Graz University of Technology

LU und Exkursion Chemische Technologie CHE.170

Polymerisation of Emulsions

based on the PhD work of Sebastijan Kovacic

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1. Emulsions

Many situations in different area of food industry, petroleum production (drilling fluids), pharmaceutics (mainly cosmetics), and environmental applications require mixing oil and water. For that reason the production and use of stable emulsions had been extensively examined. Emulsions are heterogeneous dispersions in which drops of liquid are dispersed in continuous 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 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 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 type).[2] Emulsions with no aqueous phase, so-called anhydrous or oil-in-oil emulsions can also be prepared where 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 formation of rust and other mechanical systems.[3]
The type of emulsion that is preferred depends upon a number of factors including temperature, electrolyte concentration, proportions of components, nature of components and surfactant structure. The 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. Interface between phases in both emulsion types lining the stabilizer molecules which differ in chemical structure. Most meta-stable emulsions that are used in practice contain oil, water and stabilizers which 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 protective film around droplets and keeping the emulsion from

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[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.

breaking. The liquid in which the surfactant has a higher solubility tends to be the continuous phase, 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 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 surfactant determine its affinity for particular phase. The first who has quantified surfactant affinity for aqueous or oil phase of the emulsion and gave answer to the preferred emulsion morphology was Griffin by introducing the hydrophilic-lipophilic balance concept (HLB).[5] Drawback of Griffin's method is that contains only certain classes of surfactants where a direct link between structure of the surfactant and its HLB can be found. Concept which obeys emulsion as a whole system and interprets surfactant affinity to the both phases is the phase inversion temperature (PIT) concept. The PIT concept was proposed by Shinoda and Kunieda as a method for the classification of non-ionic surfactants and to predict correlation between emulsion morphology and temperature.[6] While HLB is a surfactant property, PIT is an emulsion property. The intermediate temperature, at which surfactant affinity for both phases in the emulsion is equal, is the phase inversion temperature. Deficiency of PIT, despite of its importance during preparation of a stable emulsion, is its inapplicability to ionic surfactants.

Besides temperature and surfactant affinity, there are other variables that influence surfactant distribution at the interface and therefore the emulsion morphology: the salinity of the aqueous phase, the polarity of the oil phase, the HLB value of the surfactant and the co-surfactant. Salager suggested merging all variables into one framework which would yield 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 oil phase

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

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 water phase (subscript w) or oil phase (subscript o). With this equation it is easier to define surfactant affinity to the individual emulsion phase where 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 emulsion solution is diluted while during concentrating, the

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[4] Bancroft, W.D., The theory of emulsiofication 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]

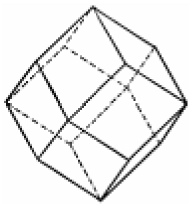
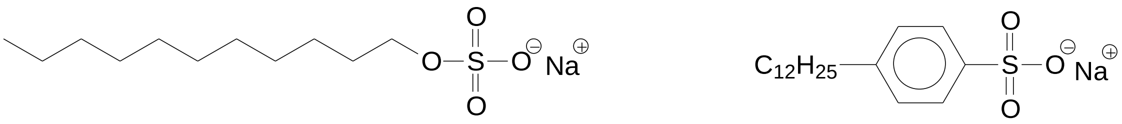


Figure 1. *Rhombic dodecahedron shape*

Emulsions exhibit 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 are 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 kinectic stability.

1.1 Surface active agents (surfactants)

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



Sodium Dodecyl (ester) Sulfate

Sodium Dodecyl Benzene Sulfonate

Figure 2. *Amphiphilic molecules*

For a surfactant to act as an emulsifier it must satisfy certain conditions. It has to show good surface activity and produce a low interfacial tension at interface. This means that it must have tendency to migrate into the interface rather than stay dissolved in either one of the bulk phases. Next feature that must be considered prior to selection is the ability to form as highly as possible condensed interfacial film, either by itself or with other adsorbed molecules that are present, with lateral interactions between molecules comprising the film. The most condensed interfacial film between oil and water is formed when maximum number of surfactant molecules is packed and are oriented vertically.[10] Surfactant concentration at a boundary depends upon the surfactant structure and the chemistry of the two phases that meet at the interface. Surfactant must migrate to the interface at such rate that interfacial tension is reduced to a level of stability during the emulsion preparation. Rate of migration depends on whether the surfactant is placed into the oil or water phase.

