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ORIGINAL CONTRIBUTION

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Synthesis of spherical microcapsules by photopolymerization in aerosols

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Abstract The preparation of polymer microcapsules of well defined size in the range of 10–50 μm with different shell thickness to core diameter ratios is described. An aerosol of monodisperse droplets of a homogeneous ternary liquid system which contained a hydrophobic component and a hydrophilic component dissolved in a high-volatile mutual solvent, was produced by dispersing with a vibrating-orifice aerosol generator. After the evaporation of the solvent in a nitrogen atmosphere the particles demix and form a two-phase droplet of core-shell type. These droplets were illuminated with UV light and polymerized to highly monodisperse microcapsules with a solid polymer shell and a liquid core. The properties of the resulting particles (size, size distribution, shell thickness, shape and surface characteristics) were investigated by scanning electron microscopy, Raman spectroscopy on single optically levitated particles, and confocal Raman micro spectroscopy. The microcapsules were highly monodisperse and have spherical shape.

Key words Photopolymerization – vibrating orifice aerosol generator – core-shell particles – Raman spectroscopy – optical levitation – confocal micro Raman spectroscopy – microspheres

Introduction

Micrometer-sized particles have many applications in biomedical, biological, chemical and technical fields. The investigation of the preparation, characterization, and applications of core-shell particles has attracted increasing attention in the scientific community due to their interesting morphology and applications in various aspects. Generally monodisperse polymer particles with core-shell structures were prepared by seeded emulsion polymerization [1, 2]. Microcapsules are particles with core-shell structure with a polymer shell and a liquid core. Microcapsules with a stable shell can be prepared by interfacial polycondensation, interfacial polymerization or by an interfacial coacervation/crosslinking method. All methods include three main steps: e.g., production of oil containing poly(vinylalcohol) microcapsules prepared by the coacervation/crosslinking method includes the following steps [3]:

- dispersion of the oil phase in an aqueous poly(vinylalcohol) solution,
- addition of the electrolyte phase inducer (e.g., sodium sulfate), and
- crosslinking of the coacerved polymer membrane with glutaraldehyde.

The size, size distribution, shell thickness and morphology of the particles are determined by the experimental conditions, for example, type and concentration of the emulsifying agents, temperature, size and concentration of the colloidal polymer aggregates. Weatherley et al. [4]

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prepared nylon 610 capsules of controlled size by interfacial polymerization in a high-voltage electric field. The size of the particles was controlled by the size of the droplets, which were produced by electrostatic dispersion. The size distribution of these droplets depends very sensitively on the applied electrical field strength and is normally not very monodisperse.

Here we will present a technique for the preparation of monodisperse microcapsules with a solid polymer shell and a liquid core with the method of photopolymerization in two-component aerosols. In aerosols the size and the shell thickness of the particles can be predetermined by the diameter of the monomer droplets and the particles are free of additives, e.g., surfactants. Three methods are suitable for the preparation of two-component aerosols: charged aerosols, condensing one phase around another and ternary liquid systems [5]. The method of the ternary liquid system consisting of a hydrophilic and a hydrophobic component dissolved in a mutual solvent was used for the preparation of two-component aerosols.

Preparation of monodisperse polymer colloids in aerosols was first investigated by Matijevic and coworkers [6–8]. In our previous work we presented a study of preparation of monodisperse polymer particles by photopolymerization in aerosols [9]. The monomer droplets were produced with a vibrating-orifice aerosol generator and polymerized to polymer colloids. The resulting particles were highly monodisperse and spherical. Photopolymerization reactions on single levitated aerosol microparticles were followed online by Ward et al. [10] and Esen et al. [11].

Experimental

Materials

In our experiments we used as hydrophobic component an acrylic-based photocurable resin (SOMOS 3100 from DuPont), which is commonly used in laser stereolithography for the Rapid prototyping technique [12]. As hydrophilic component we used glycerol (86–88% p.a.) from Riedel de Häen. The two components were dissolved in ethanol. Ethanol (p.a.) was obtained by Baker. All chemicals were used without further purification.

