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Different types of water in the film formation process of latex dispersions as detected by solid-state nuclear magnetic resonance spectroscopy

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Abstract The properties of polymer films prepared from latex dispersions are influenced by the drying or film formation process. In order to investigate this process, various systems of aqueous latex dispersions were dried until a specific solid content was reached. The samples investigated were based on vinyl acetate, vinyl acetate/ethylene and pure acrylics employing different surfactants and polyelectrolytes as stabilisers of the dispersions. The role of water in these partially dried films was investigated using ^{1}H and ^{2}H solid-state NMR spectroscopy. Different types of water could be distinguished in the spectra. The drying latex films were found to contain interfacial external water, water at ionic and nonionic groups at surfactants in the polymer/water interface and also water inside the swollen polymer. These different types of water were examined separately using various NMR techniques.

Key words Latex dispersions · Film formation · ^{1}H and ^{2}H solid-state nuclear magnetic resonance · Water in polymer films

Introduction

Aqueous latex dispersions contain several types of polymers, stabilising and dispersing surfactants [1] and cosolvents. The choice of these components depends on the application of the final dispersion such as in adhesives, paper coatings and paints [2]. The macroscopic properties of the final film are influenced not only by the chemical composition, the molecular dynamics and the structure of the multiple components, but also by the initial latex particle morphology and by the kinetics of the latex film formation process [3].

In the first stage of the film formation process [4, 5], the loss of water causes an increase in polymer concentration and so the polymer particles come into close contact and are forced to pack. In the second stage, if the evaporation of water is continued, the latex particles will then be deformed into a compact array of particles. Finally, interdiffusion (third stage) of polymer chains across the particle boundaries and breakup of the surfactant layers lead to a homogeneous film. The molecular dynamics of the water as a solvent is an important parameter in the film formation process with respect to the kinetics of water evaporation and to the mobilisation of the polymer. Water is located between the latex particles and in the case of hydrophilic polymers or polymer components it may also be located inside the particles. The hydroplasticising effect [6] of polymer swelling and mobilisation by water is especially important in the last stages of the film formation process, because the interdiffusion of the polymer chains is relieved.

Here, we report a study concerning the behaviour of water in the drying process of different latex dispersions. Polymer films were made from latex dispersions, which still contained a known amount of water at various solid contents. Different types of polymers and polymer/water interface systems were investigated by ^{1}H and ^{2}H solid-state NMR spectroscopy. The dispersions investigated were based on poly(acrylate), poly(vinyl acetate) or poly(vinyl acetate-ethylene) copolymers. The polymers are influenced by different hydroplasticising properties of the polymer/water system. Hydrophilic comonomers such as sodium ethylene sulphonate or methacrylic acid (MAA), which form stabilising polyelectrolytes, and various surfactants such as sodium dodecyl sulphate (SDS) or surfactants with poly(ethylene oxide) (PEO)-containing chains were chosen to examine different polymer/water interfaces.

Solid-state NMR

^{1}H NMR spectroscopy of solutions yields narrow spectral lines since the isotropic molecular motion averages the dipolar coupling of nuclear spins. The resulting frequencies depend on the isotropical chemical shift. In solids or gels, however, the dipolar coupling is no longer averaged by isotropic molecular motions. Depending on the mobility of the sample, the nuclear transition frequencies can be broadened up to 30–50 kHz line width. One possibility to reduce the line width in ^{1}H solid-state NMR spectra is to spin the sample at the magic angle [magic-angle spinning (MAS)] of 54.7° [7, 8]. Components with a homogeneous line width smaller than the spinning frequency form a narrow line, and the frequency resolution is dramatically improved. ^{1}H solid-state NMR under MAS yields detailed information about the structure and dynamics in spatially heterogeneous systems [9, p. 402] such as aqueous latex dispersions. Dissolved or gel-like components form narrow lines containing chemical structure information in the chemical shift. The rigid components yield broad lines with information about the dynamics at spinning frequencies below the static line width.

^{2}H solid-state NMR spectra are dominated by the nuclear quadrupolar interaction along the chemical bond of deuterons with respect to the magnetic field. If the chemical shift is ignored, a simple liquid will yield a single narrow line since the quadrupolar interactions are isotropically averaged by rapid molecular motions [10]. Rapid anisotropic motions also decrease the line width but lead to spectral patterns that are characteristic of the type of motions [11]. Selection between different types of molecular motion can be performed by varying temperature. The dynamics of one component, such as water, in a complex system can be conveniently investigated by ^{2}H NMR after selective deuteration, i.e. replacement of H_2O by D_2O.