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[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.

Surfactant simultaneously serves three functions in stabilizing an emulsion. They play an essential role in determining whether oil in water is the continuous phase. They control many of the attractive and repulsive forces between droplets that govern the flocculation and coagulation. They determine the mechanical properties of the interfacial films that control coalescence rates.

Two other general guidelines have to be taken into account during surfactant selection. 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 surfactant and water soluble surfactant often produce better and more stable emulsions than an individual surfactant.[11]

A frequently used method for 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]

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

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

1.2 Stability of the emulsions

Emulsions are heterogeneous systems which will eventually phase separate into two clear, 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 surfactants additions which sufficiently reduce the interfacial tension.

From thermodynamics it is know 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.

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[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 occurs 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).

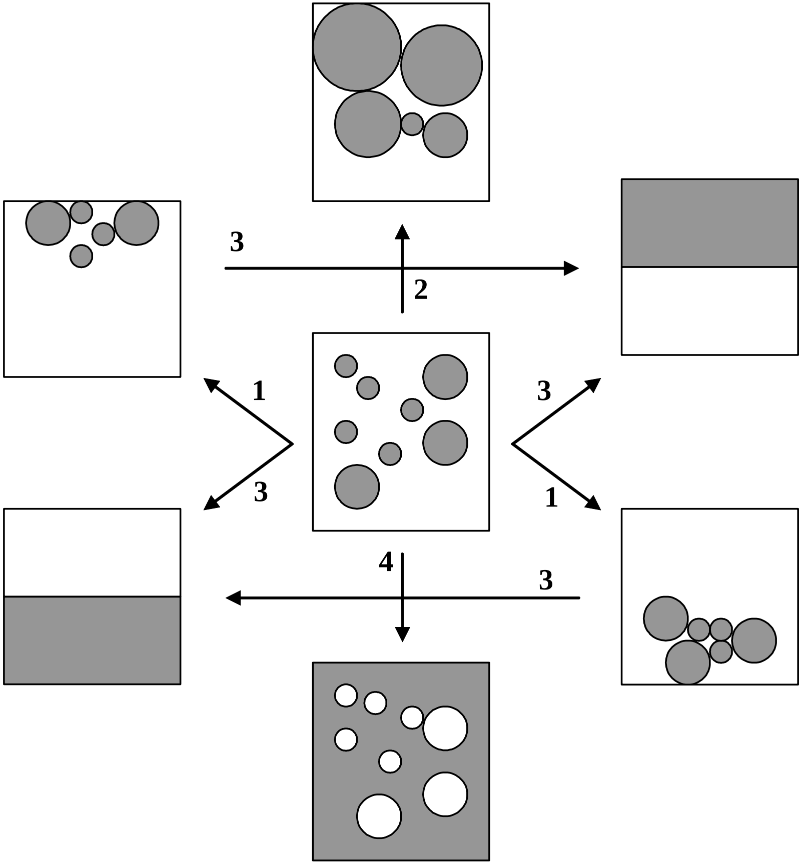

Figure 3. *Degradation of emulsion: 1 phase separation (creaming, sedimentation); 2 Ostwald ripening; 3 aggregation processes (flocculation, coagulation, coalescence); 4 phase inversion*

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. While aggregation is process where smaller droplets clump together like a grape and form one bigger aggregate. The major difference between aggregation and coalescence is that aggregation process does not form a new bigger droplet. For that reason there is no reduction of the total surface area in the case of aggregation process while in the case of coalescence process the total surface area is reduced. The emulsion that is stable against coalescence and aggregation is called kinetically stable emulsion.

