Flow-induced deformation of microcapsules

Abstract The radical polymerization of surface-active aminomethacrylates can be used to synthesize ultrathin crosslinked membranes at the interface between oil and water. We have systematically measured the kinetics of the surface gelation and the rheological properties of the stabilized films. The membranes, thus prepared, exhibit striking rubber-elastic properties. These are ideal conditions for the formation of a new type of microcapsule. In a series of experiments we have investigated the influence of the membrane elasticity on the shear-induced deformation of these artificial cells.

Key words Ultrathin films – surface polymerization – surface rheology – microcapsules – shear induced deformation

Introduction

Ultrathin membranes are interesting model systems for numerous applications in industry and science. In former investigations, we have used the photopolymerization of surface active methacrylate diesters, in order to synthesize these structures at the interface between oil and water [1]. It turns out that these crosslinked films are very well characterized in respect to their rheological properties, but due to the rather long polymerization times of about 20 h, it is rather difficult to synthesize microcapsules with these techniques. A more successful way of forming artificial cells is based on a combined redox- and radical reaction which is induced by the addition of Ce$^{4+}$-salts to aminomethacrylates. Starting point of this polymerization are surface active methacrylate diesters, which are strongly adsorbed at the interface between oil and water. A typical molecule, showing this type of behavior, is N,N-bis-(2-methacryloyloxyethyl)-hexadecylamine. This compound is soluble in dodecane, but quasi insoluble in polar liquids like water. Due to the discrepancy between the hydrophilic oxygen atoms and the hydrophobic paraffin chains these molecules are strongly adsorbed at the interface between oil and water.

At the present state, the exact mechanism of the Ce$^{4+}$-polymerization seems still to be unknown. As alcohols are often used to form radicals with cerium salts, we first tested this type of reaction, but we did not get polymerized films with this technique [2]. With aminomethacrylates, however, a spontaneous gelation process sets in. In analogy to three-dimensional polymerizations, there might be an initiation process of the following type:
As Ce$^{4+}$-ions do not react with pure methacrylates, we suppose that the radical is formed at the nitrogen atom. In this way, the monomers might be transformed to charged radicals, which can polymerize by further reaction steps with double bonds of the metacrylic groups. As the crosslinking process occurs within a few minutes, it is easy to form microcapsules using this polymerization technique.

**Experimental part**

The monomers were synthesized by reacting N,N-bis(2-hydroxyethyl)-hexadecylamine with methacrylic acid in tetrahydrofuran after addition of small amounts of dicyclohexylcarbodiimide. The molecules were purified by medium pressure liquid chromatography (MPLC). As solvents we used dodecane and water, which were carefully purified and stored under argon atmosphere. The water was twice distilled over potassium permanganate and kept under argon.

Microcapsules were prepared by the interfacial polymerization of oil droplets which are suspended in water. The chemical reactions are identical compared to that of the planar interface.

The rheological measurements were carried out in different types of surface rheometers, which are explained in detail in ref. [1]. The microcapsules were observed in a rheoscope, which is schematically shown in Fig. 2.

**Experimental results**

The kinetics of surface gelation were detected by measuring the two-dimensional storage modulus $G'$ as a function of the reaction time (time sweep). In these experiments, a sinusoidal deformation with small amplitude is applied to the sample at a constant angular velocity $\omega$. As the two-dimensional shear modulus does not depend on the frequency, the data describe the formation of cross-linking points as a function of time. A typical curve, showing such data, is given in Fig. 3.

It is evident that the polymerization proceeds rapidly with time constants of the order of a few minutes. In contrast to crosslinking reactions initiated by UV-irradiation the kinetics are very fast. It is interesting to note that the crosslinked network structure exhibits rubber-elastic properties. Figure 4 gives some insight into the dynamic features of these membranes.