Experimental

Preparation of the latexes

Six latex dispersions containing vinyl acetate or vinyl acetate-ethylene as monomers were prepared according to the procedure in Ref. [12] in an emulsion polymerisation with 0.2 wt% ammonium persulphate (APS) as the initiator. The compositions of the different samples are shown in Table 1. The pH was adjusted using 0.2 wt% sodium acetate to a pH of 4–5 for the samples VAc-1 and VAE-1 with $Na_4P_2O_7$. During the synthesis the ethylene pressure of the poly(vinyl acetate-ethylene) dispersion was 20 bar. This resulted in a polyethylene content of 8.7 wt% or 22.6 mol%.

The second type of dispersion was prepared from methyl methacrylate and *n*-butylacrylate. The emulsion polymerisation was performed with 0.35 wt% APS as the initiator. In this case, the pH was adjusted to pH 8 with ammonia. All the dispersions contained different surfactant systems to stabilise the dispersions. They are listed in Table 1 with respect to each system.

Typical surfactants were SDS, several PEO-containing compounds and finally polyelectrolytes. One PEO surfactant was a C_{11}-oxoalcohol with 28 mol EO, and another one was Hostapal BV® [sodium tri(*t*-butyl)phenol-PEO sulphate with typically 7 mol EO]. MAA and sodium ethylene sulphonic acid salt (NaESA) were used as comonomers in the emulsion polymerisation. MAA and NaESA form polyelectrolytes, which stabilise the latex dispersions.

Particle sizes and particle size distributions were measured by photon correlation spectroscopy (PCS). The particle diameters were found to be in the range 150–200 nm as for all dispersions. The glass-transition temperatures, T_g, of all the samples were

Table 1 Investigated latex systems. The chemical composition of the samples for the various polymers [poly(vinyl acetate) (*PVAC*), polyethylene (*PE*), poly(methyl methacrylate) (*PMMA*), poly(*n*-butylacrylate) (*P*(*n-BA*))], comonomers [sodium ethylene sulphonic acid salt (*NaESA*), methacrylic acid (*MAA*)] and surfactant systems [sodium dodecyl sulphate (*SDS*), poly(ethylene oxide) (*PEO*), Hostapal BV] and the amounts of $(NH_4)_2S_2O_8$ initiator are given. All weight percentages given were normalised with respect to the amount of polymer (100 wt%). PEO-1 is a C_{11}-oxoalcohol ethoxylated with an average of 28 mol EO. Hostapal BV® is a sodium tri(*t*-butyl)phenol-PEO sulphate with an average of 7 mol EO. The particle sizes were measured by photon correlation spectroscopy and were found to be in the range 150–200 nm diameter. VAc-2 (483 nm) and RA-1 (83 nm) differ from this value

Sample	Polymer	Comonomer	Surfactants	Initiator
VAc-1	PVAc 100 wt%	NaESA 0.5 wt%	1 wt% SDS 2 wt% PEO-1	0.2 wt%
VAc-2	PVAc 100 wt%	–	0.5 wt% SDS	0.2 wt%
VAc-3	PVAc 100 wt%	–	3 wt% Hostapal BV®	0.2 wt%
VAc-4	PVAc 100 wt%	NaESA 2 wt%	3 wt% Hostapal BV®	0.2 wt%
VAE-1	PVAc 91.3 wt% PE 8.7 wt%	NaESA 0.5 wt%	1 wt% SDS 2 wt% PEO-1	0.2 wt%
RA-1	PMMA 50 wt% P(*n*-BA) 50 wt%	MMA 2 wt%	1.5 wt% SDS	0.35 wt%

determined by differential scanning calorimetry with a scanning rate of 20 K/min. They were found to be 313 ± 2 K for poly(vinyl acetate) dispersions, 287 ± 2 K for poly(vinyl acetate-ethylene) dispersions and 295 ± 2 K for the polyacrylate dispersion.

Sample preparation

Most latex dispersions dry in a spatially inhomogeneous manner, drying inward from the surface. A skin surrounds the wet dispersion. The reasons for this spatial inhomogenity are the increased concentration of latex particles close to the surface as evaporation of water proceeds and the compressive capillary forces [13] that deform the particles. This compression accelerates the closing of the capillaries and the formation of a skin. Due to the fact that NMR spectroscopy is a spatially averaging method, we chose to prepare homogeneous latex films. These films contained different water contents. Dispersions (1–2 g) with an initial solid content of 50 wt% were filled to a height of 5 mm in glass tubes. The water was slowly evaporated by heating the samples at 333 K (60 °C) for several hours while stirring them less than once per minute to prevent macroscopic skin formation. This drying process was stopped after different times corresponding to different solid contents. The solid content of each sample was determined by gravimetric analysis. The accuracy of the preparation was cross-checked by ^{1}H solid-state NMR spectroscopy. As shown later, the homogeneous films contained different types of water with several discrete resonance frequencies with respect to their chemical proximities. The spatially inhomogeneous films contained a broad superposition of separate frequencies. Samples with D_2O as the solvent were prepared by adding D_2O to the dispersions followed by evaporating most of the D_2O / H_2O mixture. This procedure was performed several times. In this way we produced H_2O/D_2O exchange rates greater than 80 mol%.

