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SHORT COMMUNICATION

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On-line detection of emulsion polymerization by solid-state NMR spectroscopy

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Abstract The on-line detection of emulsion polymerization processes by means of solid-state NMR spectroscopy is demonstrated for the first time using poly(butyl acrylate) as a model system. Relatively short time intervals are accessible via ^{1}H detection while the use of ^{13}C NMR spectroscopy results in an increased spectral resolution. Details of sample preparation and experimental techniques are given, while remaining artifacts of the preliminary results will be addressed in further investigations.

Key words Emulsion polymerization – solid-state NMR spectroscopy – on-line detection – poly(butyl acrylate)

Introduction

Emulsion polymerization is an important method within the wide variety of synthetic techniques. Beside several well-known experimental advantages, e.g. viscosity and heat transfer, particles with well-defined structures are obtainable by this approach. Details about mechanisms and kinetics of polymerization processes are known from various studies [1] including investigations by off-line and on-line methods as well as theoretical studies. On-line methods for the measurement of chemical and physical properties of polymerization reactions are advantageous because they may provide a direct process control in industrial applications without the need to isolate specific samples. Examples of the various techniques used for on-line monitoring of emulsion polymerization are calorimetry [2], chromatography [3], densitometry [4], dielectric spectroscopy [5], electrical conductivity [6], turbidity measurements [7] and ultrasound propagation [8].

Solid-state NMR spectroscopy is an additional method that provides unique information about morphological and dynamic properties of polymer particles by taking advantage of the high selectivity of the method to details of the chemical structure.

Previously reported investigations by Winnik et al. demonstrate the use of NMR techniques to perform a step-by-step characterization of an emulsion polymerization process [9]. An on-line detection of copolymerization processes by liquid-state ^{1}H NMR was performed recently by Kruft et al. [10]. However, suitable conversion ratios for further calculations were limited to values between 4%

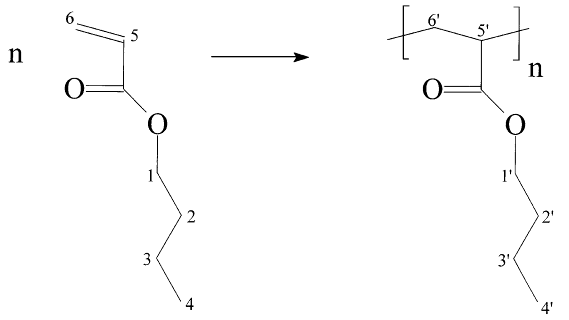

Fig. 1 Schematic conversion of butyl acrylate to poly(butyl acrylate) with designation of the various sites

and 6% due to troublesome integration of polymer signals for lower conversions and due to the so-called composition drift effect [11] for higher conversion ratios. So far, solid-state NMR techniques have not been used as a tool for on-line investigation of emulsion polymerization processes. The purpose of this communication is to demonstrate an on-line application of solid-state NMR spectroscopy for detection of the emulsion polymerization process of butyl acrylate. For this purpose, vanishing signals of the olefinic double-bond in butyl acrylate (Fig. 1) as well as the growing signals of the newly formed saturated polymer main chain are followed. In this simple case the polymerization process can be followed by means of both ^{1}H and ^{13}C NMR spectroscopy. For characterization of the quasi-solid-state emulsions with high polymer content, solid-state NMR methods are advantageous in comparison with liquid-state NMR spectroscopy. Especially, the technique of magic angle spinning (MAS) [12] provides a line narrowing and therefore a higher resolution not available in liquid-state NMR spectra of similar samples.

