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ORIGINAL CONTRIBUTION

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Measurement of diffusion coefficients of additive molecules in colloidal polymer particles by electron paramagnetic resonance

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Abstract Nonpolar paramagnetic additives mixed into the aqueous serum of colloidal polymer dispersions are absorbed by the polymer particles with a rate that depends on the diffusion coefficient of the additive in the polymer. The absorption leads to an immobilization of the additive which can be detected in the electron paramagnetic resonance spectrum. By fitting the time dependence of the immobilized fraction to the appropriate diffusion model, it is possible to determine the diffusion coefficient of the additive in the polymer if the polymer particles are approximately uniform in size. This opens up a new way to determine diffusion coefficients in the range between 10^{-14} and 10^{-17} cm^2s^{-1}, as are expected for low-molecular-weight additives in polymers below their glass-transition temperature.

Keywords Diffusion coefficient · Polymer latex · Electron paramagnetic resonance · Spin probe · Additive

Introduction

Low-molecular-weight additives are often used to improve polymer performance. Additive leaching thus leads to a degradation of the performance and may ultimately limit the lifetime of the polymer [1]. Furthermore, such leaching can cause environmental problems. As the rate of additive loss is related to the diffusion rate of the additive molecules in the polymer, it is of some interest to determine the diffusion coefficients at the temperature of application, which is quite often below the glass-transition temperature of the polymer. Such diffusion coefficients, which are typically smaller than 10^{-12} cm^2s^{-1}, are also required to predict the rate of drug release from a polymer or the rate of permeation of small molecules through a polymer layer. The well-established sorption techniques [2, 3, 4] are restricted to diffusion coefficients between 10^{-7} and 10^{-11} cm^2s^{-1}. Techniques such as observing the diffusive decay of a holographic pattern by forced Rayleigh scattering [5, 6] or nonradiative energy transfer between two different dyes [7] can access the required range of diffusion coefficients between 10^{-12} and 10^{-16} cm^2s^{-1}; however, they are limited to optically transparent samples. Measurements on tracer molecules that diffuse from the serum into the particles in aqueous polymer dispersions (latices) provide an attractive alternative, as owing to the mesoscopic particle dimensions the tracer concentration in the particles evolves on experimentally convenient time scales of some 10 s to hours. In principle, any detection technique is feasible that can distinguish between the tracer molecules in the serum and in the polymer. In this work, we used electron paramagnetic resonance (EPR) spectroscopy, for which a large variety of tracers (nitroxide spin probes) with different molecular size, shape, and functionalization are available [8, 9, 10]. Our technique is similar to a method introduced by Pekcan and Yusuf [11,12] on polymer particles in nonaqueous solutions, but differs in the quantification of the spectra and in the diffusion model applied.

Experimental

Materials

Poly(butyl methacrylate) (PBMA) latex samples were prepared by BASF AG, Ludwigshafen, from butyl methacrylate, acrylic acid, and styrene or methyl methacrylate by emulsion polymerization at 80 °C using sodium persulfate as initiator. Sodium dodecyl sulfate (SDS) was added as surfactant in a molar ratio of 1:200 with respect to monomer concentration. The resulting dispersions were posttreated with hydrogen peroxide and ascorbic acid after neutralization with sodium hydroxide, yielding a pH of 7.5. The residual monomer content was below 300 ppm. The mean particle size and the particle size distribution were measured using a Malvern Zetasizer 5000, which has a range from 0.005–5 μm. The glass-transition temperature, T_g, of the dried polymer samples was determined by differential scanning calorimetry with a Mettler compensation calorimeter (DSC-30) using a heating/cooling rate of 10 $Kmin^{-1}$. T_g was obtained from the turning point of the second heating cycle. The characteristics of the samples are given in Table 1.

The spin probe 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was selected for its nearly spherical shape, small size (radius of about 0.3 nm), and moderate solubility in water owing to the slightly polar N–O group. It was used as received (Aldrich). An aqueous solution of the spin probe was added to the polymer dispersions to give a concentration of 1 $mmoll^{-1}$ dispersion.

