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Film-forming Colloidal Dispersions Studied by Tracer Methods

Tobias Baumgart[1], Sibylle Cramer[2], Thilo Jahr[3], Andrei Veniaminov[3], Jörg Adams[1], Jürgen Fuhrmann[1], Gunnar Jeschke[2], Uli Wiesner[2], Hans W. Spiess[2], Eckhard Bartsch[*,3], Hans Sillescu[3]

[1]Institut für Physikalische Chemie, TU Clausthal, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld, Germany; [2]Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, Germany; [3]Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Jakob-Welder-Weg 15, 55128 Mainz, Germany

SUMMARY: We have studied the dynamics of small probe molecules in film forming latex dispersions by non-radiative energy transfer, forced Rayleigh scattering and electron paramagnetic resonance. First results indicate that on drying the dynamics of the different probes expose characteristic changes at comparable water contents. This could be used for correlating dispersion and film properties in subsequent experiments.

Introduction

Formation of polymer films from latex dispersions has become an important technological process for production of coatings and paints, partially due to the aim of avoiding organic solvents for environmental protection and for economic reasons. There exists a large body of empirical knowledge about the film-formation process1) and a general mechanism has been proposed2), with three subsequent stages occurring on decreasing the water content: formation of a dense packing of particles, particle deformation, particle coalescence and polymer interdiffusion. Even though, many facets of the underlying physical and chemical principles are but poorly understood. This is due to the complexity of the process even in model dispersions as it involves a heterogeneous system composed of a polymer phase, an aqueous phase and the interface (sometimes denoted as "hydrophilic membrane") which contains surfactant and other hydrophilic components. Tracer methods are particularly suited to study the physics of heterogeneous systems as they allow to selectively probe specific compartments or processes by a judicious choice of probe molecules. This has been amply demonstrated by the use of fluorescence techniques to monitor polymer interdiffusion in film forming dispersions1).

In this contribution we report on first results of applying a combination of three complementary tracer techniques (Non-radiative energy transfer - NRET, forced Rayleigh scatttering – FRS, electron paramagnetic resonance – EPR) to study the dynamics of small probe molecules in identical film-forming dispersions. The major aim was to see in how far the techniques are able to catch important features of the film formation process that could be used as indicator for correlations between the formulation of the latex dispersion and the material properties of the corresponding films (e.g. wetting behavior, small molecule transport, surfactant distribution and dynamics) in subsequent experiments. Special emphasis was laid on

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correlating the results of the different techniques as each offers its own advantages and limitations.

Materials and Methods

The studied aqueous latex dispersions, kindly provided by BASF AG (Ludwigshafen), were prepared by emulsion polymerization using n-butyl methacrylate (BMA), acrylic acid (AA), methyl methacrylate (MMA) and n-butyl acrylate (BA) for monomers (initiator: sodium persulfate; surfactant: sodium dodecyl sulfate (SDS), 1 part per hundred monomers; solid content ~ 29 wt%; residual monomer < 300 ppm). Ascorbic acid and hydrogen peroxide were added for deodoration after the polymerization. The pH was then adjusted to 7.5 by adding an appropriate amount of sodium hydroxide. Particle radii R, polydispersities σ and glass transition temperature T_g as determined by capillary hydrodynamic fractionation and DSC were:

$R = 42$ nm, $\sigma = 7$ %, $T_g = -57$°C for P(BAcoAA) (monomer composition: BA:AA = 99:1; molar ratio);

$R = 101$ nm, $\sigma = 4.4$ %, $T_g = 35$°C for P(BMAcoAA) (BMA:AA = 99:1);

$R = 99$ nm, $\sigma = 5.6$ %, $T_g = 64$°C for P(BMAcoMMAcoAA) (BMA:MMA:AA = 71:28:1).

Probe molecules were introduced by stirring crystalline (FRS, NRET) or dissolved (in water, EPR) material into the dispersions at ambient temperature (FRS, EPR) or at 70°C (NRET), respectively. Films of the labeled dispersions were prepared in accordance to the requirements of the different tracer techniques, leading to slightly different film thicknesses (NRET: 150-300 µm; FRS: 400 µm; EPR: 1-2 mm). Tracer concentrations were 0.3 mol/L (related to solid content, NRET), 2 mmol/L (FRS) and 1 mmol/L (EPR), respectively. Water content was varied by stopping the drying process at different times and remnant water was determined gravimetrically taking completely dried films as reference.

For NRET-experiments films from a 1:1-mixture of phenanthrene- and perylene-doped dispersions were examined in a SPEX-Fluorolog II fluorescence spectrometer. Perylene fluorescence intensities were continuously accumulated ($\lambda_{\text{excitation}} = 293$ nm, $\lambda_{\text{emission}} = 471$ nm).