NMR measurements

The ^{2}H solid-state NMR spectra were measured on a Bruker CXP 300 spectrometer and the ^{1}H NMR spectra were measured on a Bruker MSL 300 spectrometer. Both instruments operated at a magnetic field strength of 7.05 T. All ^{2}H NMR measurements were recorded under static conditions with a T_1 selective solid-echo pulse sequence ($[90°]_{5\,\mathrm{times}} - \tau_1 - 90°_{\pm x} - \tau_2 - 90°_{\pm y} - \tau_2 -$ acquire) [11, 14, 15] at different temperatures. By setting $\tau_1 = 10$ ms we could selectively observe the fast-relaxing (and therefore mobile) components in a T_1 filter experiment. In other experiments τ_1 was set to 3 s and all water components could be observed. The 90° pulse length was about 3 μs and the pulse delay, τ_2, in the solid-echo sequence was 20 μs. ^{2}H NMR spectra were measured in a temperature range of 180–300 K. Before each measurement, which took between 0.5 and 8 h, the sample was allowed to equilibrate for 0.5 h. Selection between different types of molecular water dynamics at low temperatures was performed by varying the temperature. The different components of the spectra were quantitatively determined by standard deconvolution techniques.

The ^{1}H solid state NMR spectra of our samples were measured under MAS in a 7-mm rotor with a rotor frequency of 3000 Hz in the temperature range 290–340 K. The samples were stable against the centrifugal forces in the MAS experiment at high solid contents (above 80 wt%) especially when the temperature was below the T_g of the polymer. No time-dependent change in the spectra of these samples before and after the acquisition was found. The temperature was controlled by a Bruker VT-100 unit with an accuracy and stability of ±2 K. The ^{1}H 2D-exchange experiment ($90° - \tau_1 - 90° - t_m - 90°$ acquisition − recycle delay) [9, 16, 17] was performed in time-proportional phase incrementation mode by incrementing τ_1. A mixing time, t_m, of 200 ms was used for spin diffusion and molecular diffusion [9, p. 425]. The 90° pulse length was about 4.5 μs and the recycle delay 2 s. The dynamic and chemical exchange of magnetisation in ^{1}H 2D-exchange spectra in combination with MAS contain information about intermolecular interactions. Slow molecular motions and spatial proximity of molecules are detected. t_m is limited by the T_1 relaxation time of the sample.

Results and discussion

Temperature dependence of ^{2}H NMR spectra

Typical ^{2}H NMR spectra of water as a function of temperature in a wet polymer film prepared from latex dispersions are shown in Fig. 1. The poly(vinyl acetate-ethylene) dispersion VAE-1 in Fig. 1 (Table 1) was dried to a solid content of 77 wt%. Different dynamics of water were found in the ^{2}H solid state NMR spectra of the prepared wet latex films. The dynamics of water and its associated temperature behaviour depend on the chemical surroundings. In chemically heterogeneous systems such as latex dispersions, the differences in water dynamics can easily be detected by measuring the samples at various low temperatures from room temperature down to 170 K. All spectra presented are normalised to the same height.

The spectrum at the top corresponds to a temperature above the freezing point of the external water. From room temperature to 234 K the external liquid water outside the polymer particles is the most mobile component and dominates each spectrum. When the samples were cooled, a large freezing point depression of the external water was found resulting from the surfactants, salt and polyelectrolytes.

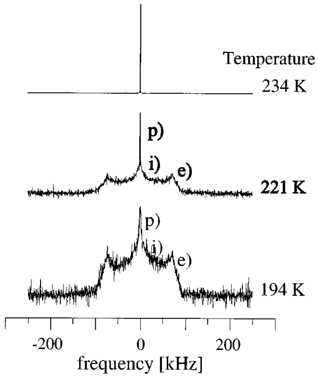


Fig. 1 Temperature-induced change in the water dynamics in polymer films at low temperatures as detected by ^{2}H NMR spectroscopy. The H_2O has been exchanged by D_2O to measure exclusively the mobility of water. Three different dynamics of water in the spectra of D_2O in water-containing polymer films (solid content 77 wt%) made from dispersion VAE-1 were found: *e* ice (external water), *i* immobilised water (interface) and *p* mobile water (inside the polymer). All spectra are normalised to the same height as described in the text

Below the freezing point of the external water we were able to distinguish three different types of water in the spectra at 221 and 194 K (Figs. 1–3). The dominant contribution to the spectrum comes from the frozen external water (e). Due to the rigidity of this component at temperatures below 223 K, a broad Pake pattern [9, p. 30] is observed. Superimposed on this pattern is a narrow peak corresponding to the mobile water inside the swollen polymer (p). The intermediate region of mobility contains partially immobilised water in the interface (i).