Preparation of particles

A homogeneous mixture of the three components SOMOS 3100, glycerol and ethanol was dispersed with a vibrating-orifice aerosol generator [13], which was modified according to Lin et al. [14]. The size of the produced two-component droplets is given by

$$d = \sqrt[3]{\frac{6FC}{\pi f}} \tag{1}$$

where d is the droplet diameter, F the liquid flow rate, C the volumetric concentration of the aerosol substance in the solution, and f is the frequency of the vibrating orifice. After the evaporation of the solvent (ethanol) the remaining two components separate and form layered droplets. The core size and shell thickness were controlled by altering the volumetric ratio of the total SOMOS 3100 and glycerol in the solution droplets. The thickness of monomer layer is given by

$$s = 0.5d[1 - (1 + k)^{-1/3}] \tag{2}$$

where s is the shell thickness and k is the volume ratio of the monomer to glycerol. The polymerization reaction was induced by eight UV-light strip lamps (36 W, 120 cm in length, λ = 320–380 nm). The photopolymerization reaction of multiacrylate monomers follows the general scheme for classical free radical-initiated polymerization in three essential steps: initiation, propagation and termination. Because oxygen inhibits the polymerization the experiments were carried out in a nitrogen atmosphere.

Characterization

Electron microscopy

A scanning electron microscope (SEM), Cambridge Stereoscan 250 Mk 3, was used to examine the particles. The particles were placed on an aluminium sampleholder and were coated with a thin layer of gold (Bio-Rad SC 500, 20 mA, 4 min, Ar gas atmosphere). Particle size, shape and surface characteristics were estimated from SEM photographs. For the measurement of the shell thickness, the particles were cracked before the sample was coated with gold. The monodispersity of the particles was determined by measuring each hundred particles.

Raman spectroscopy

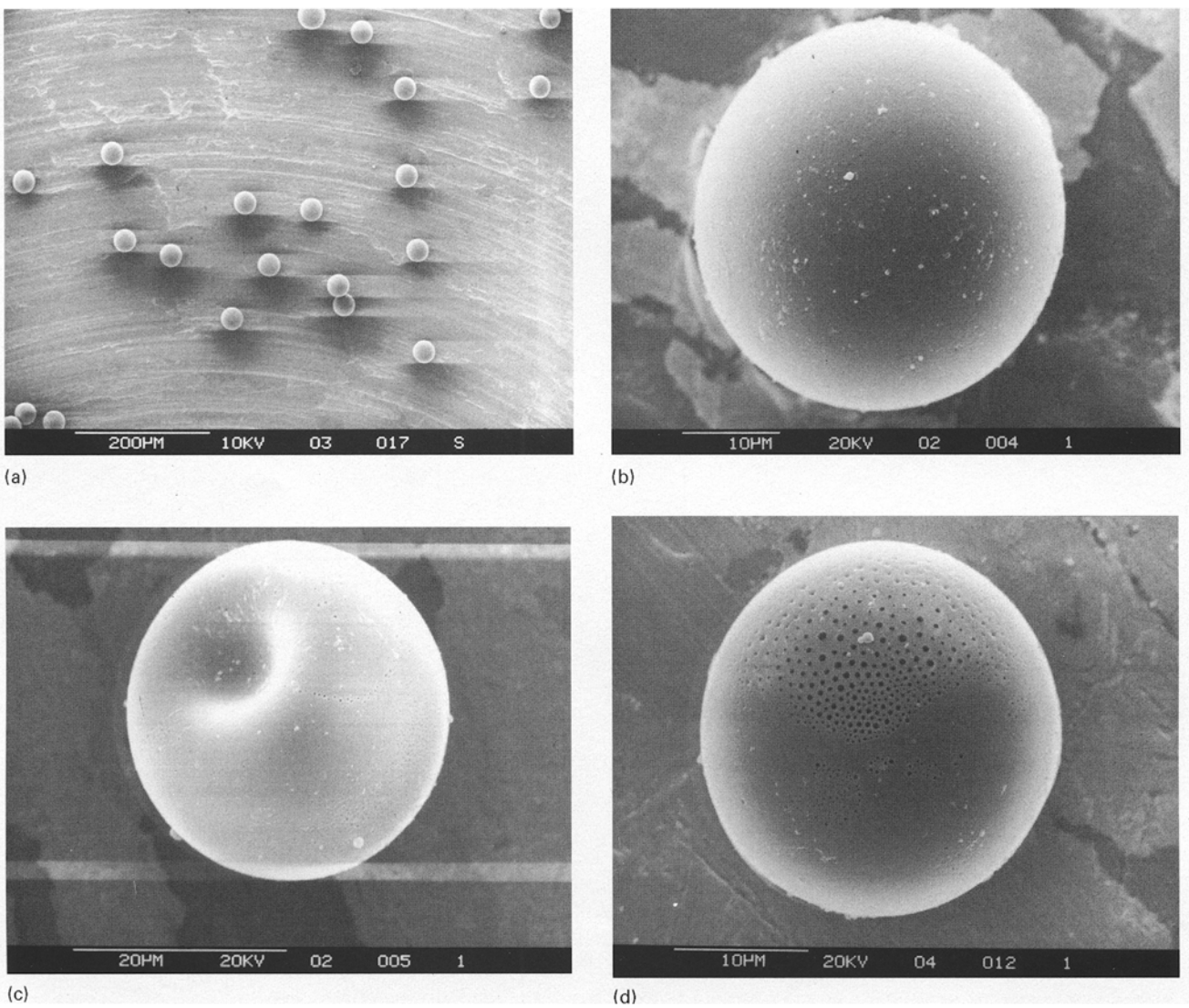
The experimental setup used for the Raman spectroscopic investigations on optically levitated single particles was described in detail elsewhere [15, 16]. Basically a vertically adjusted beam of an argon-ion laser (LEXEL 3000-5) is used for levitation of the microparticle and simultaneous excitation of the Raman scattering. The power of the laser was typically 1.0–1.5 W at a wavelength of λ = 514.5 nm. A feedback stabilization was realized to control the