Experimental

Sample preparation

The emulsion polymerization of butyl acrylate was prepared by mixing the components (0.5 g butyl acrylate, 0.5 g 3%-solution of sodium dodecyl benzenesulfonate, 5 mg $K_2S_2O_8$, 1.5 ml water) at ambient temperature. To avoid the dominating proton signal of water, samples for ^{1}H NMR spectra were prepared with D_2O instead of H_2O. For solid-state NMR measurements, small portions of the mixture were filled into standard ZrO rotors with a volume of 0.5 ml. Then, the filled rotors were inserted into the NMR probe head. Finally, the reaction was started by increasing the temperature to several defined values above 320 K which results in a radical formation by decomposition of the initiator.

Solid-state NMR spectroscopy

All solid-state NMR experiments were carried out at temperatures between 323 and 343 K on a Bruker MSL-300 spectrometer with a standard Bruker ^{1}H–^{13}C double-resonance MAS probe head, using 90° ^{1}H and 90° ^{13}C pulse lengths of 3.5 μs. Due to mechanical properties of the emulsion-filled rotors MAS spinning rates were limited to some 1000 Hz. The magnitude of the magnetic field was 7.05 T, which results in resonance frequencies of 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively. NMR signals of butyl acrylate and poly(butyl acrylate) were detected in ^{1}H one-pulse and ^{13}C one-pulse spectra. For ^{13}C spectra dipolar decoupling [13] was used to eliminate the heteronuclear ^{13}C–^{1}H dipolar coupling. Typically, 32 scans with a repetition delay of 2 s for ^{1}H detection and 512 scans with a repetition delay of 1 s for ^{13}C detection were accumulated.

Results and discussion

^{1}H NMR spectra

On-line detection of emulsion polymerization processes by ^{1}H NMR is favorable because the high sensitivity of ^{1}H nuclei allows a relatively short time interval between two subsequent spectra. However, some problems may arise from the dipolar couplings between different ^{1}H sites which increase ^{1}H NMR line widths. Such dipolar couplings are averaged out to a great extent in the liquid state while they are dominant in the solid state. For the emulsion process under investigation, ^{1}H line widths will increase with progressing conversion, i.e. increasing solid content of the emulsion. A quantitative analysis of ^{1}H NMR data depends crucially on the remaining resolvable lines in the quasi-solid-state spectrum after mostly completed polymerization. For investigation of samples with increasing solid content, solid-state NMR is favorable in comparison with liquid-state NMR because an additional line narrowing is provided by the technique of MAS. Figure 2 shows typical ^{1}H NMR spectra before the polymerization was started (a) and after completed reaction (b). Monomeric butyl acrylate shows characteristic peaks between 4.8 and 6.1 ppm while poly(butyl acrylate) can be identified by the resolvable signal of H6′ at 2.1 ppm.

The necessity of a satisfactory signal-to-noise ratio, i.e. the need to accumulate, e.g. 32 scans for each ^{1}H spectrum, limits the above-mentioned minimal time interval to 1 min. Therefore, the rate of the investigated polymerization process has to be adjusted by the amount of initiator and by the reaction temperature. The temperature was raised from ambient temperature to the investigated values

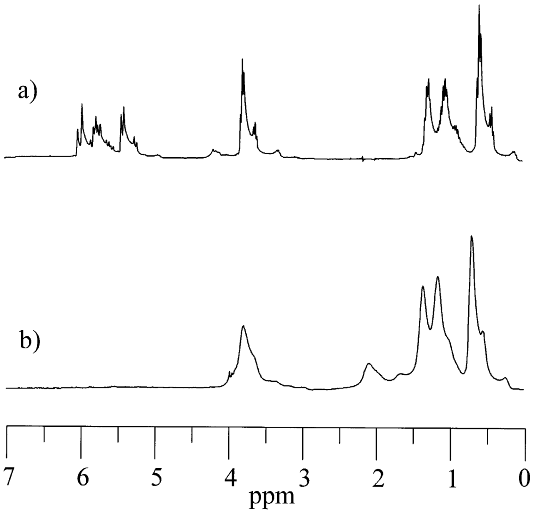

Fig. 2 Typical ^{1}H one-pulse NMR spectra before the polymerization was started (a), i.e. showing pure butyl acrylate with characteristic peaks between 4.8 and 6.1 ppm and after complete conversion (b), i.e. showing pure poly(butyl acrylate) which can be identified by the resolvable signal of H6′ at 2.1 ppm

