POLYETHYLENE NANOPARTICLE DISPERSIONS STUDIED BY X-BAND CW-ESR SPECTROSCOPY

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Introduction

Electron spin resonance spectroscopy (ESR) has been widely used to study properties of polymers, e.g. microviscosity or polarity, on a local scale as sensed by spin probes. The underlying principle is the very high sensitivity of rotational and lateral diffusion of a spin probe to its environment.[1] Nitroxide free radical spin-probes have been studied most intensely for this purpose because of their rather high chemical stabilities. In general, three lines are observed in a continuous-wave (CW) ESR nitroxide spectrum due to hyperfine coupling between the electron spin and the nuclear spin of ^{14}N, which is characterized by the splitting between the outermost extrema in the spectra ($2A_{zz}$'). In addition, the shape of the ESR spectra can be strongly altered by interactions between spin probes and the surrounding medium. The film formation process from dispersions,[2] and phase transitions,[3,4] particularly glass transitions, in polymers have been studied by ESR probe or label techniques.

We have recently reported aqueous dispersions of nanoscale polyethylene (PE) crystals, consisting of a single lamella of only 6 nm thickness and with a lateral pseudo-diameter of ca. 12 nm.[5] In addition to these dispersions (**I**) composed of linear PE, dispersions (**II**) with similar overall particle size but composed of branched (50 methyl branches per 1000 carbon atoms), low crystalline PE are accessible.[6] The uptake of fluorescence probes as guest molecules by the dispersed particles was observed by optical spectroscopy.[6] The environment experienced by these guests can be switched by the melting/crystallization[7] of the PE nanoparticles, and the temperature at which this occurs can be controlled by the degree of branching of the polymer. Here we present preliminary results on spin probes as a reporter for the interactions of guest molecules with the PE particles.

Experimental

Nitroxide spin probe **1** was prepared according to [8]. **2** was used as received from Aldrich. PE dispersions were prepared according to [9]. In brief, an aqueous surfactant-containing solution of the water soluble catalyst precursor [{^{2}-*N,O*-6-C(H)=N(2,6-{3,5-R$_2$C$_6$H$_3$}$_2$C$_6$H$_3$)-2,4-R'$_2$C$_6$H$_2$O}NiMe(L)] (R = CF$_3$ for preparation of dispersion **I**, R = CH$_3$ for preparation of dispersion **II**; L = di- or trisulfonated triphenylphosphine) was exposed to 40 atm ethylene pressure at 15 °C for 30 min, which affords polyethylene dispersions with particle sizes of ca. 10 nm as determined by dynamic light scattering (DLS, 173° backscattering). The bulk crystallinity of the polymers from dispersion **I** and **II** are 60% and <20%, respectively, as determined by differential scanning calorimetry (DSC). Surface tensions of the as prepared dispersions are > 60 mN m^{-1}, that is they contain no free surfactant micelles.

Spin probes were added to the PE dispersions as a solid. After equilibration at room temperature overnight, the dispersions were filtered through a 0.45 μ filter to remove undissolved excess probe. Continuous wave ESR spectra were recorded using a MiniScope 200 CW ESR spectrometer (Magnettech GmbH, Berlin) operating in the X-band (~9.4 GHz) with a modulation amplitude of 0.05 mT. Temperatures were controlled via a variable temperature unit (Magnettech). The spectrum at a given temperature was recorded after thermal equilibration for 10 min. After measurements at high temperatures, the dispersions were studied again by DLS to ensure that no coagulation had occurred.

Results and Discussion

Two nitroxide free radical spin probes, **1** and **2**, with different polarity were employed. Aqueous suspensions of pyrene-TEMPO (**1**) do not show any ESR signal due to its very low solubility in water. However, in the presence of SDS micelles a characteristic fast regime spectrum with anisotropic rotational features was obtained at 20 °C. In dispersion **I** the probe performs much more anisotropic motion, as evident, for example, from a drastic intensity decrease of the high field line. In addition, the apparent hyperfine coupling constant ($2A_{zz}$') appears even larger than in SDS micelles, although the probes taken up

by the particles sense much less polarity than in micelles according to the aforementioned fluorescence studies.[6] This probably results from an extra broadening effect due to the high microviscosity of the polymer phase and restricted slow motion in the particles, which is supported by the increase of the widths of all three lines, particularly of the high field line.