The film of sample VAE-1 (Table 1) with NaESA as comonomer contains a large interfacial layer at the water/particle interface. The observation of an increased interface size with increasing amounts of NaESA comonomer derives from a comparison of the particle diameter measured by PCS and aerosol spectroscopy [12] as hydrodynamic and hard-core diameters. The interface consists of water-soluble polyelectrolytes, formed by vinyl acetate with 0.5 wt% NaESA comonomer, 2 wt% PEO surfactant and 1 wt% SDS.

A simplified picture for the location of these three types of water is given in Fig. 4. At room temperature mobile (liquid or gel-like) water is located outside the latex particles and less mobile water is located inside. For temperatures below the freezing point of the external water, rigid ice is found outside the latex particles. In contrast to this, partially mobile water is still found inside the polymer. This is in agreement with Radloff et al. [18], who found that water bound to cellulose and cellulose/poly(vinyl alcohol) blends did not freeze. This dynamic behaviour of water in a polymer matrix was also found in water-containing epoxy resins [19, 20].

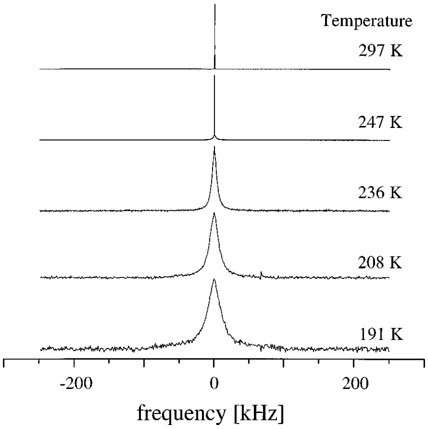


Fig. 2 ^{2}H NMR spectra of D_2O in swollen pure poly(vinyl acetate) as a function of decreasing temperature. Only a mobile component is found in the spectra. The line width increases when the temperature decreases

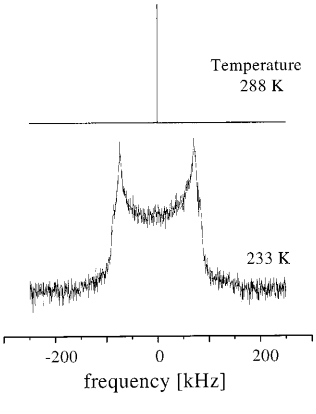


Fig. 3 ^{2}H NMR spectra of D_2O in the surfactant system of VAE-1 after dialysis of the dispersion. Below the freezing point of the water the ice shows a typical Pake spectrum

Assignment of spectral components

The assignment of the spectral components was checked with D_2O spectra of water in related but pure chemical environments. An analysis of the different water components was performed as a function of temperature and chemical composition. First pure poly(vinyl acetate) with a weight-average molecular weight of 125 kg/mol was swollen for 4 days in D_2O. The surface of the swollen polymer was dried before the measurements to exclude external water at the surface. According to Schaechtling [22, p. 380], about 3 wt% of water is soluble in poly(vinyl acetate). The ^{2}H NMR spectra of the D_2O inside the pure polymer are shown in Fig. 2. A narrow line corresponding to a mobile water component is present at all temperatures. Nevertheless, there is a temperature dependence of the line width for this mobilised water inside the polymer. With decreasing temperature the mobility of this type of water decreases. This results in an increasing line width. The water mobility inside the polymer is a function of the local mobility of the polymer.

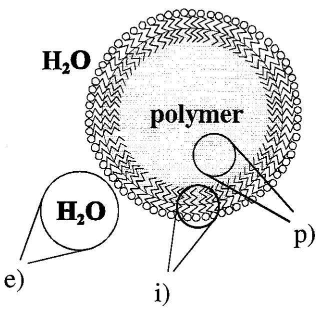


Fig. 4 Schematic presentation of water located in different types of chemical surroundings in the latex dispersions

The spectra of pure water used as a solvent for salt, surfactants and polyelectrolytes differ from those given in Fig. 2. Typical ^2H NMR spectra of D_2O in the surfactant system of VAE-1 are depicted in Fig. 3. The sample was prepared by dialysis of the dispersion, evaporation of the water and finally exchange of H_2O by D_2O. Again a strong freezing point depression of about 35 to 238 K depending on the surfactant, salt and polyelectrolyte concentration is found from the spectra. The calculated freezing point depression of the pure salt solution is less than 5 K. Two spectra are given for comparison: the spectrum of liquid water at 288 K and the Pake-like spectrum of rigid ice at 233 K. It can be concluded that component e in Fig. 1 is the frozen external water.