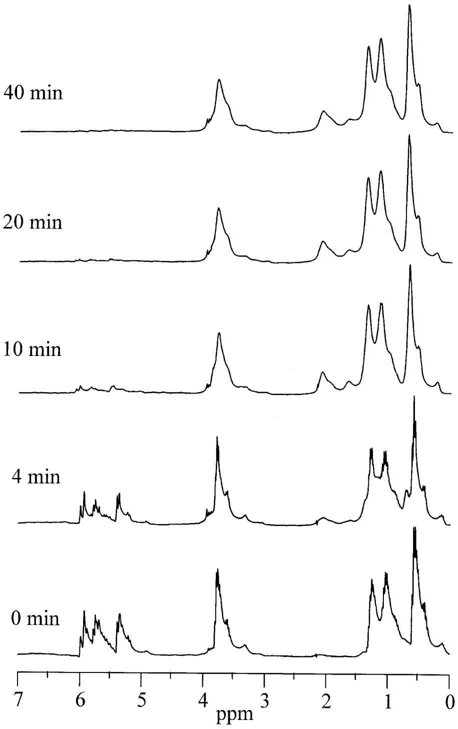

Fig. 3 ^{1}H one-pulse NMR spectra after indicated reaction times at 343 K

(323, 328, 333 and 343 K) while carefully preventing any overheating.

At a temperature of 323 K no conversion was observed, while the reaction was completed after 50 min at higher temperatures. A characteristic series of ^{1}H one-pulse NMR spectra from the measurement at 343 K is shown in Fig. 3. With increasing conversion the narrow monomeric signals between 4.8 and 6.1 ppm decrease while the broad polymeric signal at 2.1 ppm increases. Additional changes can be observed for the line widths of several signals, e.g. the O–CH$_2$ signal at 3.7 ppm and some signals in the aliphatic region between 0 and 1.5 ppm. The characteristic increase of the ^{1}H NMR line width is based on an increasing content of polymerized material in the sample which results in a decreasing mobility, i.e. a stronger dipolar coupling.

Signal intensities as detected in the ^{1}H NMR spectra are determined from the signals mentioned before by integration over the respective spectral ranges. Results for the investigated reaction temperatures are given as a function of reaction time for poly(butyl acrylate) in Fig. 4a and for monomeric butyl acrylate in Fig. 4b. With increasing reaction temperature the polymerization rate increases which results in a faster decay of the butyl acrylate signal and a faster growth of the poly(butyl acrylate) signal. For all series the polymerization processes are completed after 50 min, i.e. no further changes of signal intensities are detected. At the highest temperature of 343 K most of the conversion takes place within the first 25 min.

The curves displayed in Fig. 4 are not perfectly smooth but display some artificial kinks and discontinuities. Most likely, these apparent artifacts have to be attributed to a varying electronic match of the probe head due to the change of sample composition and filling factor. These parameters affect both the absolute size of the signal received and the phasing, thus introducing some error in the signal values.

^{13}C NMR spectra

As demonstrated so far, on-line detection of an emulsion polymerization process is feasible by ^{1}H NMR with a relatively high time resolution. To increase spectral resolution it is advantageous to use ^{13}C NMR. However, due to the smaller sensitivity of ^{13}C nuclei the minimal time between two spectra with a satisfactory signal-to-noise ratio is restricted to a higher value of 9 min.

Figure 5 shows typical ^{13}C one-pulse NMR spectra before the polymerization was started (a) and after complete conversion (b). As demonstrated in Fig. 5a, monomeric butyl acrylate can be identified by the signal of the olefinic double bound (C5 and C6) at 129 ppm, while poly(butyl acrylate) (Fig. 5b) exhibits characteristic backbone signals at 39 ppm (C6′) and 42 ppm (C5′).