In this case word “stable” describes the extent, to which smaller droplets can remain uniformly distributed in emulsion. Furthermore can be kinetically unstable emulsions termed as dynamically stable under agitation where droplets break up counteracts coalescence. Emulsion instability can be also described by other processes which encounter to the changing of emulsion properties. Creaming results from density difference between the dispersed and continuous phase and produced 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 aggregate moves as a single unit. So, 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. Or, 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 lead to 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 thermodynamical point of view we can distinguish between two emulsion systems. Thermodynamically stable systems are known as microemulsions, while thermodynamically unstable or metastable systems are known as macroemulsions, where can also be counted high internal phase emulsions or HIPEs. These three types of the emulsions differ in structural length scale; microemulsions involve droplets in range between 5 and 100 nm while macroemulsions and high internal phase emulsions in range between 100 nm and 10 µm.

Microemulsions are thermodynamically stable liquid dispersions of an oil phase or a water phase, where dispersion phase is included in aggregates of surface active agents the concentration of which is generally much higher compared with coarse emulsions.[15,16] Microemulsions have nothing in common with coarse emulsions except that both can be considered as liquid-liquid dispersions. Droplets involved in microemulsions are in a size range of 5 nm - 100 nm, and has very low oil/water interfacial tension. Because the droplets sizes are less than the wavelength of visible light, microemulsions are transparent. Formation of microemulsions is readily and sometimes spontaneously, generally without high energy input. Microemulsions tend to decrease Gibbs free energy ($\Delta G<0$). Small droplet sizes make the specific area larger which increase surface tension and increase Gibbs free energy which is in agreement with equation,

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

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

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[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, Young-Laplace equation predict 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,

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

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

$\Delta p = 2\gamma/Rs$ Equation 5

where Δp is pressure difference inside and outside of the curvature drop's surface, γ is surface tension and R stands for 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,

$dG = \gamma dA - TdS$ 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 spontaneously only when 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 with respect to separation into two distinct layers. According to the emulsions instability, their fate is pretty much clear: it will separate by one of two mechanisms 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 µm – 10 µm. 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]

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[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 stabilization of an emulsion and addition of surfactant is one which is most commonly used. Production of macroemulsions with higher volume fractions of internal phase, up to 0.99, will require an additional amount of surfactant as will usually macroemulsions preparation. 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 high concentration of high internal phase droplets and droplets deform into non-spherical shapes and only 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:

$$\pi / \sqrt{18} \approx 0.74048 \qquad \text{Equation 7}$$

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 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 far from 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 influenced mainly by surfactant properties.[26] Viscosity can be influenced by

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[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. Coloid. 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 proportion[28] and by droplets size or temperature of internal phase.[29] To prepare stable HIPEs a surfactant which should not be soluble in droplet phase is needed, while preventing emulsion inversion at higher droplets concentration. Increasing concentration of surfactant leads to increased viscosity of the continuous phase which resulting in the obstruction of Brownian motion.[30] Brownian motion enables droplets to come into the contact with each other and this can lead to the emulsion instability mentioned earlier by one of the four mechanisms. Another positive side of increased concentration of surfactant in the continuous phase of HIPE is to provide a barrier which disturbs the van der Walls 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 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 the electrolyte into the aqueous phase which causes inhibition of Ostwald ripening process.[33] Mixtures of co-surfactants usually yield more stable emulsions than single surfactant, but this is only the estimation based on observation during emulsion preparation, where creaming and milky appearance are taken as a parameter of stability.[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 agricultural as sprays with pesticide properties.

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[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. Coloidl. Interacef. Sci.*, **1991**, 145, 260-269.

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

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

2 Porous materials

One of the most useful and widely used applications of high internal phase emulsions is as template for the preparation of highly porous materials, so-called polyHIPEs.[35,36] Usually, preparation procedure of macroporous polymers is performed by the bulk polymerisation (radical polymerisation or condensation) in the presence of the pore producing solvents or via polymerisation in solution.[37] By this polymerisation procedure porous polymer up to 65% of porosity can be prepared. Another way to produce highly porous polymers (more than 74.05%) is the polymerisation of continuous phase or both phases of a high internal phase emulsions (HIPEs).

PolyHIPE monoliths. Characteristic polyHIPE monoliths incurred as a result of continuous phase polymerisation around the droplets of the dispersed phase of HIPE. 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.[38] Mixing is followed by polymerisation of continuous phase, which depends upon the initiation system used; thermal, redox, catalytic, UV, or microwave induced initiation and is washed generally by Soxhlet extraction and vacuum dried.