EPR spectroscopy

Continuous wave EPR spectra were recorded using a Bruker ESP380 instrument operating in the X-band (about 9.5 GHz) using a rectangular cavity of the type 4102 ST/8725, a modulation amplitude of 0.1 mT, and a microwave power of 2 mW. The temperature was 294 K for all the experiments. The lower ends (9 mm) of the EPR sample tubes with 4-mm outer diameter were flattened to an outer thickness of 2.7 mm. With these homemade flat cells the resonator Q value was only slightly deteriorated by the aqueous sample.

Results and discussion

The EPR spectrum observed immediately after addition of an aqueous TEMPO solution (lowest trace in Fig. 1) to the polymer dispersions investigated exhibits a bimodal structure, which is best seen by comparing the central line of the triplet (arrow) with the corresponding line in the spectrum of TEMPO in aqueous solution (Fig. 2a). In the course of a few hours, this bimodality becomes even more apparent, as the fraction of the more immobile component, corresponding to the broader lines, increases (Fig. 1). All the spectra in such a time-evolution series can be fitted by a superposition, $w_a I_a(B_0) + w_b I_b(B_0)$, of the spectrum of TEMPO in aqueous solution and the spectrum of TEMPO in the polymer. The latter spectrum (Fig. 2b) was measured after drying the dispersion on the resulting polymer film. A plot showing the typical quality of these fits is also shown in Fig. 2c. Localization of TEMPO in the polymer phase of the film is evidenced by the dependence of the spectral lineshape on the T_g of the polymer [13]. The spectral changes can thus be assigned to diffusion of the spin probe from the serum into the polymer particle. No evidence for a significant third fraction associated with the surfactant layer on the polymer particles was found.

The immobilized fraction, M_t, as a function of time can be determined from the time-dependent weighting coefficients, w_a and w_b, of the spectra corresponding to probes in the aqueous and polymer phase, respectively.

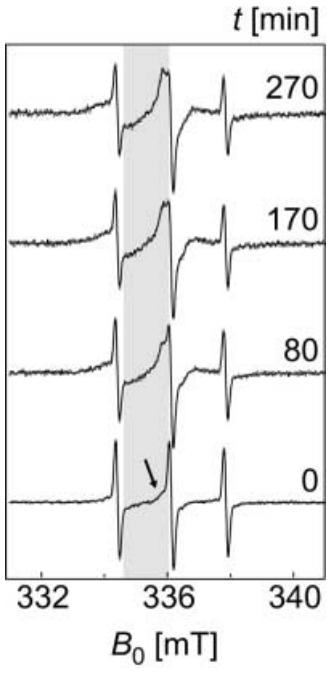

Fig. 1 Time evolution of the electron paramagnetic resonance (*EPR*) spectra of 2,2,6,6-tetramethylpiperidine-1-oxyl (*TEMPO*) in dispersion P(BMA)Co1-1. Time $t = 0$ corresponds to the spectrum measured immediately after addition of the TEMPO solution to the dispersion. The *bar* designates the field region where changes in the lineshape are most apparent. The *arrow* shows a shoulder due to the immobilized fraction observed already in the first spectrum

Table 1 Characteristics of the latices studied (diameter, ∅, particle size distribution, *PSD*, glass-transition temperature, T_g, solid content, *SC*)

Latex	Monomer ratios (wt%)	∅ (nm)	PSD	T_g (K)	SC (%)
P(BMA) Co1-1	BMA:71, AA:1, S:28	179	0.01	320	28.7
P(BMA) Co1-2	BMA:71, AA:1, S:28	103	0.04	320	30.2
P(BMA) Co2-1	BMA:71, AA:1, MMA:28	201	0.39	337	29.1
P(BMA) Co2-2	BMA:71, AA:1, MMA:28	132	0.01	338	29.7

