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Investigation of heterogeneous radical polymerization of methyl methacrylate with polydimethylsiloxane as stabilizing agent in supercritical CO_2 by turbidimetry†

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Experimental results of a turbidimetric *in situ* investigation of the heterogeneous radical polymerization (dispersion polymerization) of methyl methacrylate and polydimethylsiloxane–monomethacrylate in supercritical carbon dioxide are presented. The experiments were carried out at 60 °C and 330 bar. Turbidity spectra were measured directly in the autoclave to determine the average particle diameter σ_τ and the particle density N_{AV}/V during the first five minutes of polymerization. The results show that the particle density increased until a maximum was achieved, whereas the particle diameter increased during the first stage. Moreover, a comparison with kinetic data suggests that the particles nucleate through coagulation of polymer that is formed in the homogeneous phase.

Keywords: turbidimetry; dispersion polymerization; methyl metharylate; supercritical carbon dioxide

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INTRODUCTION

The polymerization in supercritical carbon dioxide (sc-CO_2) has been investigated intensively in recent years with an emphasis on the preparative aspects. Sc-CO_2 is a very poor solvent for most polymers, hence, except some fluorinated polymers and polydimethylsiloxane (PDMS), they precipitate during polymerization.[1] A review of the results in this area is given by Canelas and DeSimone.[1]

Using amphiphilic CO_2-soluble surfactants, as has already been done in the polymerization of vinyl polymers,[1] well-defined particles can be synthesized. DeSimone and coworkers obtained narrow particle size distributions by adding polydimethylsiloxane–methacrylate macromonomer (PDMS—MA) to methyl methacrylate (MMA).[2] Depending on the reaction conditions, they observed particle diameters of 1–2 μm.

On the basis of experimental results and modeling of dispersion polymerization, two different mechanisms for particle formation have been assumed. First, the particle formation is completed very soon at low conversion (∼0.1%).[3] Second, a more elaborate mechanism takes into account the nucleation through aggregation that is combined with the coagulation of small nuclei and unstable aggregates to form larger stable particles.[3–5] Up to now, particle formation in heterogeneous polymerization has not been understood satisfactorily, and a quantitative investigation of the early stage of this process is needed to elucidate the mechanism. Turbidimetry allows a fast *in situ* determination of particle size at high particle number densities.[6] It is thereby possible to investigate dispersion polymerization of MMA at an early stage. In this communication we present the first results of our studies employing turbidimetry.

THEORY

If an incident light beam with intensity I_0 transmits

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through a polymer dispersion of path length l, it will be weaken to the intensity I_t because of light scattered from particles. In dispersion where not light is absorbed, the turbidity τ depends on the scattering intensity $I(\theta)$ of the particles:

$$\tau = 2\pi \int_0^{\pi} R(\theta) \sin\theta d\theta \qquad [1]$$

where $R(\theta)$ denotes the Rayleigh ratio. The experiments were performed at low particle number densities. Therefore, the effect of particle interaction on the turbidity can be neglected to a good approximation. The turbidity measured can be correlated directly to the particle number density N/V and the total scattering cross-section C_{SCA} of monodisperse particles:[6,7]

$$\tau = \frac{N}{V} C_{SCA} \propto \frac{N}{V} V_P^2 Q(\sigma_\tau, \lambda^2, m) \qquad [2]$$

where V_P is the particle volume, Q the integrated formfactor, σ the diameter of the particles and m denotes the relative refractive index of the particles (the ratio of the refractive of the particles n_P to the solution n_0). Knowing the relative refractive index m, the integrated formfactor Q can be calculated using Mie theory.[6] The ratio of two turbidities at two wavelengths is proportional to the ratio of the formfactors Q, and the particle size can be determined from the following relation:[8]

$$\frac{\tau(\lambda_1)}{\tau(\lambda_2)} = \frac{\left(\frac{m_1^2-1}{m_1^2+2}\right)^2 \left(\frac{n_{0,1}\pi}{\lambda_1}\right)^4 Q_M(\sigma, \lambda_1^2, m_1)}{\left(\frac{m_2^2-1}{m_2^2+2}\right)^2 \left(\frac{n_{0,2}\pi}{\lambda_2}\right)^4 Q_M(\sigma, \lambda_2^2, m_2)} \qquad [3]$$

The refractive index of both phases was obtained by assuming volume additivity using the Lorenz–Lorentz mixing rule:[9]

$$\left(\frac{n_{12}-1}{n_{12}+2}\right)^2 = \sum \phi_j \left(\frac{n_i-1}{n_i+2}\right)^2 \qquad (4)$$

with ϕ_i being the volume fraction of compound i and n_i the refractive index of the compound i.