Resulting polyHIPE material (Figure 4) posses open pore system, means that bigger pores (so-called cavities) which arise as a result of extraction of dispersed phase after the polymerisation of continuous phase are connected with smaller interconnecting pores (Figure 5). In some cases we can get a closed and isolated pore system which is largely depended on the amount of added surfactant during HIPE formation. Most probable theory of open cellular architecture formation states that the amount of surfactant added should exceed 7 vol. % according to monomer mixture. Increasing the proportion of surfactant causes the thinning of oil (monomer) layer between droplets and at some critical point of added surfactant the monomer layer becomes very thin. The polymer film which forms during the polymerisation of the continuous phase shrinks slightly because of monolith volume contraction and consecutively breaks between neighbouring former droplets to form interconnecting pores.[39] Another explanation is that interconnecting pores formation is a post

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[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**.

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

[37] (a) Svec F., Frechet J.M.J., Continuous rods of macroporous polymer as high-performance liquid chromatography separation media, *Anal.Chem.*, **1992**, 64, 820-822. (b) F.Svec, T.B.Tenikova, Z.Dely, *Monolithic Materials: Preparation, Properties, and Application, Elsevier, Amsterdam,* p.173, **2003**.

[38] 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.

[39] (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.

polymerisation process and are generated as a result of extraction and drying in vacuum.[40]

The open-cell structured monolithic polymers are characterized by low dry bulk density, less than 0.1 g cm^{-3}, which is due to complete interconnectivity between all neighbouring cavities and could be even lower, as low as 0.01 g cm^{-3}.[41] PolyHIPE materials posses large pore volume up to 10 cm^3/g and cavities size range from 5 to 100 µm. In spite of high porosity, the specific surface area of non-modified polyHIPE materials is relatively small, between 3-20 m^2/g. Modification in terms of increasing polyHIPEs surface area, is due to the addition of porogenic solvents into the continuous phase of HIPE during HIPE formation. Introducing the porogenic solvents during the synthesis of polyHIPE materials affect the formation of secondary pores in polymer matrix due to the phase separation in polymer matrix during the polymerisation and can yield materials with up to 720 m^2/g.[42]. Even extremely high surface areas can be achieved through hyper-crosslinking of the material which is a post-polymerisation process and results in materials with surface area up to 1100 m^2/g.[43]

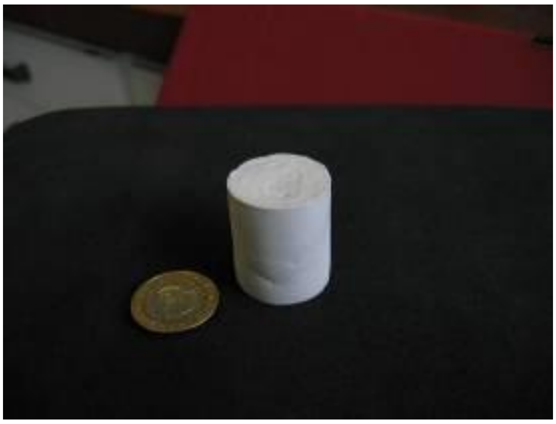

Figure 4. *Photograph image of polyHIPE monolith*

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. Beside styrene/DVB based polyHIPEs, examples of W/O derived polyHIPEs from 4-vinylbenzyl chloride (VBC),[44] aryl

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acrylates,[45] glycidyl methacrylate (GMA)[46] and propylene fumarate[47] were prepared. While W/O HIPE morphologies and related chemistries are well researched, also O/W HIPEs was used to prepare monolithic polyHIPE materials with various chemistries including acrylic acid (AA),[48] polysaccharide,[49] 2-hydroxyethyl methacrylate (HEMA),[50] or *N* -isopropyl acrylamide (NIPAM).[51]