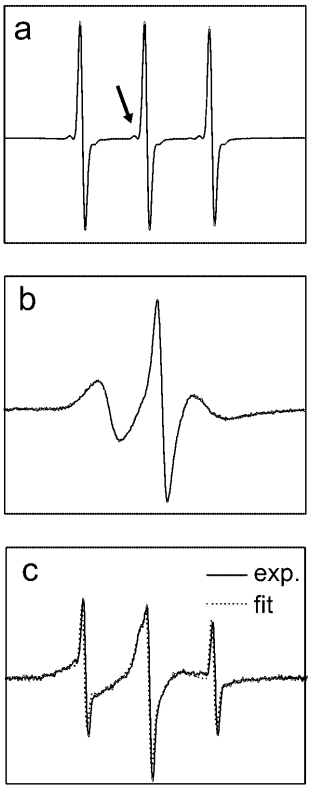

Fig. 2 Fit of bimodal EPR spectra by a superposition of spectra of the mobile and partially immobilized probe. **a** Spectrum of TEMPO in aqueous solution. The *arrow* marks the main difference with the lowest trace in Fig. 1. **b** Spectrum of TEMPO in the dried film of dispersion P(BMA)Co1-1. **c** Spectrum of TEMPO in dispersion P(BMA)Co1-1 at $t = 80$ min (*solid line*) and fit by a superposition of 70% of the spectrum shown in **a** and 30% of the spectrum shown in **b**

We find

$$M_t = \frac{w_b(t) \iint I_b d^2B_0}{w_a(t) \iint I_a d^2B_0 + w_b(t) \iint I_b d^2B_0}. \quad (1)$$

This normalization with the double integrals over the whole EPR spectra is required to obtain correct fractions since the derivative of the absorption spectrum is measured in EPR and peak amplitudes are not proportional to concentrations. Owing to the significantly different linewidths in the spectra of the mobile and immobilized components, the equation based on peak amplitudes, which was used in earlier work [11, 12], thus leads to erroneous results.

To model the diffusion of the spin probe into the polymer particles, we assume that the particles are uniform in size, that the influence of the surfactant layer can be neglected, and that the surface of the polymer particles is homogeneous. The fraction of immobilized spin probes approaches $M_\infty < 1$ at very long times, indicating that at equilibrium a significant fraction of the probes resides in the serum. In the following we assume that the surface of the polymer particle is always at equilibrium with the surrounding liquid. Furthermore, as the diffusion of the probe in the serum is several orders of magnitude faster than in the polymer, no significant concentration gradient is built up in the serum.

We may then use the model for diffusion from a well-stirred solution of limited volume into a sphere of radius r [14]. The time evolution is described by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp\left(-Dq_n^2 t/r^2\right)}{9 + 9\alpha + q_n^2\alpha^2}, \quad (2)$$

where the q_n are the nontrivial solutions of the equation

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}, \quad (3)$$

and the parameter α is given by

$$\alpha = \frac{1}{M_\infty} - 1. \quad (4)$$

This parameter is thus related to the equilibrium constant for the distribution of the spin probes between the solution and the spherical particles. We found that both D and and the starting time, t_0, relative to the time of the first measurement, had to be treated as fit parameters. For numerical simulations, we computed the sum in Eq. (2) up to $n_{max} = 100$, which ensures convergence at all experimentally accessible times t. Fits with $n_{max} < 8$ gave significantly different parameters and higher root-mean-square errors.

This diffusion model fits the experimental data well, as can be appreciated from the agreement of the solid line with the data points in Fig. 3. The diffusion coefficients and apparent starting times for all four samples investigated are summarized in Table 2. The simplified model used in earlier work [11, 12], which assumes constant concentration in the serum, does not agree with our data (dashed line). This simplified model would be a good approximation only for $M_\infty \ll 1$. For our samples, it gives values of D that are too large by a factor of 3–6.

There are few data in the literature for diffusion coefficients of additives significantly below the T_g of the polymer. However, the order of magnitude (10^{-16}–10^{-15} cm^2s^{-1}) for reduced temperatures, T/T_g, between 0.87 and 0.92 is in the same range as reported (10^{-16} and 10^{-14} cm^2s^{-1}) for the slightly larger tracer 2,2′-bis(4,4-dimethylthiolan-3-one) at $T/T_g = 0.95$ in polystyrene (10^{-16} cm^2s^{-1}) and poly(bisphenol A carbonate) (10^{-14} cm^2s^{-1}) [6].