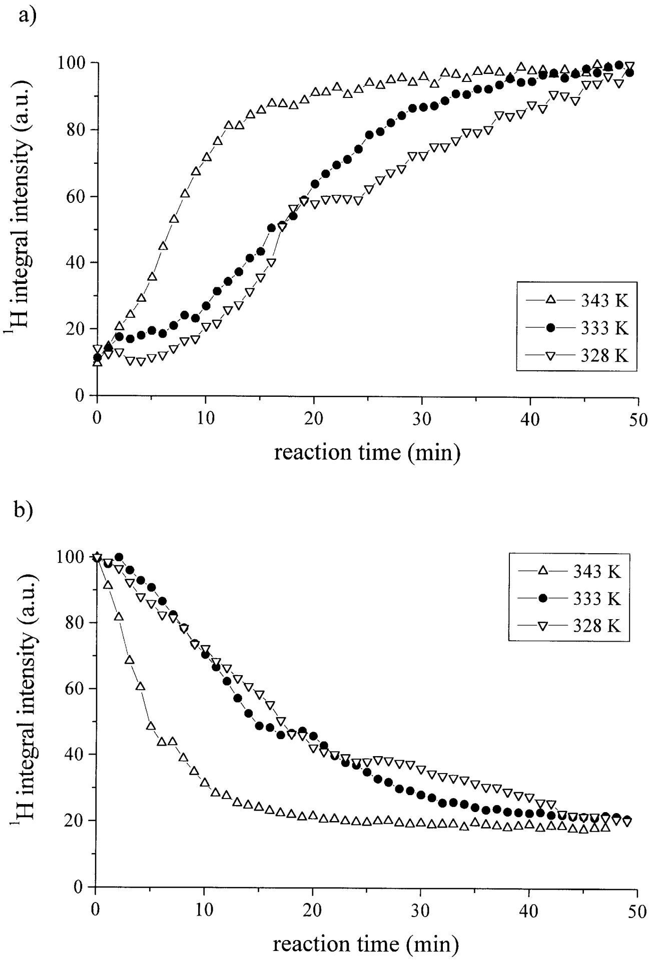

Fig. 4 Integrated signal intensities of poly(butyl acrylate) (a) and of butyl acrylate (b) as a function of reaction time at 328, 333 and 343 K (Analogous data for 323 K are not presented because intensities remain constant for all reaction times.) Experimental values are determined from ^{1}H NMR signals at 2.1 ppm and between 4.8 and 6.1 ppm for the polymer and the monomer, respectively. All intensities are scaled to a maximum value of 100

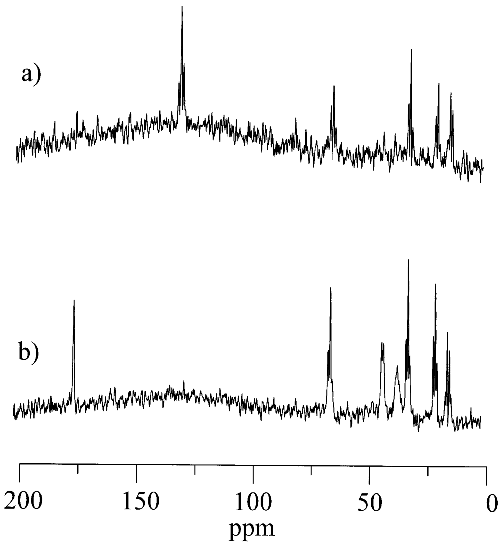

Fig. 5 Typical ^{13}C one-pulse NMR spectra before the polymerization was started (a), i.e. showing pure butyl acrylate with olefinic double-bond signals (C5 and C6) at 129 ppm and after complete conversion (b), i.e. showing pure poly(butyl acrylate) with characteristic backbone signals at 39 ppm (C6′) and 42 ppm (C5′)