In spite of different kind of chemistries used in polyHIPE preparation, a number of reactions have been employed for surface functionalization. The system which is very well known and has been extensively studied involves Styrene/DVB chemistry. For that purpose it was often used for chemical modification or functionalization in order to fulfil a particular application. It was functionalized with a wide variety of functional groups such as sulfonic groups,[52] nitro groups and halogens.[53] It was also used as

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supports for reactions in batch-mode or flow-through set-up,[54] as supports for initiators,[55] as filtration media,[56] supports for peptide synthesis,[57] as absorbents in aqueous media,[58] as matrixes for tissue engineering,[59] supports for human neuritis growth,[60] and as microbioreactors in flow-through mode.[61]

Surface functionalization was carried out on monoliths as well as grinded materials in batch mode or in flow-through set-ups. Flow-through techniques have many advantages over conventional batch-mode systems. Some of them are continuous production of desired products, high reactivity, use of automated synthesis and, most importantly, easy separation of the supported and non-supported species at the end of reaction.[62]

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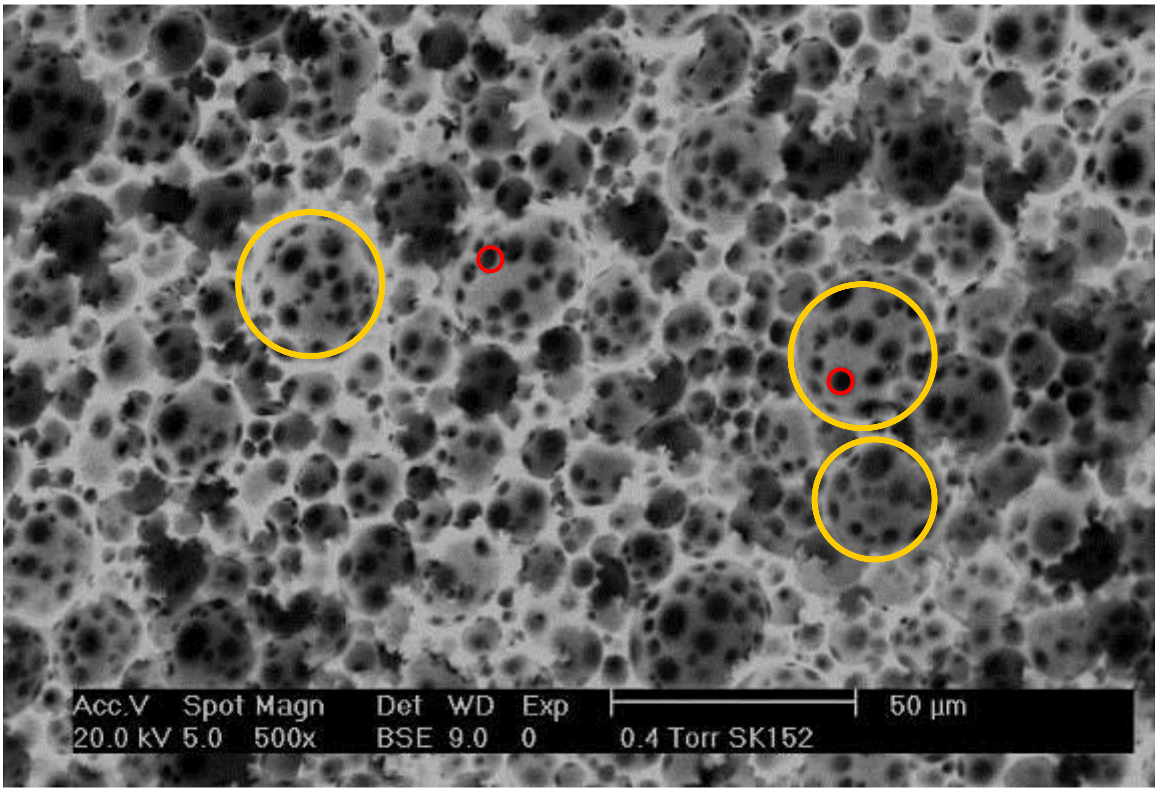

Figure 5. *SEM image of acrylamide polyHIPE material with typical cavities (yellow circles)-interconnecting pores (red circles) architecture*

Preparation of polyHIPE columns (Figure 6) by 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 scavengers,[63] reagents[77] and chromatographic supports.