In FRS experiments the diffusion coefficient of the photochromic dye α-2,5-Dimethyl-3-furylethylidene(isopropylidene)succinic anhydride (ACR540) was determined from the diffusive decay of the FRS intensity, which is given by an exponential in the case of Fickian diffusion3). A standard setup4) was used, applying an argon ion laser (488 nm line) with intensity densities of ~ 100 mW/mm^2, irradiation time ~ 100 ms, and laser spot size ~ 0.2 mm^2.

As ionic and surfactant spin probes the potassium salts of 4-carboxy-2,2,6,6-tetramethyl-piperidine-N-oxyl (K-TEMPO) and of 2-(3-carboxypropyl)-2-tridecyl-4,4-dimethyl oxazolidine-3-oxyl (K-5-DOXYL-stearate) were chosen. The non-ionic probes 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl

(TEMPOL) were used for comparison. EPR measurements were performed at ambient temperature with a Bruker ESP 380 spectrometer at X-band frequencies (about 9.75 GHz).

Results and Discussion

I. Non-Radiative Energy Transfer

The aim of the NRET-experiments is the observation of the interdiffusion of small tracer molecules between polymer particles at early stages of the particle coalescence . In contrast to the interdiffusion of polymer chains[5,6] it can be expected that the diffusion of small molecules reveals more information about the barrier properties of the emulsifier layer covering the particles because of the faster evolution of the energy transfer (ET) during a temperature jump experiment. The NRET and thus the concentration of the acceptor perylene in the vicinity of the donor phenanthrene is quantified via the normalized ET efficiency $E_n(t)$ which is calculated from the on-line measured steady state fluorescence intensities I_A of the acceptor:

$$E_n(t) = \frac{I_A(t) - I_A(0)}{I_A(\infty) - I_A(0)} . \tag{1}$$

Fig. 1a shows $E_n(t)$ for a series of annealing experiments on dried P(BMAcoMMAcoAA) film (water content below 1 wt%) obtained from a 1:1-mixture of phenanthrene and perylene doped dispersions. In these experiments the temperature was increased at t = 0 s from 25°C to the desired temperature.

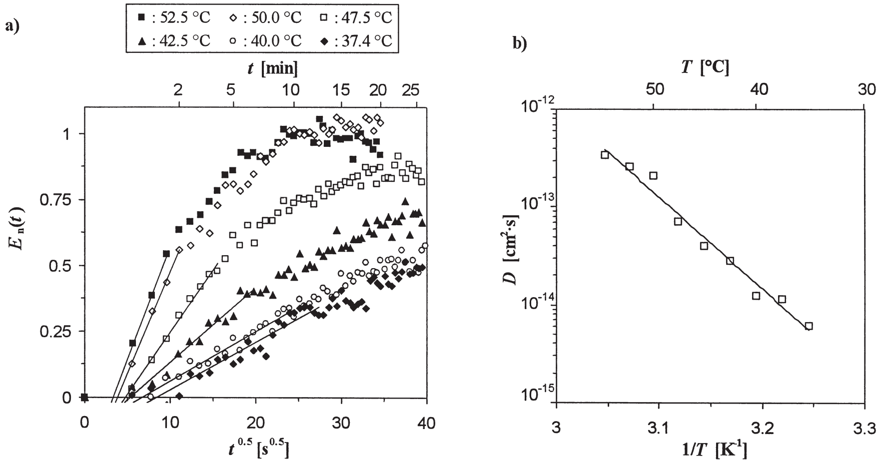

Fig. 1: a) Normalized energy transfer efficiency $E_n(t)$ between phenanthrene and perylene incorporated into P(BMAcoMMAcoAA) latexes plotted vs. $t^{0.5}$ for different temperatures.The initial rise can be described by straight lines (—) according to Eq.2. b) *Arrhenius*-plot of the diffusion coefficients.

The investigated temperature range is below T_g of the polymer (64°C) and hence below the minimal film-forming temperature (MFT). From the slope of the $E_n(t)$ versus $t^{0.5}$ plot the self-diffusion coefficient D of the tracer molecules can be determined according to$^{7,8)}$:

$$E_n(t) = K_x\sqrt{Dt} + a\sqrt{\Delta t}\ . \tag{2}$$

The constant K_x includes the photo-physical properties of the donor-acceptor system (FÖRSTER-radius), the initial acceptor concentration in the acceptor containing particles and the size of the polymer particles; a is a normalization constant. At longer times the diffusion fronts of tracer molecules from different particles meet within a given particle leading to a deviation from Eq.2. The temperature dependence of D is that of an activated process as shown by the *Arrhenius*-plot in Fig.1b. The activation energy E_a of 179 kJ/mol is in the same range as the activation energy for the diffusion of pyrene in bulk poly(isobutylmethacrylate)$^{7,8)}$.