position of the particle within several μm. The inelastic scattered light was recorded at a scattering angle of $\Theta = 90°$ and an aperture angle of $\Omega = 40°$. A triple Raman spectrometer (DILOR XY500) with an attached liquid-nitrogen cooled CCD-camera (Wright Instruments Ltd., 1152×298 Pixel) was used to record the Raman spectra. The spectral data were processed using specially developed software.

Confocal Raman micro spectroscopy

An argon-ion laser at a wavelength of $\lambda = 514.5$ nm (Spectra Physics 171) was used in a confocal 180 degree scattering geometry. A triple Raman spectrometer (DILOR XY800) with a confocal entrance optic which was equipped with a Nikon $40 \times$ SLWD microscope and a liquid-nitrogen cooled CCD-camera (Wright Instruments Ltd., 1152×770 Pixel) was used for the detection of the Raman-spectra. The solid microparticles were collected on a quartz sample holder and placed for positioning on an XYZ-stage. A single particle was placed in the focus of the laser beam. The laser power was typically 200–300 mW. The focus diameter of the laser beam was < 10 μm. Moving the microparticle with the manual stage in defined steps allowed recording of the Raman spectra at different volume elements along the axis of rotation of the microparticles.

Fig. 1 SEM-photographs of the microparticles produced by photopolymerization in the aerosol phase



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Results and discussion

Electron microscopy

Figures 1 and 2 show SEM photographs of particles prepared under different experimental conditions with the method described above. The particles are spherical and monodisperse (Fig. 1a). The percentage of multiplets (two or more agglomerated particles) was determined to be approximately 7%. The surface of the particles is normally smooth (Fig. 1b). In some cases, additional to smooth spheres, rather dent depression (Fig. 1c) or porous particles (Fig. 1d) could be observed. A reason could be that the shell-thickness is irregular and the evacuation for SEM leads to the dent depression and solvent which encapsulated in the glycerol-core diffuses to the particle surface, respectively. The shell thickness, which can be determined by Eq. (2), was measured on cracked microparticles (Fig. 2).