An additional change of intensity can be observed for the carbonyl signal at 175 ppm which cannot be detected for the monomeric butyl acrylate. However, the latter effect is no hint at changes of the chemical structure but has to be assigned to different relaxation times which affect the intensity of the carbonyl signal [14]. Additional lines, so-called "wiggles", are experimental artifacts due to the long free induction decay (FID) of mobile components [15]. The sample preparation for different reaction temperatures (323, 328 and 338 K) was performed as described before. The first ^{13}C one-pulse NMR spectrum of each series was recorded immediately after thermal equilibrium was reached. Subsequent spectra were recorded until no further changes were detected, i.e. the polymerization process was completed. Entire results for the three series are shown in Figs. 6a–c.

At a temperature of 323 K (Fig. 6a) no conversion is observed. Even after reaction times as long as 15 h the NMR signal intensities remain constant as compared to the initial spectrum. Increasing the reaction temperature to a value of 328 K (Fig. 6b) results in significant changes of the NMR spectrum for reaction times longer than 18 min. Due to the evidence of this measurement, the conversion of butyl acrylate is completed after 54 min when the signal of the olefinic double-bond at 129 ppm is no longer detectable. Finally, increasing the temperature to a value of 338 K (Fig. 6c) a similar behavior is found. However, at this temperature changes of the ^{13}C NMR spectrum occur already for reaction times longer than 9 min and the conversion is completed after 27 min, which is in good agreement with the data from ^{1}H NMR measurements discussed before. The integrated signal intensities of butyl acrylate and poly(butyl acrylate) at different reaction times are determined from the ^{13}C NMR spectra. Results for the two poly(butyl acrylate) signals C5′ at 42 ppm and C6′ at 39 ppm are presented in Fig. 7 and show a qualitative agreement with the analogous ^{1}H data from Fig. 4a.

Due to the experimental limitations our data do not yet have the quality to allow measurements of kinetic