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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 mechanical behavior of polyHIPEs is measurement of materials tensile strength which depends on the elasticity modulus (Young's modulus)

$$F/S = E\cdot \Delta L/L_0 \qquad \text{Equation 9}$$

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,[64] while Bismarck's group prepared composite polyHIPEs with Young's modulus up to 200MPa.

PolyHIPE beads possess permanent porosity but are mechanically fragile. Inspite of this mechanically drawback, porous polymer beads are used in wide range of applications, such as stationary phase in separations,[65,66] supports in solid phase

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organic and peptide synthesis,[67] as ion-exchanged resins,[68] scavengers[69] and supports for catalysts immobilisation.[70]

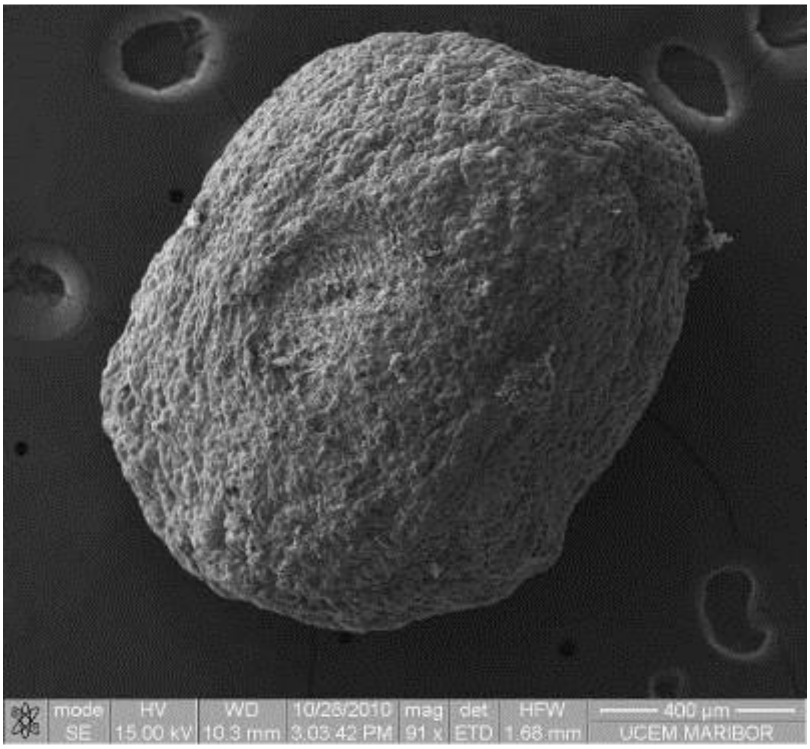

Figure 7. *SEM image of the polyHIPE beads*

Porous beads are mostly prepared by suspension polymerisation of monomer droplets which contains porogenic solvents and are suspended in second continuous phase where they are polymerized.[71] An alternative strategy which yields polyHIPE beads (Figure 7) with porosity up to 90 % is a dispersion of HIPE into the third medium (forming W/O/W or O/W/O three phase systems or double emulsion) where they are subsequently solidified by polymerisation.[72] After Li and Benson patented the preparation procedure in 1998 not much research has been done on polyHIPE

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beads, probably because of emulsion instability during formation. Later on there have been several attempts to introduce functional groups to polyHIPE beads by copolymerisation of functional monomers with styrene and DVB or by grafting the functionalized macromolecular chain on the walls of previously prepared polyHIPE beads.[73] Functionalities were also introduced by post-polymerisation functionalization of polyHIPE beads surface by different chemistries.[74]

