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THERMOSENSITIVE POLYMER GELS – FROM THE THEORY TO THE APPLICATION

PhD theses

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Introduction and aims

Development of the so-called “functional materials” was initiated by the needs of new structural materials and rather special industrial expectations and aims. One of the challenging tasks is to manufacture and characterize new multifunctional materials possessing “intelligence” at the material level. Several scientists focus their attentions on polymer gels.

Polymer gels are cross-linked polymeric networks which swell by imbibing into a high affinity solvent. These gels are unique multifunctional materials for their capability of responding to several environmental stimuli, e.g., temperature, pH, solvent composition or electrical stimuli, etc. Not only the volume of the gel but related properties, like mechanical and optical characteristics may also change as a consequence of the stimulus.

These interesting characteristics of polymer gels may be used in a variety of applications, for instance, in controlled drug release, in molecular separation processes, for tissue culture or as artificial muscles, etc. There are several possible technical applications, like valves, selective absorbers, sensors, actuators, interfaces or large area displays.

The main aim of my PhD work was to modify the volume phase transition temperature of poly(N-isopropylacrylamide) hydrogel (34 °C) and to study the optical properties as a function of temperature. Temperature sensitive polymer gels and interpenetration networks were synthesized, which show a reduced volume change at their phase transition due to the temperature dependent interaction between the polymer network and the swelling agent. Alternative polymer gel systems were also prepared. In these systems the phase transition and thus the change of optical properties occur within the swelling agent. The thermal properties of poly(2-acrylamido-2-methylpropylsulfonic acid) gels were also studied.

The thermal properties, particularly the temperature induced volume phase transition, of the gels were characterized by cloud point measurements, differential scanning calorimetry (DSC), stress-strain measurements (unidirectional compressing) and swelling degree measurements.

Scientific results

1. Swelling degree and compressive elastic modulus (G) of poly (2-acrylamido-2-methylpropylsulfonic acid) polyelectrolyte gels [PAMPS] were studied in distilled water as a function of temperature (T) at several [monomer]/[cross-linker] ratio. At each [monomer]/[cross-linker] ratio, a linear relationship was found between the G/RT and the equilibrium polymer concentration (ϕ_e).

2. Swelling degree and compressive elastic modulus (G) of poly (2-acrylamido-2-methylpropylsulfonic acid) polyelectrolyte gels [PAMPS] were studied in distilled water as a function of [monomer]/[cross-linker] ratio at several temperatures. At each temperature, the power law of swollen gels ($G \propto \phi_e^m$) was found to be valid. However, the value of the exponent, m=1.1-1.3, was smaller than that of the neutral polymer gels in good solvent (m=2.25), as well as the theoretical minimum of m for polyelectrolyte gels (m=1.5).

3. Phase transition temperatures of poly(N-isopropylacrylamide) [PNIPAAm] based polymer gels were changed in wide temperature interval. The chemical structure of PNIPAAm network was modified by copolymerization with acrylamide [AAm]. The cloud point temperature was controlled between 34 °C and 68 °C. The cloud point temperature of P(NIPAAm-co-AAm) polymer gels, equilibrated with water at 27 °C, was controlled between 22.5 and 68 °C by modifying the NaCl content of the swelling agent.

4. Phase transition temperature of poly(methyl vinyl ether) [PMVE] – water mixture embedded in poly(vinyl alcohol) [PVA] hydrogel was influenced in wide temperature interval by modifying the composition of the swelling agent. The cloud point temperature of the PMVE (M_w≈46000) – distilled water mixture (mass ratio 1.5:98.5) is 35.1 °C. Addition of tetrabutylammonium bromide results in a significant increase in the transition temperature, up to 58 °C, while increasing the NaCl content of the swelling agent decreases the cloud point temperature to 25 °C.

5. Temperature sensitive PVA/PNIPAAm interpenetration networks [IPN] were prepared by a one-pot two-step method. The two steps of polymerization were separated definitely in time.
   Temperature sensitive PVA/PNIPAAm-co-AAm) and PVA/ PNIPAAm-co-AMPS) IPNs were prepared by the two-step method.

6. PVA/PNIPAAm IPNs were equilibrated in water at a given temperature. After this, the compression elastic modulus was studied as a function of temperature. At the phase transition temperature of PNIPAAm, the elastic modulus showed an abrupt increase without a macroscopic volume change of the IPNs.

7. Studies of the swelling properties of the PVA/P(NIPAAm-co-AAm) and the PVA/P(NIPAAm-co-AMPS) IPNs showed that in several cases the volume phase transition of these IPNs was not followed by significant macroscopic shrinking, moreover, in certain cases the IPNs showed positive swelling behavior within the temperature range studied.

8. Based on the differential scanning calorimetry (DSC) measurements, a linear dependence was found between the volume phase transition enthalpies and volume phase transition temperatures of P(NIPAAm-co-X) in PVA/P(NIPAAm-co-X) IPNs. In the systems studied the enthalpy of the volume phase transition does not depend on the chemical composition but on the volume phase transition temperature.

9. Electrically adjustable thermotropic windows were manufactured based on PVA/PMVE semi-IPNs and PNIPAAm hydrogels. The influence of frequency and voltage as well as the shape of the audio frequency AC current signal (sine and square) were investigated. At the phase transition temperature the resistance of PNIPAAm gel has increased more than one order of magnitude due to the formation of a collapsed skin layer.

Possible technical applications

I succeeded in constructing an intelligent gel-glass that is able to moderate the amount of transmitted light and radiated heat. This environment sensitive glass, which is composed of a smart hydrogel layer placed between two glass or plastic sheets, becomes opaque when the temperature exceeds a critical value. It becomes transparent again if it is cooled down. The adaptive properties of gel-glasses make them promising materials in protection from strong sunlight and heat radiation. Based on the phase transition of polymer gels, a novel electrically adjustable window was also developed. These windows substantially reduce glare and thus increase the thermal and visual comfort. Another promising area is their application in greenhouses and hot water supplies for optical and thermal control. These materials are also good candidates for large displays.

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