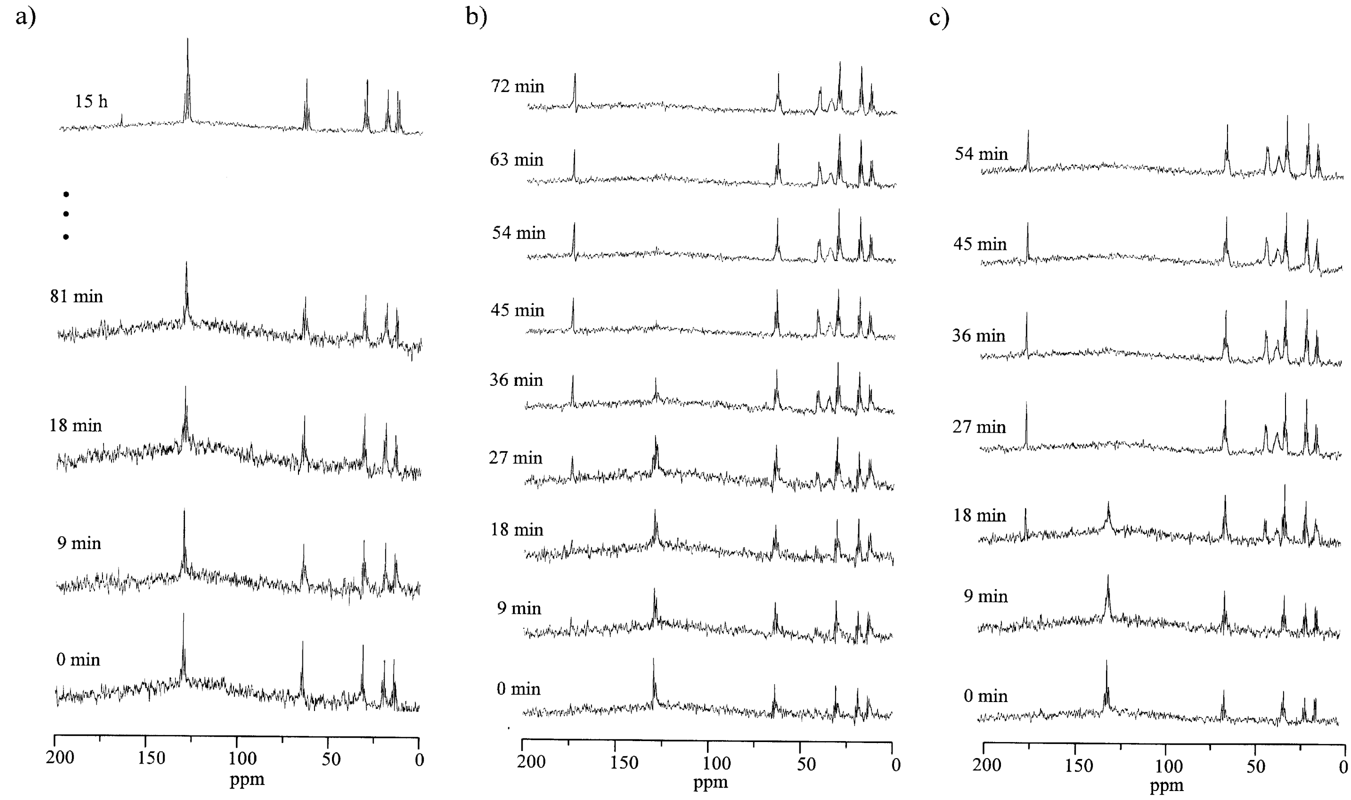

Fig. 6 ^{13}C one-pulse NMR spectra after indicated reaction times at 323 K (a), 328 K (b) and 338 K (c)

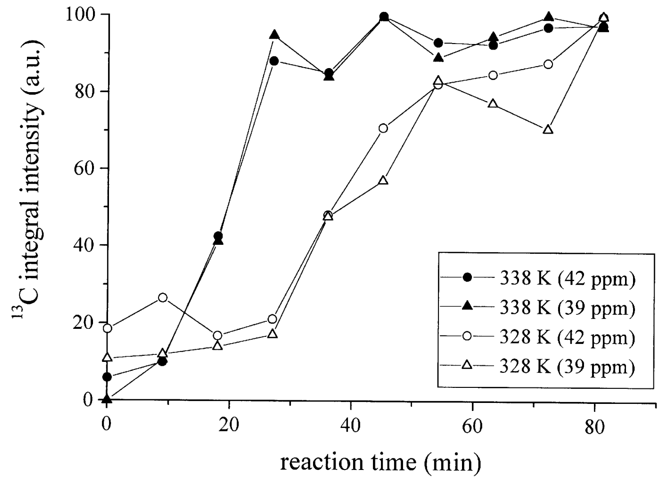

Fig. 7 Integrated signal intensities of poly(butyl acrylate) as a function of reaction times at 328 and 338 K (Analogous data for 323 K are not presented because intensities remain constant for all reaction times.) Experimental values are determined from ^{13}C NMR signals of C6′ + C5′ (39 + 42 ppm) and scaled to a maximum value of 100

parameters. This is evident from Figs. 4 and 7, where the times for half conversion as observed for the ^{1}H and ^{13}C data, respectively, differ by almost a factor of two.

Conclusions

In this communication we demonstrated the on-line detection of the emulsion polymerization process of butyl acrylate by means of solid-state NMR spectroscopy. Detection via ^{1}H NMR allows relatively short time intervals between subsequent spectra while the use of ^{13}C NMR leads to an increased spectral resolution at the cost of a reduced time resolution. Further investigations considering the artifacts observed in the ^{1}H spectra are under way. Clarification of this point will allow a reliable quantitative on-line detection by ^{1}H solid-state NMR spectroscopy. Using such experimental data a calculation of kinetic parameters of emulsion polymerization processes will be accessible.

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