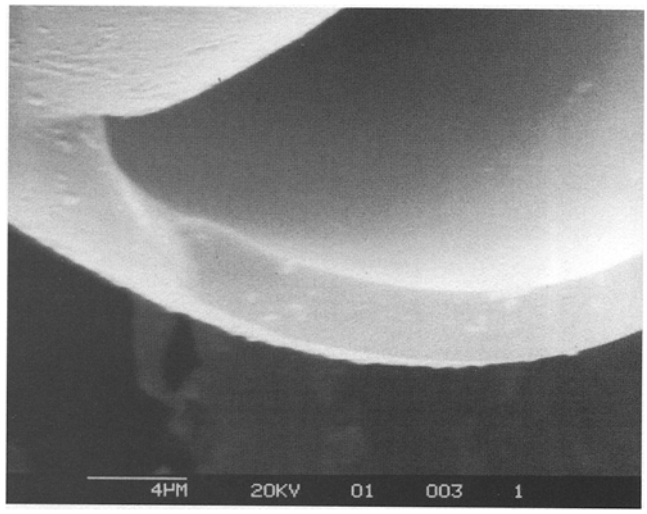

Fig. 2 SEM-photograph of a cracked microparticle

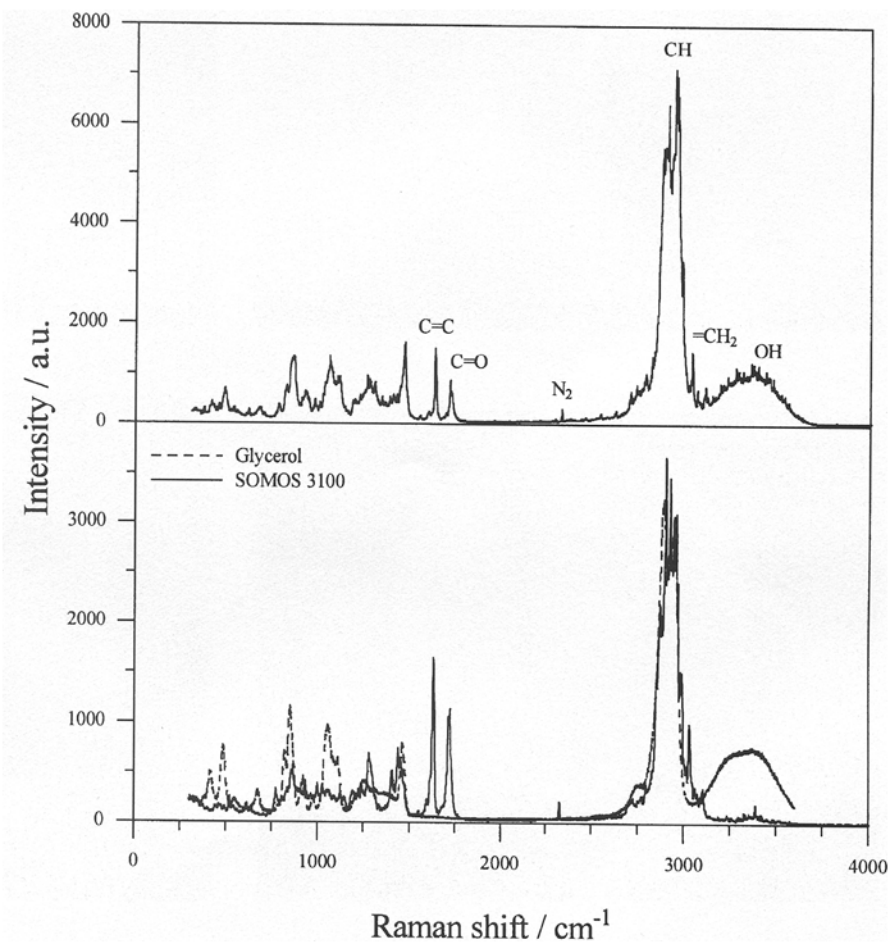

Fig. 3 Raman spectra of a two-component droplet consisting of SOMOS 3100 and glycerol (upper figure). The lower figure shows Raman spectra of glycerol measured in a cuvette and SOMOS 3100 measured on a single optically levitated droplet, respectively