An important feature in Fig.1a is the time lag Δt between the temperature jump and the beginning of the linear increase of $E_n(t)$. This time lag decreases with increasing temperature. It can not be explained by the heating characteristics of the sample and the sample holder. We speculatively interpret this delay as indication for an interdiffusion barrier for the hydrophobic probes most likely due to the hydrophilic interface. Only after this barrier has been removed by diffusion controlled dewetting of the particle surfaces from surfactant molecules and associated water can the diffusion of the fluorophores from one particle to the other take place. The water content at which this occurs during the film formation process is estimated to be less than 1% from comparative gravimetrical analysis.

II. Forced Rayleigh Scattering

FRS measurements were performed at 40°C (T_g + 5 K) on partially filmed P(BMAcoAA) dispersions with water contents between 0 wt% (homogeneous polymer film) and 10 wt% (at higher water contents the samples became too turbid to be measured) prepared by drying at measuring temperature for different amounts of time.

The completely homogenous film (0 % water) yields a FRS intensity decay $I(t)$ indicative of normal Fickian diffusion, i.e. $I(t) = I_0[\exp(-t/\tau)]^2$ with the decay time τ showing q^2 behavior ($\tau^{-1} \propto q^2$; scattering vector $q = 2\pi/\Lambda$, Λ: grating distance). A gradual transition to anomalous diffusion with a different q-dependence and stretched exponential signal decays $I(t) = I_0[\exp(-(t/\tau)^{\beta})]^2$, $0.7 \leq \beta < 1$, takes place with increasing rest water content (Fig. 2a). Literally taken, Fig. 2a implies that the apparent diffusion coefficient depends on the length scale of the experiment (the grating distance Λ). Detailed interpretation of this anomalous diffusion behavior requires appplication of diffusional models treating diffusion in heterogeneous systems which is deferred to future work. Surprisingly, the apparent diffusion coefficient is higher for motion on larger length scales (large grating periods Λ) than on small length scales, which is counterintuitive. However, on the basis of the present data it seems that the diffusional behavior of small probe molecules is capable to capture an essential feature of the film formation process – namely the transition from a heterogeneous dispersion to a homogeneous polymer film. It is noteworthy that this transition takes place at a water content (2-3%) where significant changes in the EPR signal are observed for the same system (see below).

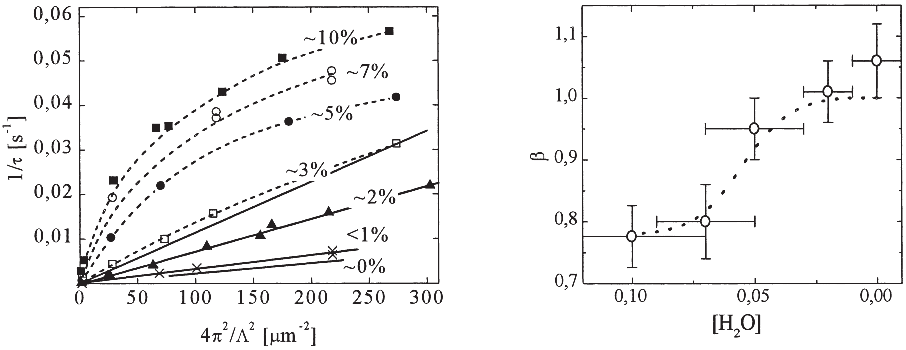

Fig. 2: a) FRS diffusional grating decay rates τ in P(BMAcoAA) films vs. squared grating vector q for different water contents (given at the curves). Solid straight lines indicate q^2 behavior while curved dashed lines are guides to the eye indicating anomalous diffusion. The crossover occurs between 2 and 3% water. b) Line shape parameter β indicating the transition from heterogeneous to homogenous polymer film on decreasing the water content.

III. Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) experiments can access polymer and surfactant dynamics during film formation because the motion of spin probes is influenced by both the dynamics of their environment and by specific interactions with it[9)]. If the motion of the spin probes is slow on an EPR time scale (rotational correlation times $t_c > 10^{-4}$ s), the spectra are broadened by anisotropic interactions. For nitroxides, the most important contribution is the anisotropy of the hyperfine interaction. With increasing mobility, anisotropic interactions are averaged and finally a much narrower isotropic spectrum is obtained for motion that is fast on the EPR time scale ($t_c < 10^{-10}$ s). Motion in the intermediate region is most easily characterized by the total spectral width 2 A_{zz}.