1 pyrene-TEMPO   **2** DOXYL-cyclohexane
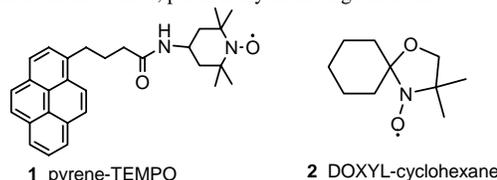
With increasing temperature, narrowing of the whole spectra was observed. The extreme separation $2A_{zz}$' decreased from 38.5 G at 20 °C to 34.5 G at 150 °C. This can be related to a faster rotational motion at higher temperature, and probably also to an increased contribution due to a lower-polarity environment, the latter corresponding to the polymer phase rather than the particle interface. Note that, in comparison to the isotropic spectrum in SDS micelles at 110 °C, the spectrum in dispersion **I** at 150°C still shows residual anisotropy, i.e. a larger linewidth and lower amplitude of the high field line. This confirms the incorporation of probe **1** in the PE particles and its restricted rotational motion in the polymer phase. Interestingly, in the temperature range where the crystallization in the particles[7] occurs during cooling from high temperature (T_c = 75 °C for dispersion **I**), a two-component feature of splitting of the high field line was observed (Figure 1, spectrum at 80 °C). This may be explained by assuming that at temperatures corresponding to only partial, incomplete crystallization during cooling, a fraction of particles exists in which the probes are located more towards the molten interior of the particles, and another fraction in which they are located in the amorphous periphery covered with surfactants. Simulation with a suitable model can afford quantitative information of the probe distribution.
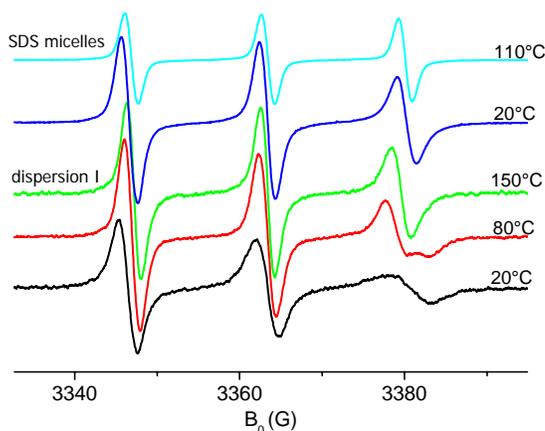

Figure 1. ESR spectra of probe **1** in SDS micelles and in dispersion **I** at different temperatures (spectra taken during cooling cycle).

DOXYL-cyclohexane (**2**) is slightly more hydrophilic than pyrene-TEMPO (**1**). In neat water, an isotropic spectrum with large extrema separation and narrow peak-to-peak linewidth was observed due to the high polarity and low viscosity of water. The spectra in both dispersion **I** and **II** show much more anisotropic features with an extra broadening effect resulting from restricted slow motion of the probe in the particles, as was observed in the case of probe **1** as well. The restraining effect seems to be slightly stronger in dispersion **I**, which is compatible with a higher degree of crystallinity of the particles.[4] However, after applying two heating/cooling cycles exceeding T_m, different effects on the spectral lineshape are observed in dispersion **I** and **II**, respectively (Figure 2).
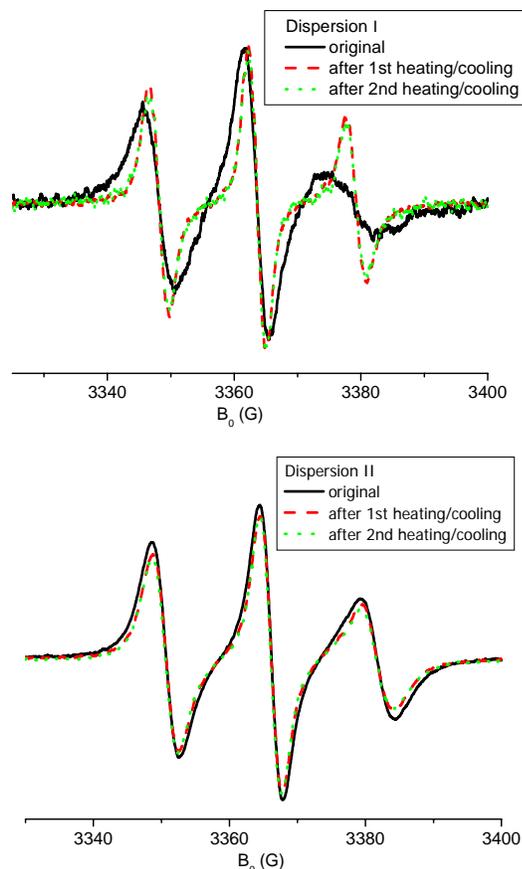
Figure 2. ESR spectra of probe **2** obtained at a temperature of 20°C in dispersion **I** (top) and **II** (bottom) before and after applying one and two heating/cooling cycles.

In dispersion **II**, after applying two heating/cooling cycles the spectra taken at 20°C were not changed in terms of lineshape and linewidth. In contrast, in dispersion **I**, after one heating/cooling cycle significant line narrowing was observed for all three lines, and in particular for the high field line. In addition, the relative amplitude of the high field line increased to a large extent, which indicates somewhat less restricted and faster motion. The second heating/cooling cycle did not result in further change of the spectrum. This observation suggests that the distribution of probes in the particles of dispersion **I** may have changed after the first heating/cooling cycle. Such a change in the distribution might result from a change in the lamella thickness of the crystalline phase. In this context, the spatial distance distribution of the probes can be elucidated by pulse ESR studies.

In summary, spin probes with adequate hydrophobicity are taken up by the PE nanoparticles in aqueous dispersions. Quantitative determination of the distribution of the probes in each phase is rather complex due to significant surface contributions with the very small particles investigated. A comprehensive picture of the probe location in a given system and its temperature dependence requires further studies.

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