The apparent starting times, t_0, which have to be added to t in Eq. (2), are significantly longer than the actual time between the mixing of the TEMPO solution with the dispersion and completion of the first EPR measurement (approximately 1.3 min). This indicates

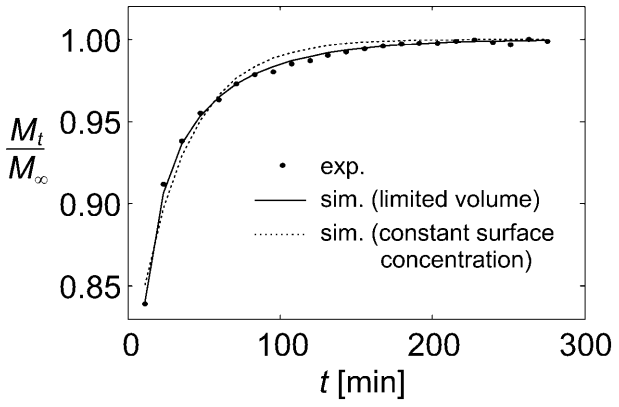

Fig. 3 Time evolution of the immobilized fraction of TEMPO spin probes in dispersion P(BMA)Co1-1 (*filled circles*) and fit by a diffusion model for spherical particles of uniform size in a solution of limited volume (*solid line*) corresponding to $D = 1.37 \times 10^{-15}$ cm^{2}s^{-1}. The *dashed line* is a fit by a simplified model assuming constant probe concentration in the serum. Note that a large fraction of the spin probes are already immobilized at the time of the first measurement

Table 2 Diffusion constants, D, and apparent starting times, t_0, of the diffusion process for the samples listed in Table 1

Latex	D (10^{-15} cm^{2}s^{-1})	t_0 (min)
P(BMA)Co1-1	1.37	–6.5
P(BMA)Co1-2	1.06	–11.5
P(BMA)Co2-1	0.69	–7.3
P(BMA)Co2-2	0.30	–9.6

that a substantial fraction of the spin probes is immobilized faster than the diffusion kinetics suggests. Using the experimental data for the particle size distribution, we checked that the effect cannot be explained by deviations from the assumption of a uniform particle size. We tentatively assign this effect to fast adsorption of a fraction of the tracers on the polymer surface.

We also checked if the apparent diffusion coefficient, D, depends on particle size. For copolymer P(BMA)-Co1, which contains styrene as a comonomer, the apparent diffusion coefficient decreases by 25% when changing the average particle diameter by 74% from 179 to 103 nm (Table 2). Although the deviation between the two values may be acceptable for most practical applications, it is larger than the expected statistical error. An even larger decrease of D with decreasing particle size is observed for copolymer P(BMA)Co2, which contains methyl methacrylate as a comonomer.

Since aging effects may well induce differences in diffusion coefficients as large as this [6], this unexpected trend in D may be due to differences in the preparation procedure for the latices with different particle size. Alternatively, one of the model assumptions may not be strictly fulfilled. In fact, the surface of the polymer particles is not homogeneous, as the surface coverage by the surfactant is less than 100%. As the amount of surfactant per monomer used in the preparation of the dispersions was the same, the smaller particles have a significantly smaller surface coverage compared to the larger particles. Therefore, the apparently slower diffusion in the smaller particles may be a consequence of surfactant-assisted adsorption of the spin probe on the polymer surface. Exact values would then be obtained for a surface coverage of 100% and would be close to the results for the larger particles. Finally, the trend of D could also be due to non-Fickian diffusion as observed by Quijada-Garrido et al. [3] for an additive in isotactic polypropylene. However, in this case the good agreement between the diffusion model and the experimental data seen in Fig. 3 would be surprising. The experimental error in determining the immobilized fraction of spin probes as a function of time causes an error of the diffusion coefficient well below 10% and is thus significantly smaller than the estimated uncertainties of about 30–40% caused by aging effects and surface inhomogeneities.

Conclusion

Diffusion coefficients between approximately10^{-16} and 10^{-15} cm^{2}s^{-1} were measured by EPR spectroscopy for nearly spherical additive molecules with a radius of 0.3 nm inside dispersed polymer particles at reduced temperatures between 0.87 and 0.92. The method should be applicable for diffusion coefficients within the range from 10^{-17} to 10^{-14} cm^{2}s^{-1} for particle sizes between 50 nm and 1 μm. Owing to the high sensitivity of EPR, tracer concentrations of only 1 mmoll^{-1} dispersion are required, so plastification by the tracer is negligible and even very weakly polar tracers can be added as aqueous solutions to the serum of the dispersion. The method should also be applicable to polymers containing pigments and for the characterization of diffusion into core–shell particles, which are cases for which no alternative method has been established.

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