Water in different polymers

The spectrum of the mobile water (p) in Fig. 1 is a function of the polymer. Both ^2H NMR spectra in Fig. 5 correspond to latex films with similar solid contents and polymer/water interfaces. They differ in the composition of the polymer. The samples VAc-1 and VAE-1 (Table 1) contain the same amount of surfactant and similar amounts of stabilising polyelectrolyte: VAc-1 is a pure poly(vinyl acetate) latex and solution NMR measurements showed that VAE-1 is an approximately statistical copolymer with 91.3 wt% vinyl acetate and 8.7 wt% (or 22.6 mol%) ethylene. The different chemical structures of the polymers result in different spectra of the mobile low-temperature water component (p). A larger amount of mobile water can be detected inside VAc-1 by the analysis of the peak areas; less can be detected in VAE-1. The ratio of ice (e) to the mobile components i and p is reduced by a factor of 2.8 by copolymerising ethylene to the polymer as shown in Fig. 5. Most of the mobile water, i and p, in VAE-1 is found in the intermediate region of mobility, i. This corresponds to the fact that about 3 wt% water is soluble in poly(vinyl acetate) [22, p. 380] but only 0.002–0.2 wt% is soluble in polyethylene [22, p. 708]. The reduced number of polar hydrophilic groups in poly(vinyl acetate-ethylene) explains the reduced amount of water inside the polymer. The ^2H NMR line width of the mobile component p decreases from 7.2 kHz in VAc-1 to 2.6 kHz in VAE-1 by statistically adding ethylene to the polymer. This indicates a higher mobility of the polymer in VAE-1. The samples differ in the T_g, with 312 K for dry VAc-1 and 288 K for dry VAE-1; however, with respect to the low temperatures in the ^2H NMR experiment, differences in the local mobility of the polymer must be responsible for this behaviour. In both samples the water inside the polymer mobilises the acetate side group especially. Higher local mobility of the polymer is in accordance with higher mobility of the water inside the polymer. In contrast to the reduced amount of water inside the polymer, no decrease in the water peak intensity in the intermediate mobility region in the ^2H NMR spectrum of VAE-1 is found with respect to similar interface systems (Table 1). Both polyelectrolyte/surfactant interfaces are swollen by water.

Similar trends are observed in the ^2H NMR spectra of D_2O in other polymer systems as displayed in Fig. 6. VAc-2 (Table 1) is a poly(vinyl acetate) latex dispersion; the polymer of latex RA-1 consists of 50 wt% MMA and 50 wt% *n*-butylacrylate. The T_g are 312 K for dried VAc-2 and 295 K for dried RA-1. The amount of mobile water at low temperatures is reduced in RA-1. This corresponds to the fact that D_2O is less soluble in RA-1. Water is soluble to the extent of 1.7–2 wt% in poly(methyl methacrylate) [22, p. 427], which is the hydrophilic component of RA-1. The line width in RA-1 is largely reduced and is much more pronounced than in the case of latex VAE-1 compared to VAc-1. Again this is related to the local mobility of the polymer, but the chemical surroundings of the water inside the polymer are changed.

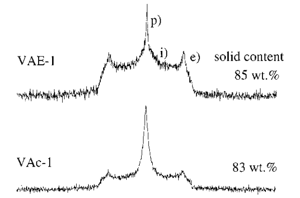


Fig. 5 ^2H NMR spectra of D_2O in dispersions containing the same surfactants (Table 1) but different polymers, VAc-1 [poly(vinyl acetate)] and VAE-1 [poly(vinyl acetate-ethylene)] at 210 K. The amount and line width of D_2O inside the polymer are reduced in the presence of the ethylene comonomer in VAE-1. The polymers differ in their number of CH_2 groups, which is greater in VAE-1, and in the number of acetate side groups, which is greater in VAc-1

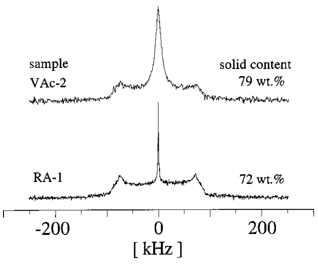


Fig. 6 ^2H NMR spectra of D_2O in a water-containing poly(vinyl acetate) latex film (*top*) and a poly(acrylate) film (*bottom*) consisting of 50 wt% methacrylic acid and 50 wt% *n*-butylacrylate made from dispersions measured at about 211 K. D_2O is less soluble in RA-1, but is of higher mobility in the changed chemical water/polymer environment of RA-1 caused by the modified polymer structure