EXPERIMENTAL

The polymerization apparatus (Fig. 1) consists of a stainless steel high-pressure autoclave (100 ml volume), two sapphire windows, a magnetic stirrer, a high-pressure pump used to fill and control the system pressure and a temperature-controlling unit consisting of a thermocouple, four heating elements and a controller.

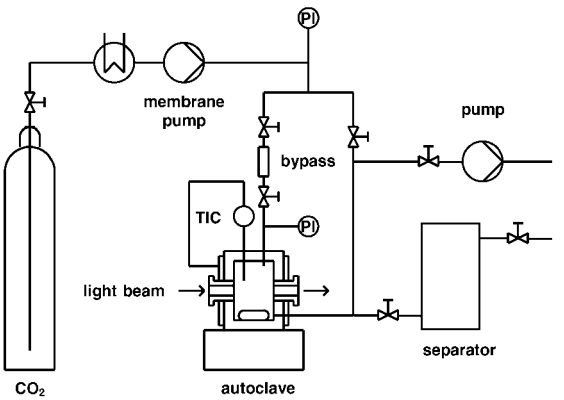

Figure 1 Scheme of the apparatus used for the study of the precipitation polymerization of MMA in sc-CO_2. The polymerization in the autoclave is directly monitored through the measurement of the turbidity. The initiator AIBN, which starts the reaction, is injected through a bypass. The reaction can be quenched through injection into the separator under pressure. The separator is filled with *n*-octane containing a small amount of methylhydroquinone to stop the radical polymerization. The autoclave is thermostatically controlled to $\pm$ 1 °C.

In order to exclude oxygen, the autoclave was heated up to 120 °C in vacuum prior to all measurements. 10 g of freshly distilled MMA, 0.65 wt% (relative to MMA) of PDMS–MA macromonomer and CO_2 were introduced to the autoclave and heated to 60 °C. To start the polymerization azodiisobutylnitrile (AIBN) was added as an initiator through a bypass. Then the extinction was measured as a function of time at various wavelengths $400 \leq \lambda \leq 900$ nm) by a UV–VIS diode array spectrometer (Zeiss MCS 522). The polymerization was carried out at 60 °C and 330 bar.

RESULTS

Figure 2 shows the plots of turbidity *versus* time at different wavelengths. There are two stages to the polymerization reaction: during the initiation stage the turbidity changes only slightly, whereas during the second stage the increase is more pronounced.

Figure 3 shows the average apparent particle size and the particle number density as a function of time. It is obvious that the size of the particles grows linearly with time. Scanning electron microscopy (see Fig. 4a) shows that the size of a single particle is 300 nm at 500 s. Within an uncertainty of

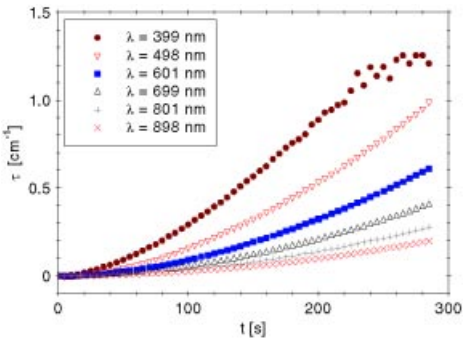

Figure 2 Analysis of the kinetics of the precipitation polymerization by turbidimetric measurements. The turbidity measured at different wavelengths given in the insets is plotted against time.

