
Abstracts

Classical bulk temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels were prepared *via* free radical polymerization in the presence of *N,N'*-methylenebisacrylamide (MBAAm) as a crosslinker. Two different initiation methods were studied: redox and photoinitiation. It was demonstrated that the desired final properties of resulting hydrogels, i.e., high monomer conversion and adjustable swelling were only achieved by selecting best suited initiation conditions. For redox polymerization, this was done by tuning the ratio of accelerator *N,N,N',N'*-tetramethylethylenediamine to initiator ammonium persulfate. The key parameters for achieving optimum photopolymerization conditions were photoinitiator concentration and UV irradiation time. With the help of *in situ* rheological measurements, optimum conditions could be further verified and quantified by monitoring the liquid-to-gel transition. Overall, photoinitiated crosslinking copolymerization was postulated to offer better options for *in situ* preparation of tailored functional hydrogels. Therefore the classical photopolymerized bulk PNIPAAm hydrogels were characterized in more details (swelling and mesh size, swelling recovery, volume expansion factor relative to synthesis state, morphology and partitioning of test solutes) as compared to redox hydrogels (swelling and mesh size). Rheology was also used to investigate the hydrogel after *ex situ* preparation, revealing “perfect” soft-rubbery behaviour. A good correlation between the mesh sizes determined from swelling and rheology was also found. Rheology has been found to be a powerful tool because it provides valuable data on polymerization and gelation kinetics as well as information about the hydrogels microstructure based on their viscoelastic character. The resulting optimum conditions from this part were utilized towards preparation and characterization of smart hydrogels that can respond to multiple stimuli and also functional pore-filling composite membranes.

Temperature-responsive PNIPAAm hydrogels were imprinted with lysozyme *via in situ* photoinitiated crosslinking copolymerization. The three-dimensional network of the hydrogels was tailored by tuning the ionic content through methacrylic acid (MAA) as template-binding comonomer while keeping the ratio between crosslinker (MBAAm) and *N*-isopropylacrylamide (NIPAAm) fixed. The rheological data demonstrated that the onset of gelation was delayed with increasing MAA content. Moderate salt concentrations (0.3 M NaCl) were found to be suited for template removal without phase separation of the hydrogel. Swelling and protein (lysozyme and cytochrome C) binding were investigated for molecularly imprinted (MIP) and non-imprinted polymers (NIP) gels at temperatures below and above the lower critical solution temperature of PNIPAAm (32 °C). MIP gels showed a much higher affinity, selectivity and binding capacity for lysozyme compared to the NIP reference materials. Protein binding capacity was strongly reduced above 32 °C, to zero for NIP and to small values for imprinted gels. Most important, specific lysozyme binding to the MIP gels caused a large concentration dependent deswelling. This effect was much smaller for NIP gels, and the response could be

modulated by the content of the comonomer methacrylic acid. It is envisioned that the alteration of swollen state of stimuli-responsive MIP hydrogels as functions of specific protein or temperature may govern the recognition-ability and binding-specificity towards establishment of novel biomimetic materials.

A copolymer of PNIPAAm and 4-vinylbenzo-18-crown-6 (vCE) was synthesized *via* redox-initiation polymerization. The influence of vCE content on the copolymerization efficiency and also on the ion-recognition properties was investigated. The copolymerization was relatively efficient in a more loosely crosslinked network (rheology and Fourier transform infrared analyses). The swelling of PNIPAAm-*co*-vCE at 37 °C was higher in the presence of cations; i.e. $\text{Ba}^{2+} > \text{K}^+$ than in pure water. The hydrogel copolymers were more sensitive at the higher ion concentration (0.02 M). The cation recognition and selectivity were further enhanced by the increase of vCE content in the hydrogel copolymers. Overall, this approach is interesting for the development of novel sensors or materials for controlled release applications.

Hydrogel pore-filled composite membranes (HPFCM) based on polyethylene terephthalate (PET) track-etched membranes with pore diameters between 200 and 5000 nm and temperature-responsive PNIPAAm hydrogels were successfully prepared. A prefunctionalization of the pore walls by grafted linear PNIPAAm lead to stable anchoring of crosslinked PNIPAAm prepared in a subsequent step. Proper tuning of photopolymerization conditions resulted in desired microstructure of the hydrogels and thus tailored barrier properties of the composite membranes. The very interesting separation performance of HPFCM was due to diversification of the hydrogel network as function of its composition that caused adjustable sieving properties *via* synthesis conditions and also largely switchable barrier properties in response to the temperature. The interplay between the immobilized hydrogel and various pore sizes of the membrane support was also investigated. The base membrane provides mechanical support and confines the hydrogel within its pores, and it thus allows using the hydrogel mesh size for size-selective solute transport. Completely stable and selective HPFCM were only obtained with base pore sizes of about 2 μm or smaller. The size-selectivity (molecular weight cut-off) of the same HPFCM was higher under diffusive than under convective flow conditions; this is presumably mainly caused by elastic deformation of the hydrogel network. The cut-off from diffusion experiments was well correlated to mesh-size of the hydrogel determined from the Darcy model applied to permeability data obtained under convective flow conditions. Upon temperature increase beyond 32 °C, flux increased and rejection decreased very strongly; this remarkable change between macromolecule-size selective ultrafiltration and microfiltration/filtration behaviour was fully reversible. The smart performance of HPFCM could be interesting for the separation of multi-component mixtures or for controlled release due to the tunability of the sieving coefficient by changing the temperature.