monolithic poly(styrene–divinylbenzene) polyHIPE materials, *J. Mater. Chem.* **1996**, 6, 719-726.

⁴⁷ Mercier, A., Deleuze, H., Mondain-Monval, O. Preparation and functionalization of (vinyl)polystyrene polyHIPE[®]: Short routes to binding functional groups through a dimethylene spacer, *React. Funct. Polym.*, **2000**, 46, 67-79.

⁴⁸ (a) Bhumgara, Z., Polyhipe Foam Materials as Filtration Media, *Filtration and Separation*, 1995, 32, 245-251. (b) Walsh, D. C., Stenhouse, J. I. T., Kingsbury, L. P., Webster, E. J. PolyHIPE foams: Production, characterisation, and performance as aerosol filtration materials, *J. Aerosol Sci.*, **1996**, 27/1, 629-630.

⁴⁹ Small, P. W., Sherrington, D. C., Design and application of a new rigid support for high efficiency continuous-flow peptide synthesis, *J. Chem. Soc., Chem. Commun.*, **1989**, 21, 1589-1591.

⁵⁰ Sergienko, A. Y., Tai, H. W., Narkis, M., Silverstein, M. S., Polymerized high internal-phase emulsions: Properties and interaction with water, *J. Appl. Polym. Sci.*, **2002**, 84/11, 2018-2027.

⁵¹ (a) Busby, W., Cameron, N. R., Jahoda, C. A. B., Emulsion-derived foams (polyHIPEs) containing poly(ϵ -caprolactone) as matrixes for tissue engineering, *Biomacromolecules*, **2001**, 2, 154-164. (b) Bokhari, M. A., Akay, G., Zhang, S., Birch, M. A., The enhancement of osteoblast growth and differentiation in vitro on a peptide hydrogel-polyHIPE polymer hybrid material, *Biomaterials*, **2005**, 26, 5198-5208.

⁵² Akay, G., Erhan, E., Keskinler, B., Bioprocess intensification in flow-through monolithic microbioreactors with immobilized bacteria, *Biotechn. Bioeng.*, **2005**, 90, 180-190.

Preparation of polyHIPE in mold polymerisation of HIPEs, as columns for use in flowthrough mode, yielded highly permeable supports with high surface area which have been used as scavengers⁵³ and chromatographic supports (Figure 6).



Figure 6. Column for flow-through set-up with the polyHIPE inside

Besides chemical and morphological characteristics, polyHIPE monoliths have to possess also appropriate mechanical properties. A common test for determining the mechanical behaviour of polyHIPEs is the measurement of the tensile strength which depends on the elasticity modulus (Young's modulus)

$$F/S = E \cdot \Delta L/L_0$$

Equation 9

where is L_0 original length, ΔL increased length of test material by tensile force, S cross-sectional area, F is the force, and E is the Young's modulus.

Many groups tried to improve relatively poor mechanical properties of polyHIPEs which range with Young's modulus between 3-6 MPa. The groups of Silverstein and Deleuze were trying to improve mechanical properties of polyHIPEs by preparation of interpenetrating polymer networks (IPN) which yielded materials with Young's modulus up to 38.4 MPa,⁵⁴ while Bismarck's group prepared composite polyHIPEs with Young's modulus up to 200 MPa.

PolyHIPE beads possess permanent porosity but are mechanically fragile. In spite of this mechanical drawback, porous polymer beads are used in wide range of

⁵³ (a) Krajnc, P.; Brown, J.F.; Cameron, N.R., Monolithic scavenger resins by amine functionalizations of poly(4-vinylbenzyl chloride-co-divinylbenzene) PolyHIPE materials, *Org. Lett.*, **2002**, 4, 2497-2500. (b) Lucchesi, C.; Pascual, S.; Dujardin, G.; Fontain, L., New functionalized polyHIPE materials used as amine scavengers in batch and flow-through processes, *React. Funct. Polym.*, **2008**, 68, 97-102. (c) Kovačič S., Krajnc P., Macroporous monolithic Poly(4-vinylbenzyl chloride) columns for organic synthesis facilitation by in situ polymerisation of High Internal Phase Emulsions, *J. Polym. Sci. Part A, Polym. Chem.* **2009**, 47, 6726.

⁵⁴ (a) Silverstein, M. S., Tai, H., Sergienko, A., Lumelsky, Y., Pavlosky, S., PolyHIPE IPNs, hybrids, nanoscale porosity, silica monoliths and ICP-based sensors, *Polymer*, **2005**, 46, 6682-6694. (b) Lepine, O., Birot, M., Deleuze, H., Preparation of macrocellular PU-PS interpenetrating networks, *Polymer*, **2005**, 46, 9653-9663.

applications, such as stationary phase in separations,⁵⁵ supports in solid phase organic and peptide synthesis,⁵⁶ as ion-exchanged resins,⁵⁷ scavengers⁵⁸ and supports for catalysts immobilisation.⁵⁹