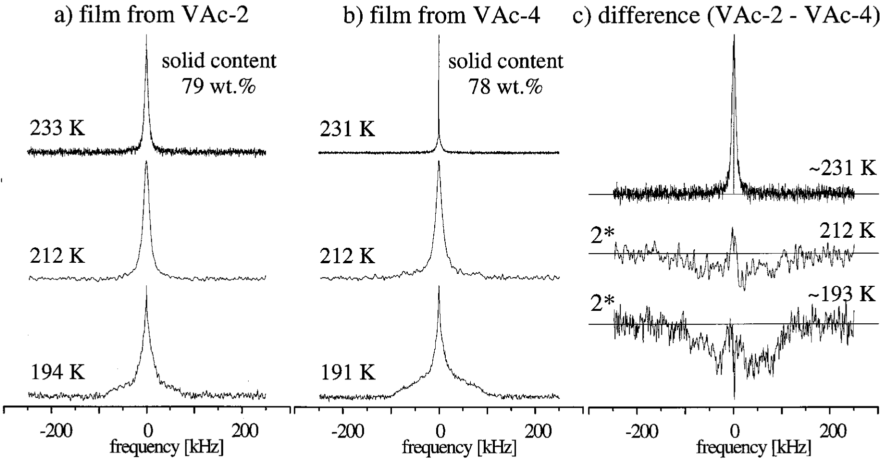
Water in the interface from ^2H and ^1H NMR spectroscopy

Different copolymers and surfactants in the interface region modify the domain of intermediate mobility in the ^2H NMR spectra of D_2O in wet polymer films. This corroborates the assignment in Fig. 1. Spectra of poly(vinyl acetate) films with a solid content of about 78 wt% are presented in Fig. 7. The T_1 selective solid-echo spectra contain only fast-relaxing components, selected by a short preparation time of 10 ms after the saturation pulses (see Experimental); therefore, only mobile components are detected in the spectra of VAc-2 and VAc-4. The film made from VAc-2 contains only a small amount of 0.5 wt% SDS in the polymer/water interface (Table 1). In contrast to this, the extended interface of VAc-4 consists of 3 wt% Hostapal BV® and polyelectrolytes, built up by the copolymerisation with 2 wt% NaESA. At 231 K the water in VAc-4 is very mobile compared to that in VAc-2, which corresponds to the increased freezing point depression of the external bulk water in VAc-4 relative to VAc-2. At temperatures below 231 K, when all external water is frozen to ice, an extended amount of water in the interface is still detected for VAc-4 in Fig. 7, which can be seen in the difference of both spectra. This corresponds to the large interface.

^2H NMR spectra yield information about the mobility of water inside different polymers and provide an estimate of the size of the polymer/water interface. A more detailed view results from ^1H NMR spectra. Solution NMR methods are limited by the comparatively low spectral resolution due to the immobilised water in the interface. More detailed structural information and also high spectral resolution is achieved by ^1H solid-state NMR in combination with MAS. A typical ^1H NMR spectrum of a wet polymer film made from the dispersion VAc-3 is shown in Fig. 8. The solid content of the film made from the latex dispersion VAc-3 (Table 1) was 99 wt%. The narrow lines of the mobile Hostapal BV® interface, the PEO surfactant, can be distinguished from the broad lines of the rigid polymer. ^1H NMR is therefore sensitive to the mobile components, which are in solution or in the interface. An interesting point in Fig. 8 is that most of the residual water (1 wt%) is not visible as external water at the resonance frequency of 4.65 ppm. A detailed analysis by integration reveals that less than 0.1 wt% water is located in the PEO layer, the rest is immobilised inside the polymer [22]. The immobile water component in the ^1H NMR spectrum is identified as nonfreezable water (p) as shown in the ^2H NMR spectra of Fig. 1. At temperatures below the freezing point of the external water in Fig. 1 this water has the highest mobility.