Raman spectroscopy

A typical Raman spectrum of a single optically levitated SOMOS 3100 – glycerol particle is shown in Fig. 3. The volume ratio of SOMOS 3100 and glycerol in the droplet was approximately 1:2. The lower figure shows Raman spectra of SOMOS 3100 measured on a single optically levitated homogeneous particle and glycerol measured in a cuvette, respectively. The spectrum of SOMOS 3100 measured in a cuvette shows a high fluorescence background which can be suppressed by single microparticle analysis [16]. The spectrum of the two-component droplet shows all Raman bands observed in the spectra of the two individual components. The Raman bands of SOMOS 3100 are the C=C-vibration at a Raman shift of $\Delta\tilde{\nu} \approx 1640\ \mathrm{cm}^{-1}$, the C=O-vibration at $\Delta\tilde{\nu} \approx 1720\ \mathrm{cm}^{-1}$ and the $=CH_2$ valence bonding at $\Delta\tilde{\nu} \approx 3040\ \mathrm{cm}^{-1}$. The Raman band of glycerol is the OH-band between $\Delta\tilde{\nu} \approx 3100\ \mathrm{cm}^{-1}$ and $\Delta\tilde{\nu} \approx 3700\ \mathrm{cm}^{-1}$. All other bands between $\Delta\tilde{\nu} \approx 700\ \mathrm{cm}^{-1}$ and $\Delta\tilde{\nu} \approx 1500\ \mathrm{cm}^{-1}$ and the CH-stretching band between $\Delta\tilde{\nu} \approx 2800\ \mathrm{cm}^{-1}$ and $\Delta\tilde{\nu} \approx 3000\ \mathrm{cm}^{-1}$ are caused by both molecules. The spectrum indicates that the droplet contains both chemical species. The radial distribution of the two components inside the droplet

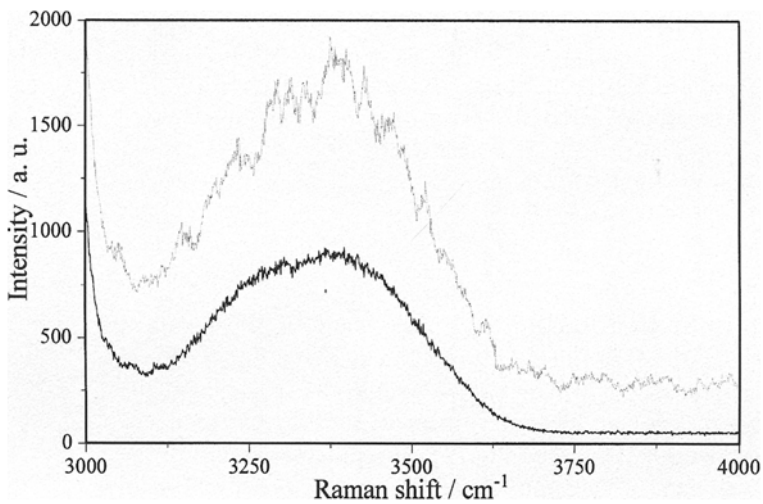

Fig. 4 Part of the Raman spectra of two-component particles measured on single optically levitated particles after the polymerization. The volume ratio of SOMOS 3100 and glycerol was approximately 1:2 (solid line) and 1:6 (dashed line)