After adding K-TEMPO to any of the provided dispersions we obtained a spectrum containing three sharp lines, implying fast isotropic motion. We therefore conclude that this ionic probe resides mainly in the aqueous phase. Spectra for completely dried films prepared from these dispersions correspond to the rigid limit even if the polymer component has a T_g well below ambient temperature. Considering what is known about probe motion in polymers above T_g, one would expect the probe to be more mobile. This immobilization is most probably caused by an interaction of carboxylate groups of the probe with the ionic endgroups of SDS since similar effects have been observed with this probe in ionomers[10)]. Samples with intermediate water content exhibit spectra corresponding to the isotropic limit for water contents above 3 %

or the rigid limit below 0.5 %, the latter being true only for the high-T_g samples. The samples with a water content between 0.5 % and 3 % show bimodal spectra, which for the high-T_g samples can be simulated by a superposition of the isotropic-limit and rigid-limit with differing weighting coefficients (see Fig.3a). For the low-T_g samples, the spectrum of the mobile component broadens before it vanishes (see Fig.3b).

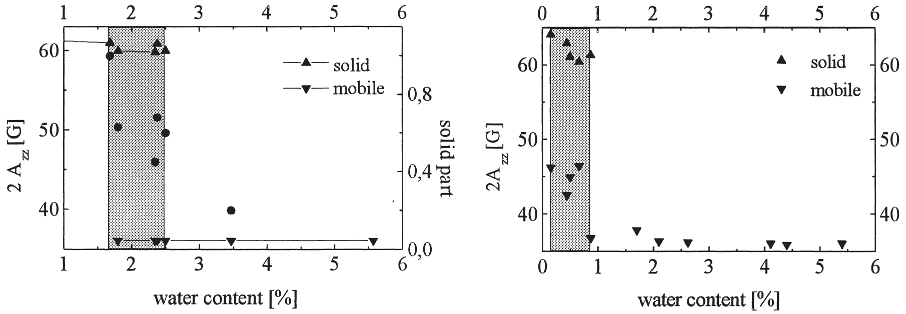

Fig.3: a) Extreme outer peak separation 2 A_{zz} *vs.* water content (triangles) and fraction of solid part vs. water content (circles) for P(BMAcoAA) doped with K-TEMPO. b) Extreme outer peak separation 2 A_{zz} vs. water content for P(BAcoAA).

A similar behavior as for K-TEMPO was found using TEMPOL. The spectra of the completely dried films now reveal some mobility, although still not as much as expected. This indicates specific interactions between the probe and its environment. TEMPOL mobility is correlated to the T_g of the polymer. TEMPO in dry films revealed significantly higher mobility than TEMPOL. The small size difference of the two probes alone cannot explain this.

In analogy to DOXYL-stearate probes in biomembranes, the spectra of the surfactant spin probe K-5-DOXYL-stearate in the dispersions indicate anisotropic motion, i. e., rotation only about the long axis of the surfactant molecule. We therefore conclude that this probe inserts into the surfactant layer on the polymer particle, which forms to a good approximation an one-dimensional liquid crystal. During the drying process the rotation about the unique axis starts to freeze and approaches the rigid limit spectrum for dry films.

These results show that the EPR spin-probe technique is a rich source of information on the dynamics of colloidal polymer dispersions as well as wet and dry films. The motion of K-TEMPO is most likely correlated to motion of the ionic end groups of SDS, and the bimodal behavior in the almost dried films can probably be interpreted as one part being immobilized in the interface between polymer particles and surfactant and the remaining mobile part being located in the interstitial voids. The motion of TEMPOL is hindered by hydrogen binding, as follows from comparison with the results for TEMPO. Whether this binding is to the surfactant or to the polar groups in the polymer itself remains to be seen. The spectra of K-5-DOXYL-stearate contain information about geometry, ordering, and dynamics of the surfactant layer on the particle. Further insight is expected from the quantitative determination of correlation times of each probe that is now in progress.

Conclusions

We have demonstrated that the dynamics of small probe molecules monitored by the different tracer methods – non-radiative energy transfer, forced Rayleigh scattering and electron paramagnetic resonance are able to capture essential features of the film formation from polymer latex dispersions. Remarkably, there is some overlap with respect to the phenomena observed with the different techniques. The water content where anomalous diffusion crosses over to Fickian diffusion in FRS experiments coincides with that where an immobile component appears in the EPR line shapes in one case; the water content where non-radiative energy transfer via interdiffusion of donor and acceptor molecules through the separating interfaces sets in compares well with that one below which EPR sees only a rigid spectrum in another case. Given the inaccuracies involved in the water content determination and keeping in mind that the determined values represent averages over a spatial distribution of water contents due to inhomogeneous drying, further experiments and a more detailed data analysis are clearly necessary to further substantiate our results. In future work we will explore systematically how changes in acrylic acid content, variation of film forming conditions and film annealing affect the observed signatures. From rewetting experiments we expect to gain information on the extent of interface healing under varying film forming conditions.

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