The ^1H NMR MAS spectra of polymer films containing water prepared from VAc-1 in Fig. 9 show complex spectra with several overlapping components of a dispersion containing various surfactants [22]. Only the mobile interface is presented here, not the broad lines of the rigid polymer. The spectra in various drying states of the dispersion correspond to different stages in the film formation process. To study this we chose samples with 74, 84 and 91 wt% solid content. The mobile water at 4.65 ppm, which can be identified with

Fig. 7 T_1 selective ^2H NMR spectra of D_2O in wet poly(vinyl acetate) films with different interfaces. The small interface of VAc-2 in *a* is generated by 0.5 wt% sodium dodecyl sulphate (*SDS*) and polymer–initiator groups. The interface of VAc-4 in *b* contains 3 wt% Hostapal BV®, the ionic polymer–initiator groups and a large amount of polyelectrolyte, formed from a copolymer of 2 wt% sodium ethylene sulphonic acid salt with vinyl acetate. Only the fast-relaxing mobile components are recorded after saturation of the slow-relaxing components followed by a solid-echo sequence (see NMR measurements). The freezing point depression of the external water is increased in VAc-4 due to the higher number of additives, which can be seen in the spectra at about 232 K. At temperatures below 212 K different amounts of water in the interface are detected in the intermediate range of mobility. The corresponding spectra are shown in *c* as the difference of VAc-2 and VAc-4 spectra; they correspond to the relative size of the interfaces



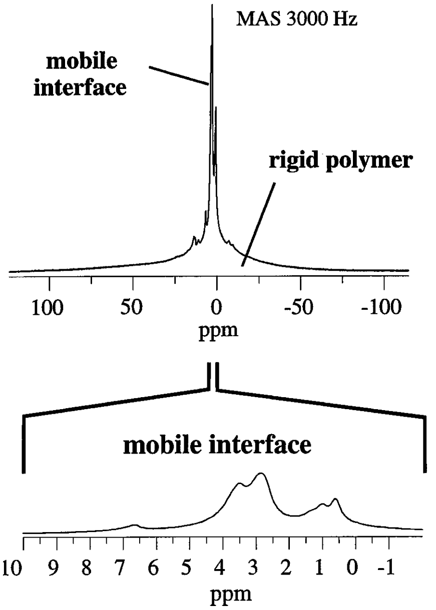


Fig. 8 The ^{1}H NMR spectrum of a water-containing polymer film made from dispersion VAc-3 was taken at a rotational frequency of 3000 Hz in the magic-angle-spinning (*MAS*) experiment. The film with 3 wt% Hostapal BV contains only 1 wt% water. ^{1}H NMR is sensitive to the mobile components in the solution and in the interface. The rigid polymer yields broad lines, the mobile poly(ethylene oxide) (*PEO*) interface provides narrow lines. Most of the residual amount of 1 wt% water is immobilised in the polymer

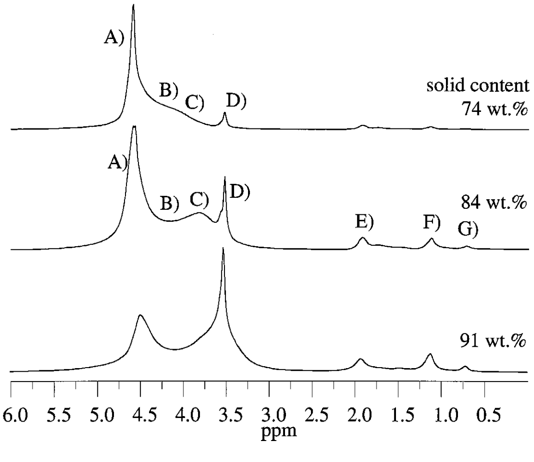


Fig. 9 ^{1}H NMR spectra of wet polymer films prepared from VAc-1 and measured at room temperature. All spectra are normalised to the same height. Water, *A*, evaporates in the drying process and the interface becomes immobilized. Analysis of the complex spectra, verified by analysis of pure systems, yields *A* water at nonionic groups, *B* water at ionic groups, *C* immobilised PEO chains, SDS and polymer–initiator end groups, *D* PEO in the surfactants, *E* mobile polymer (polyelectrolyte), *F* and *G* CH chains of all surfactants

the external and the interfacial water in the ^{2}H spectra at low temperatures, evaporates in the drying process, represented in the ^{1}H NMR spectra for the different solid contents in Fig. 9. The analysis of the complex spectra was performed by investigating the drying processes of only one surfactant containing pure aqueous surfactant solutions and latex dispersions, respectively. First, we considered the spectra of water within the pure chemical environment. Then all spectral lines were assigned supported by the identified surfactant signals. So A is found to be water at nonionic groups and D is mobile PEO of the surfactants. The shoulder B between A and D was assigned to water at ionic groups B, shifted to lower parts-per-million values. Peak C represents immobilised PEO chains, SDS and polymer–initiator end groups. Integration of the VAc-1 spectrum at 84 wt% solid content yields quantitative amounts of the different types of water in the interface. The residual 16 wt% water is distributed as follows: 8 wt% water is located at nonionic groups, 4.5 wt% is found at ionic groups and approximately 3.5 wt% is immobilised inside the polymer. The inherent error of the integration is estimated to be within 1 wt%.