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

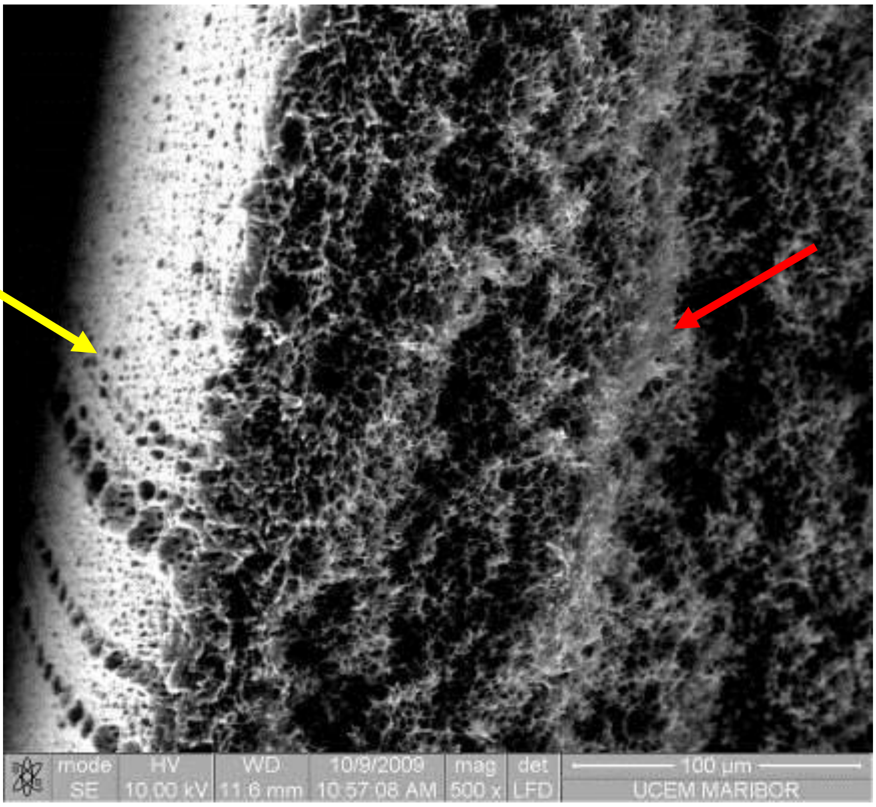

Figure 8. *Surface and interior of the polyHIPE membrane; red arrow pointed to the interior of membrane, yellow arrow pointed to the surface*

In 1989 Ruckenstein reported preparation of composite styrene/acrylamide polymeric membranes by emulsion templating for separation of mixtures of different solvents.[75] The syntheses of functionalized polyHIPE membranes of thickness between 100-200

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µm for ion selectivity were reported by group of Cameron.[76] Even thinner functionalized membranes with thicknesses of 30 µm were prepared where flexibility was tuned by different crosslinking degree and addition of plasticizer ethylhexyl acrylate (EHA).[77] Through-open polyHIPE membranes, (without the surface skin) which were difficult to obtain in the case of radical polymerized membranes, were synthesized by ring opening metathesis polymerisation (ROMP) of dicyclopentadiene (Figure 8).[78]

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Julia Wappel, Christian Slugovc