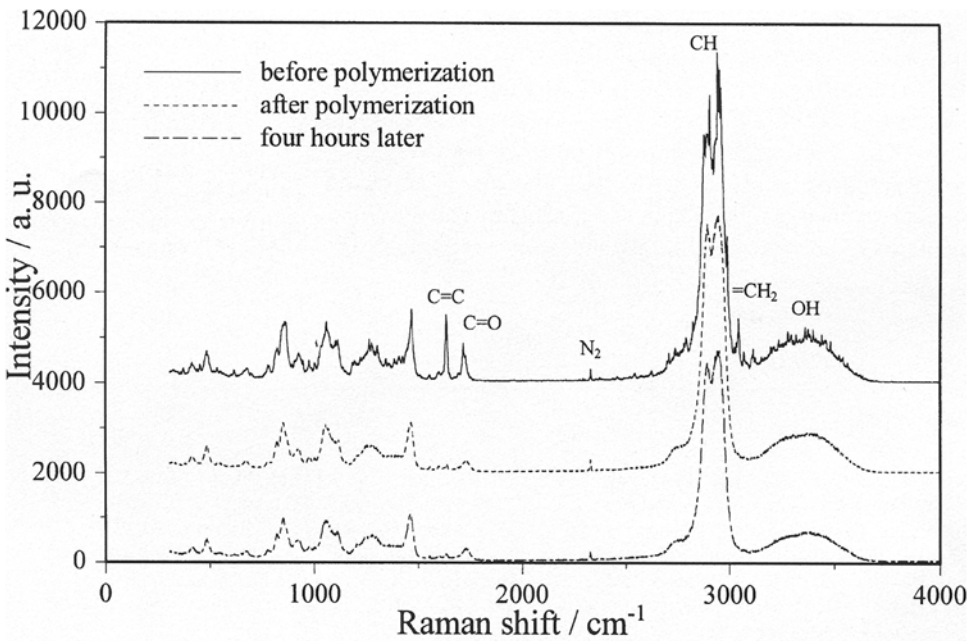

Fig. 5 Raman spectrum of a two-component particle before and after the polymerization reaction and 4 h later, respectively. The spectra before polymerization and after polymerization were shifted by adding a constant value of 4000 and 2000, respectively

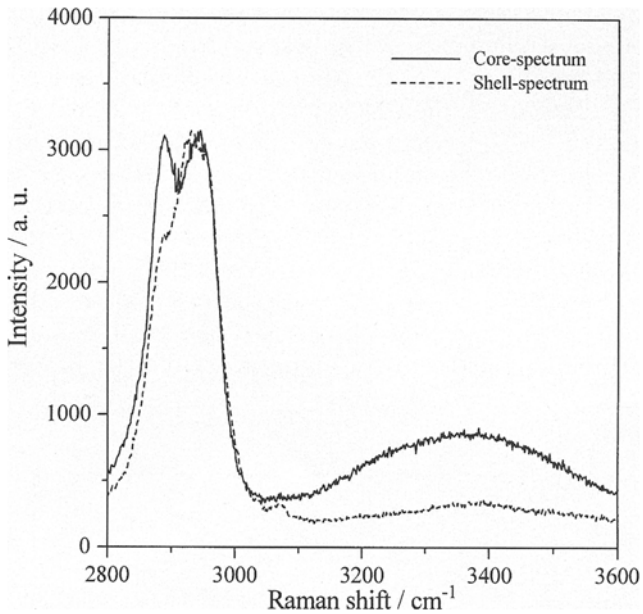

Fig. 6 Part of the Raman spectrum of a microparticle measured at two different radial positions

could be determined by time-dependent measurements of Raman spectra [17]. This method is based on structural resonances [18] which can be seen in the spectrum of the two-component droplet. Structural resonances can occur in the core and the shell [19]. The polymerization of the monomer, which can be monitored *in situ* by Raman spectroscopy [11] leads to a disappearance of the resonances. This effect is possibly caused by inhomogeneous polymerization of the optically levitated particle. By thin layers, e.g., 1 μm for a 20 μm particle structural resonances are superimposed on the spectral band shape, which can be assigned to core resonances (Fig. 4). Figure 5 shows the Raman spectrum of a two-component particle before and after the polymerization and 4 h later, respectively. The polymerization leads to a decrease in the C=C band intensity, which can be seen in the spectrum. The measurements have shown that the glycerol concentration is the same as that 4 h ago; a change in the OH-band intensity cannot be seen in the spectra. We can conclude that the glycerol is encapsulated in a nonpermeable polymer layer. A permeable layer would lead to a decrease in the intensity of the OH-band; e.g., in a droplet consisting of a glycerol core and a DOP-layer, after 400 s all of the glycerol molecules were evaporated [17].

Confocal Raman micro spectroscopy

Figure 6 shows the spectra of a microparticle, prepared by the method of photopolymerization in aerosols, at two different radial positions. The spectrum which was acquired at a radial position close to the surface of the particle shows Raman bands from the polymer. The spectrum at the center of the particle shows glycerol bands. These measurements show that the particles have a polymer shell and a glycerol core. A detailed spectroscopic analyses of layered particles is given elsewhere [20].

Conclusion

Glycerol-containing polymer microcapsules in the size range of 10–50 μm were prepared by photopolymerization of two-component aerosols. The size and shell-thickness of the particles were controlled by the volumetric ratio of the aerosol substance to the solution and monomer to glycerol, respectively. The structure of the resulting particles was investigated by scanning electron microscopy, Raman spectroscopy on single optically levitated particles and confocal Raman micro spectroscopy on single particles. The analyses of the particles proved that by the technique described in this paper highly monodisperse microcapsules can be generated.

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