In ^{1}H 2D-exchange experiments (Fig. 10) the 1D spectrum is found in the projection of the spectrum along each frequency axis [16]. The peak intensity along the diagonal represents components without exchange, which are modified because of the 200-ms mixing time for spin and molecular diffusion. The exchange peaks outside the diagonal indicate intermolecular interactions of molecules in spatial chemical surroundings. A magnetisation or a molecular transfer is performed during the mixing time of 200 ms. In Fig. 10, with a higher resolution for the 2D spectrum, A and D from Fig. 9 are separated, while B and C still overlap. The large exchange peaks between the different types of water, A and B, indicate their close proximity. No exchange peaks are found between the CH chains of the surfactant and the water.

Summary

An important factor in the film formation or drying process of latex dispersions is the dynamics of water. The molecular dynamics of the water in latex dispersions is highly influenced by the local chemical environment. Homogeneous polymer films, with different water contents, were investigated via ^{2}H and ^{1}H solid-state NMR spectroscopy. Detailed information about the distribution and dynamics of water in different polymer and surfactant systems were obtained. Three types of water in these wet films could be identified with respect to the temperature dependence of their dynamic behaviour, two could be identified with respect to their chemical shifts.

^{2}H solid state NMR spectroscopy yields information about the water mobility in different polymers; ^{1}H solid-state NMR spectroscopy provides information about

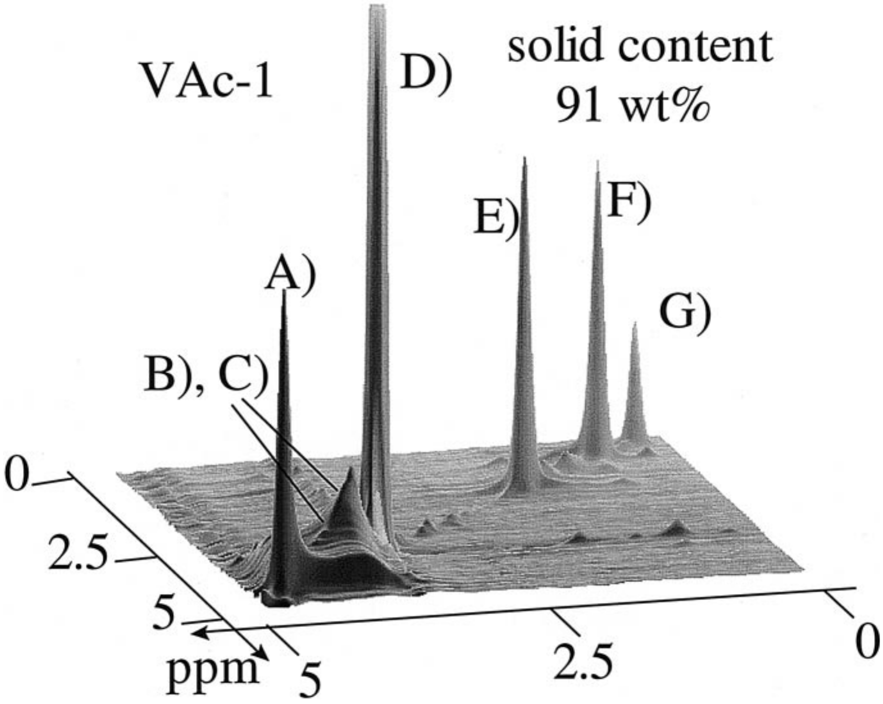


Fig. 10 ^{1}H 2D-exchange experiment with 200-ms mixing time for spin diffusion in sample VAc-1 with a solid content of 91 wt% measured at room temperature. Because of the higher resolution of the 2D experiment *A* and *D* from Fig. 9 are separated and *B* and *C* are still the overlap of different components. The exchange peaks between *A* and *B* indicate the spatial proximity of the different types of water

water in the polymer/water interface. The combination of both methods results in a complete picture of the different types of water in the film formation process. The films contained external water, water at ionic and nonionic groups in the polymer/water interface immobilised by the surfactants and water inside the polymer. The amount of water inside the polymer, known as the water absorption capacity, depends on the polarity of the polymer, its dynamic behaviour and on the local mobility of the polymer. If chemically similar water/polymer environments are compared, the mobility of the water dissolved in the polymer depends on the local mobility of the polymer. Variations in the polymer/water interface size result in different amounts of water being located inside this intermediate mobility region with motional rates of approximately 30 kHz. Information about the amount of water at ionic and nonionic groups in the polymer/water interface can be gained by integration of ^{1}H solid-state NMR spectra.

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