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polyHIPE Beads

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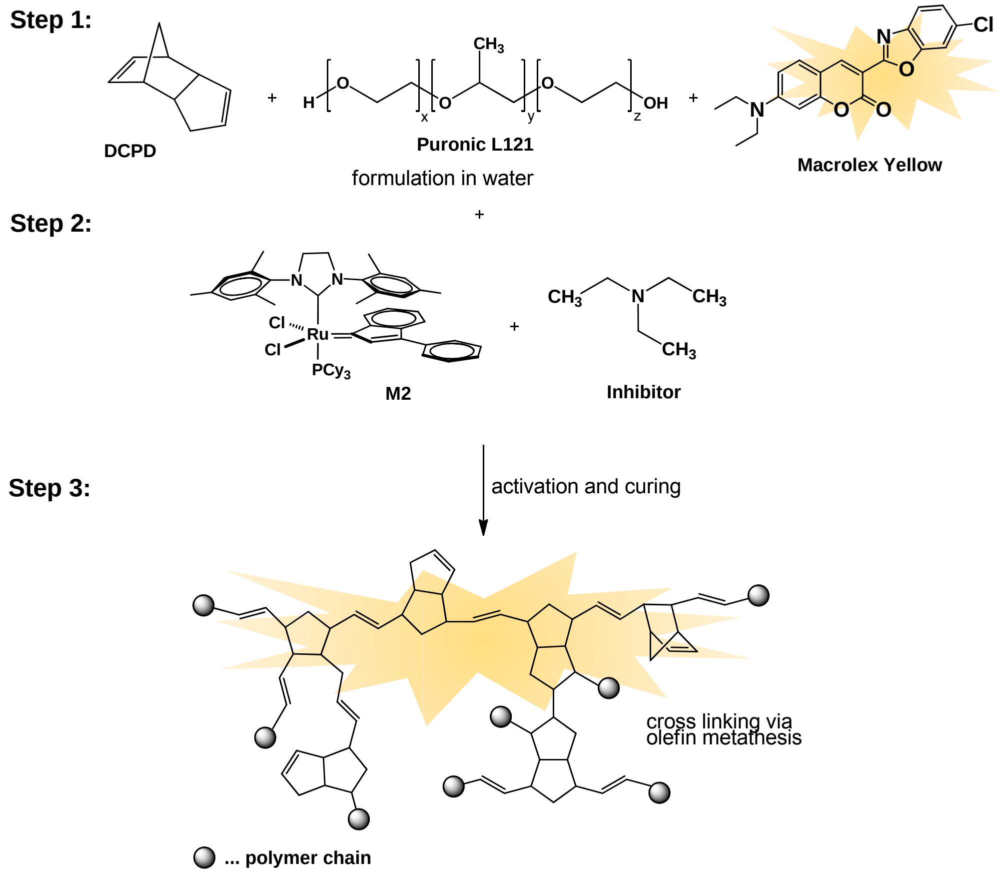

Durchführung:

Herstellung der high internal phase emusion (HIPE) mit einer Porosität von 70%:

4 mL DCPD werden mit 15 w% Tensid, Wasser und einer Spatelspitze Farbstoff (Macrolex Yellow) versetzt und anschließend für 20 min bei 400 rpm gerührt.

Berechnung der Porosität:

$$\Phi = \frac{m_{H2O}}{m_{H2O} + m_{DCPD} + m_{Tol}}$$

Zugabe des Initiators:

Als Initiator wird ein für die Olefin Metathese geeigneter Ruthenium Komplex (**M2**) verwendet. Das Verhältnis Monomer zu Initiator (M:**I**) beträgt 6000, wobei die Zugabe von 300 eq. Et_3N eine sofortige Initiierung inhibiert und nur optional nach Anweisung der BetreuerInnen zugesetzt wird.

Herstellung der Beads oder einer Membran und deren Aushärtung:

Die so hergestellte Emulsion wird unter ständiger Rührung entweder in heißes Wasser getropft, oder auf ein Substrat aufgerakelt und anschließend im Trockenschrank ausgehärtet.
[Eine etwaige Inhibierung des Initiators wird durch verschiedene Methoden (näheres dazu im Praktikum) aufgehoben].

Auswertung:

Der Einfluss der Polymerisationsparameter auf die Eigenschaften (Form, Größe,…) der Beads soll untersucht werden. Desweiteren werden die Struktureigenschaften der polyHIPEs mit Hilfe des Farbstoffs charakterisiert. Zur Verwendung der Membran gibt es mündliche Information.

Substanzdaten:

DCPD
MG: 132,20 g/mol, d = 0,979 g/mL, farbloser bis gelblicher Feststoff mit campherähnlichem Geruch, mp: 33°C, bp: 170°C, praktisch unlöslich in Wasser

Pluronic L121
MG: ~4.400 g/mol, PEG-PPG-PEG, HLB-Faktor: 1-7

Umicore M2
MG: 949,09 g/mol

Triethylamin
MG:101,19 g/mol, farblose bis gelbliche, ölige, brennbare Flüssigkeit mit fischartigem Geruch, mp: −115,0°C, bp: 89°C

Toluol
MG: 92,14 g/mol, d = 0,87 g/mL

Macrolex Yellow
MG: 368.81 g/mol, Coumarin-Farbstoff

Tabelle 1. Löslichkeit von Macrolex Yellow in g/L bei einer Temperatur von 23°C

Wasser	Aceton	Ethanol	Methylenchlorid
unlöslich	2,5	0,4	70