

Diblock and graft copolymers of n-butyl acrylate (nBA) and tert-butyl acrylate (tBA) of different chemical compositions have been synthesized and characterized by 2D chromatography. Amphiphilic block and graft copolymers with poly(acrylic acid) segments were obtained by hydrolysis of the tert-butyl groups. The influence of the topology on the aggregation behaviour in aqueous solution was investigated. Micellar structures of this type find manifold applications, e.g. in cosmetics. As these systems can be switched reversibly, it would be possible to use them as drug carriers. The active substance could be included into the micellar core and liberated depending on the pH value.

Controlled radical polymerization (ATRP) was applied for the synthesis of the block and graft copolymers. The synthesis of the block copolymers was performed by sequential addition of tBA and nBA. The synthesis of the graft copolymers was achieved by the macromonomer method. In this process the PtBA macromonomers were obtained via a new synthetic route in a two-step reaction. The high degree of functionalization of the products was confirmed by HPLC under critical conditions (LACCC). The copolymerization of the synthesized macromonomers with the comonomer nBA required a special purification technique in order to obtain high conversions. In this context, the influence of different factors, such as solvent, temperature, catalyst, and ligand, on the polymerization behaviour have been investigated in order to obtain well-defined products. For this purpose, the chain length of the backbone is kept constant by adjusting the monomer-to-initiator ratio, while the spacing of the side chains is varied. The obtained products were characterized by 2D chromatography. The results show a broad chemical distribution of the polymers, which should also have an impact on their behaviour in aqueous solution.

Acid hydrolysis of the PtBA segments of the block and graft copolymers resulted in a degree of hydrolysis of > 95 %. Dynamic light scattering in water (0.17 M NaCl solution) at a pH = 10 showed that only PnBA-g-PAA graft copolymers with an acrylic acid content of 26 mol-% form micelles. A small portion of these copolymers dissolves as unimers due to the broad chemical distribution. All copolymers with an acrylic acid content $x_{AA} \geq 47$ mol-% mainly exist as unimers under these conditions. For all structures, a portion of one weight percent of macroaggregates was proven, which is in agreement with the results of asymmetric flow field-flow fractionation (AF-FFF) and small-angle neutron scattering (SANS). The presence of these species was also confirmed by freeze-fracture transmission electron microscopy.

SANS measurements showed a strong pH dependence of the aggregation behaviour. Block and graft copolymers with an acrylic acid content $x_{AA} \geq 47$ mol-% virtually only exist as unimers in solution at pH = 8 - 10. Only at pH = 6, significant changes occur due to the different topology. Under these conditions, the block copolymers have already aggregated ($Z \sim 20$), while the graft copolymers exist primarily as dimers. In order to explain this phenomenon, the ratio of the surface charge to the volume of the particles has to be considered. While the hydrophilic blocks of the block copolymers immerse considerably in the solvent, the same amount of charges is distributed over several short side chains in the

graft copolymers. Therefore, a higher charge density at the micellar core results in the latter case. For this reason, a stabilization of the unpolar backbone is possible in these structures through the formation of smaller aggregates. Thus, the topology significantly influences the aggregation behaviour; the graft copolymers only form micelles at a pH being approximately one unit lower compared to the block copolymers of similar composition. The model of polydisperse spheres at low pH assumed from the SANS measurements was confirmed by investigating the aggregation behaviour by freeze-fracture- and cryo-TEM. Aggregation numbers similar to the results of the neutron scattering experiments were calculated. Furthermore, AFM measurements showed that both normal and inverse micelles could be deposited on a silicon wafer from aqueous and toluene solution, respectively.

In order to investigate the shear thinning behaviour, „inverse“ graft copolymers (PAA-g-PnBA) were synthesized with a hydrophilic backbone and hydrophobic side chains. The dependence of solution viscosity on the shear rate was investigated. In the range measured ($0.05 \leq \dot{\gamma} \leq 70 \text{ s}^{-1}$), the graft copolymer with a content of hydrophobic PnBA side chains of 20 mol-% shows a Newtonian behaviour throughout the whole range, whereas the graft copolymer with 40 mol-% of hydrophobic side chains shows a shear thinning behaviour. The viscosity behaviour of such structures is therefore significantly determined by the degree of hydrophobic interactions, which increases with an increasing number of hydrophobic side chains. The pseudo-plastic behaviour was examined at varying polymer concentrations. It was observed that all viscosity curves show a similar slope in the non-Newtonian region. According to the Cross equation, the same material constant results, i.e., the system shows the same interaction strength independent of the polymer concentration. On the other hand, the viscosity curves show different slopes in the non-Newtonian region by varying pH. These different interactions are ascribed to a variable solution behaviour of the backbone.

In cooperation with the group of Prof. B. Charleux (Paris), the PnBA-g-PAA graft copolymers were used as stabilizers in nitroxide-mediated radical mini-emulsion polymerization, and latices with a unimodal particle size distribution were synthesized. Under the given reaction conditions, a good reaction control was only achieved with polymeric dispersants. Higher monomer conversions were obtained while the polymerization with the low-molecular surfactant Dowfax 8390 was terminated at low conversions. If identical reaction parameters are used, only the graft copolymer with the highest content of acrylic acid ($x_{AA} = 79 \text{ mol-}\%$) yields monodisperse particles.