25%, this result agrees with the data obtained from turbidity measurements. Figure 4b shows the particles resulting after completion of the polymerization. The narrow size distribution is immediately obvious. This demonstrates that the polymerization proceeds in a well-defined manner in accord with all the other findings of this study.

From the experimental data displayed in Fig. 3 the rate of polymerization follows as $(2.7 \pm 1) \times 10^{-6}$ mol l^{-1} s^{-1}. This rate is in good accordance with the rate of polymerization in dilute solution ($v_P = 7.8 \times 10^{-6}$ mol l^{-1} s^{-1}, calculated for reaction condition[10–15]).

CONCLUSIONS

The foregoing comparison proves unambiguously

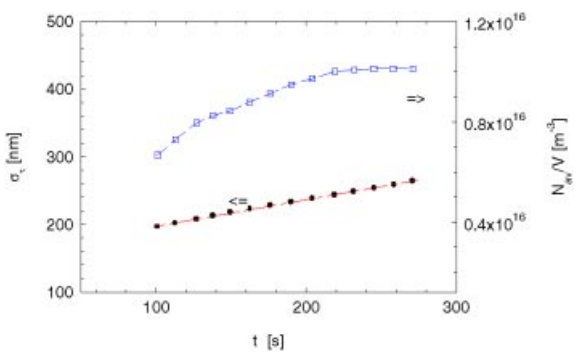

Figure 3 Plot of the turbidity-average diameter σ_τ and the average number density N_{av}/V as a function of time.

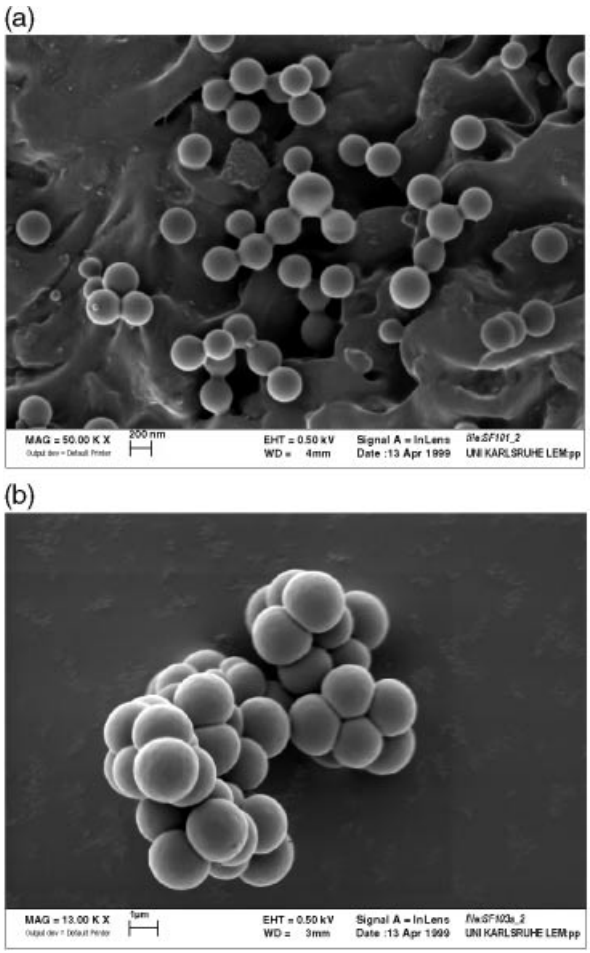

Figure 4 Analysis of the PMMA particles by scanning electron microscopy. (a) Quenched sample obtained by stopping the reaction after 500 s; (b) Sample obtained after completion of the reaction. Note the different scales of the two electron micrographs.

that the early stage of dispersion polymerization of MMA in sc-CO_2 in the presence of the macromonomer PDMS–MA can be studied quantitatively by monitoring the turbidity of the suspension directly in the autoclave.

The procedure developed here gives the turbidity-average of the particle diameter σ_τ as well as the average number density of the particles N_{av}/V. The data obtained here show that the dispersion polymerization of MMA in the presence of PDMS–MA proceeds via a homogeneous nucleation of particles from the polymer that is generated in the homogenous phase; this polymer precipitates if the molecular weight exceeds a given value.

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