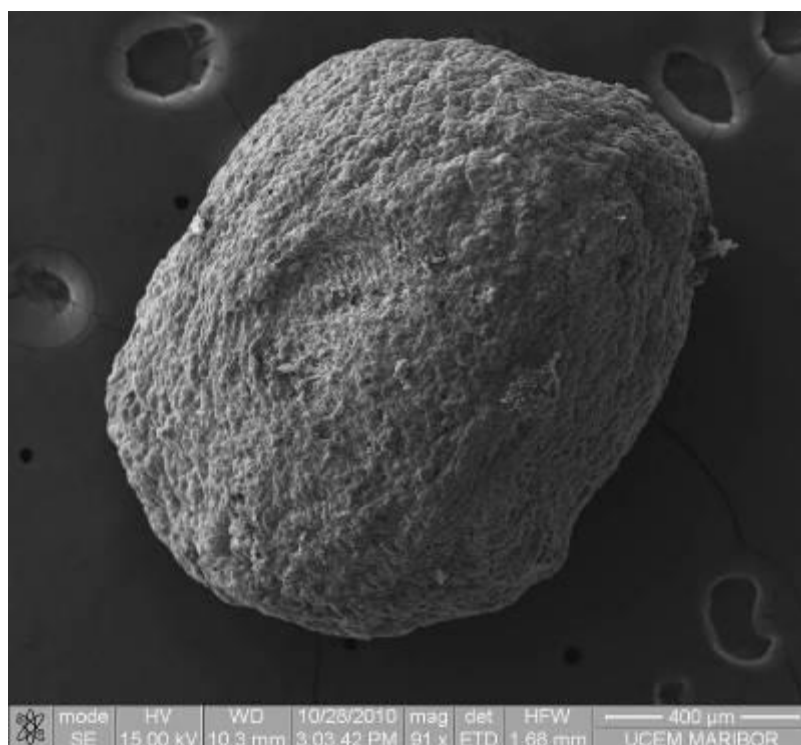


Figure 7. SEM image of the polyHIPE beads

Porous beads are mostly prepared by suspension polymerisation of monomer droplets which contains a porogenic solvent and are suspended in second continuous phase where they are polymerized.⁶⁰ An alternative strategy which yields polyHIPE beads (Figure 7) with porosity up to 90 % is a dispersion of a HIPE into the third medium (forming W/O/W or O/W/O three phase systems or double emulsion)

⁵⁵ Fontanals, N.; Marce, R. M.; Cormack, P. A. G.; Sherrington, D. C.; Borrull, F., Monodisperse, hyper-crosslinked polymer microspheres as tailor-made sorbents for highly efficient solid-phase extractions of polar pollutants from water samples, *J. Chromatogr. A*, **2008**, 1191, 118–124.

⁵⁶ Hudson, D., Matrix assisted synthetic transformations: A mosaic of diverse contributions. I. The Pattern Emerges, *J. Comb. Chem.*, **1999**, 1, 333–360.

⁵⁷ Rao, T., Praveen, R. S., Daniel, S., Styrene-divinyl benzene copolymers: synthesis, characterization, and their role in inorganic trace analysis, *Crit. Rev. Anal. Chem.* **2004**, 34, 177–193.

⁵⁸ Leeb, L., Gmeiner, P., Lober, S., Optimization of click chemistry using azide and alkyne scavenger resins, *QSAR Comb. Sci.*, **2007**, 26, 1145–1150.

⁵⁹ Haag, R., Roller, S., Polymeric supports for immobilization of catalysts, *Top. Curr. Chem.*, **2004**, 242, 1–42.

⁶⁰ Poschalko, A.; Rohr, T.; Gruber, H.; Bianco, A.; Guichard, G.; Briand, J.-P.; Weber, V.; Falkenhagen, D., SUBPOL: A Novel Sucrose-Based Polymer Support for Solid-Phase Peptide Synthesis and Affinity Chromatography Applications, *J. Am. Chem. Soc.* **2003**, 125, 13415–13426.

where they are subsequently solidified by polymerisation.⁶¹ After Li and Benson patented the preparation procedure in 1998 not much research has been done on polyHIPE beads, probably because of emulsion instability during formation.

PolyHIPE membranes. The applicability and versatility of the emulsion templating technique was also demonstrated by the preparation of open cellular porous membranes.

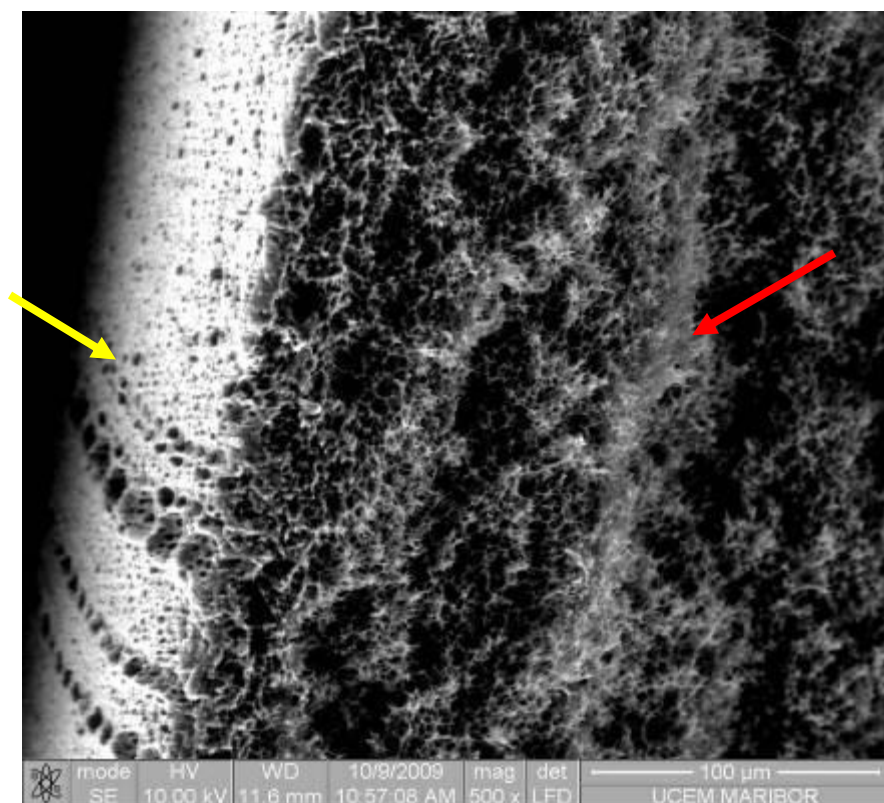


Figure 8. Surface and interior of the polyHIPE membrane; red arrow pointed to the interior of membrane, yellow arrow pointed to the surface

In 1989 Ruckenstein reported the preparation of composite styrene/acrylamide polymeric membranes by emulsion templating for separation of mixtures of different solvents.⁶² The syntheses of functionalized polyHIPE membranes of thickness between 100-200 µm for obtaining ion selectivity were reported by group of Cameron.⁶³ Even thinner functionalized membranes with thicknesses of 30 µm were prepared. Sufficient flexibility was obtained by controlling the crosslinking degree and

⁶¹ (a) Li, N. H.; Benson, J. R.; Kitagawa, N. US Patent 5,760,097, **1998**. (b) Cooper, A. I.; Zhang, H. US Patent 7,153,572, **2006**. (c) Zhang, H.; Cooper, A. I., Synthesis of monodisperse emulsion-templated polymer beads by Oil-in-Water-in-Oil (O/W/O) sedimentation polymerisation, *Chem. Mater.* **2002**, 14, 4017–4020.

⁶² E. Ruckenstein, Emulsion pathways to composite polymeric membranes for separation processes, *Colloid. Polym. Sci.*, 1989, 267, 792–797.

⁶³ C. Zhao, E. Danish, N. R. Cameron and R. Katakya, Emulsion-templated porous materials (PolyHIPEs) for selective ion and molecular recognition and transport: applications in electrochemical sensing, *J. Mater. Chem.*, **2007**, 17, 2446–2453.

addition of plasticizers.⁶⁴ Through-open polyHIPE membranes, (without the surface skin) which are generally difficult to obtain are accessible by ring opening metathesis polymerisation (ROMP) of dicyclopentadiene (Figure 8).⁶⁵

Bitte bereiten Sie zur Besprechung dieser Übung insbesondere folgende Fragen vor:

Kolloquiumsfragen zur Übung Emulsionspolymerisation

Die Beantwortung der folgenden Fragen sollte jeder/m Studierenden keine Mühe machen. Die BetreuerInnen nehmen sich aber auch die Freiheit nicht nur diese Fragen zu stellen.

1. Was ist eine Emulsion und welche Arten der Emulsion gibt es?
2. Was ist der HLB-Wert?
3. Mit welchen Mechanismen beschreibt man den Zerfall einer Emulsion?
4. Wie müssen Feststoffstabilisatoren beschaffen sein um eine Emulsion möglichst gut zu stabilisieren?
5. Wann ist eine Emulsion thermodynamisch stabil?
6. Erklären Sie den Mechanismus der Ring Öffnenden Metathese Polymerisation.
7. Nennen Sie Faktoren die ein gut ROMP-bares Monomer ausmachen.
8. Was sind „high internal phase emulsions“?

Nutzen Sie dafür diesen kurzen Abriss, eigene Recherche und insbesondere den Artikel von Silverstein et. al.

“Emulsion Templating: Porous Polymers and Beyond”

Tao Zhang, Rajashekharayya A. Sanguramath, Sima Israel, and Michael S. Silverstein, *Macromolecules* **2019**, *52*, 5445–5479.

[DOI: 10.1021/acs.macromol.8b02576](https://doi.org/10.1021/acs.macromol.8b02576)

⁶⁴ Pulko I., Krajnc P. Open cellular reactive porous membranes from high internal phase emulsions, *Chem. Commun.*, **2008**, 4481–4483.

⁶⁵ Kovačič S., Krajnc P., Slugovc C., Inherently reactive polyHIPE material from dicyclopentadiene, *Chem. Commun.*, **2010**, 46, 7504–7506.