^{1}H NMR Study of the Association of Hydrophobically End-Capped Poly(ethylene oxide)

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Introduction

Hydrophobically end-capped poly(ethylene oxide) (PEO) belongs to the family of the associative polymers and has industrial importance, for instance, as a modifier of rheological properties. When dissolved in water, hydrophobic ends associate into microdomains, which act as reversible links between polymer chains, leading to the formation of a transient network. Industrial products are principally (ethylene oxide)−urethane copolymers (HEUR) for which the large polydispersity and the presence of urethane groups may influence the association phenomena.[2] Therefore novel synthesis methods have been developed to obtain model systems without urethane groups and with small polydispersity.[1]

Properties of aqueous solutions of model PEO end-capped with alkyl groups have been studied by several techniques: fluorescence spectroscopy,[1−5] viscometry,[1−4] pulse gradient spin−echo nuclear magnetic resonance,[5−7] and dynamic light scattering (DLS).[3]

In a previous work, we investigated the associative character of poly(ethylene oxide) (PEO) end-capped with dodecyl groups using static (SLS) and dynamic (DLS) light scattering and viscometry.[8] A systematic study of the effect of functionalization has been carried out by comparing results on unmodified PEO with PEO of the same molar mass end-capped at one or both ends. The effect of the molar mass of the PEO chains was also studied, showing a reduction of the associative properties with increasing molar mass.

Here, we report for the same samples results from nuclear magnetic resonance (NMR) measurements. The chemical shift of atoms depends on their environment, which is polar in the free state and apolar in the associated state. NMR measurements can therefore give complementary information on the association of the alkyl end-groups. NMR has been used before to determine the critical micelle concentration (cmc) for classical surfactants.[9] Quite recently Petit et al.[10] have studied the associative behavior of hydrophobically modified poly(sodium acrylate) using NMR.

Experimental Section

Materials. Commercial PEO (Hoechst) with different molar masses were purified and functionalized at one (ω) or both ends (α,ω) with dodecyl groups using a method reported elsewhere.[1] The degree of substitution of the hydroxyl groups was determined by NMR and was found to range from 85% to 100%. The polydispersity of the unmodified polymers was determined by size exclusion chromatography (SEC) (see Table 1). Solutions were prepared in D_2O.

Table 1. Characteristics of the Samples

	α,ω PEO35	α,ω POE20	α,ω POE10
M_w/M_n[a,e]	1.03	1.02	1.1
M_w (kg/mol)[b,e]	34 ± 2	18.8 ± 0.7	8.7 ± 0.5
R_g (nm)[c,e]	9.4	6.7	4.2
C^* (g/L)[d,e]	16	25	45
cmc NMR (g/L)	19.5	18	6.4
cmc fluorescence (g/L)[f]	5	5	0.1
cmc LS (g/L)[g]	10	9	1.5
C_{gel} (g/L)[g]	38	24	14

[a] Obtained from SEC.[3,4] [b] Measured by static light scattering.[8] [c] Calculated from the relation $R_g = 0.215\ M^{0.583}$ given in ref 12. [d] Using $C^* = 3M_w/(4\pi R_g^3 N_a)$. [e] Measured on the nonmodified homologue. [f] From ref 1. [g] From ref 8.

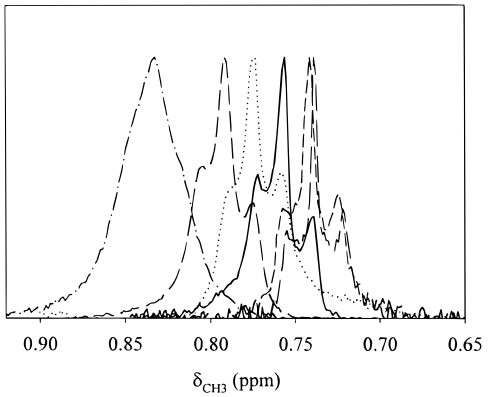

Figure 1. ^{1}H NMR spectra of the terminal methyl group of α,ω PEO20 at different concentrations in D_2O. From right to left C = 3, 10, 20, 30, 100, and 200 g/L.

NMR. ^{1}H NMR spectra were obtained on a Bruker AC400 spectrometer operating at 400.1 MHz. We used a spectral width of 8064 Hz and a flip angle of 30°. The acquisition time was 2.03 s, and the delay time was 1 s. The number of scans was 160, 320, or 960 depending on the concentration and the molar mass. The signal from residual H_2O was used as an internal reference.

Results

Figure 1 shows part of the ^{1}H spectrum of α,ω PEO20 at different concentrations in D_2O. For clarity, we have only plotted the signal of the terminal methyl group, which splits into a triplet due to the spin−spin coupling with the proton nuclei of the adjacent CH_2 group. For the other protons of the paraffinic end groups, the effect of the concentration on the signal is the same. At low concentrations, the signal is independent of the concentration within the experimental error. Above C = 18 g/L the triplet moves to larger chemical shift with increasing concentration. By analogy with classical surfactants, we call cmc the concentration above which the chemical shift increases. At all concentration we observe a single triplet, which means that the exchange of polymer chains between the free state and the associated state is fast with respect to the NMR characteristic time scale: $\tau_{NMR} = 2^{1/2}/(\pi\Delta\nu)$, where $\Delta\nu$ is the difference between the resonance frequencies in

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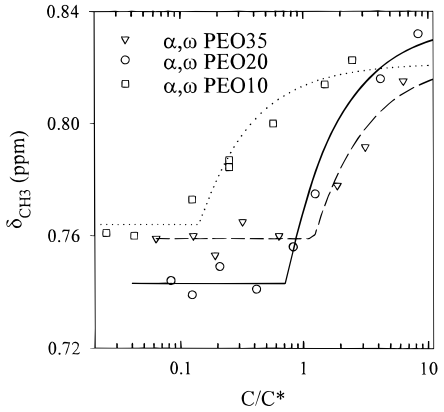

Figure 2. Concentration dependence of the chemical shift of the terminal methyl group for α,ω PEO35 (triangles), α,ω PEO20 (circles), and α,ω PEO10 (squares). Solid lines represent least-squares fits to eq 1.

the free and associated state. In our case $\Delta\nu = (36 \pm 4)$ Hz, so that $\tau_{NMR} = 12 \pm 2$ ms. τ_{NMR} is indeed larger than the resident time of a paraffin group in the hydrophobic micro domain as deduced from pulsed-gradient spin−echo NMR experiments ($\tau = 0.1$ ms).[5] It is also larger than the relaxation time of a macroscopic shear strain.[11] With increasing concentration, the triplet signal merges. The loss of resolution can be understood in terms of a decreasing mobility on the NMR time scale.

Molar Mass Dependence. In Figure 2, we have plotted the chemical shift values versus the polymer concentration for three molecular weights. The results can be fitted assuming a distinct two-phase model like that used for classical surfactants:[9]

$$\delta = \delta_u \qquad C < \text{cmc}$$

$$\delta = \text{cmc}\ \delta_u + (C - \text{cmc})\ \delta_m \qquad C > \text{cmc} \qquad (1)$$

Here δ_u and δ_m are the intrinsic chemical shifts of free and associated terminal methyl groups, respectively. Cmc values increase with the molar mass (see Table 1) which reflects the decreasing associative character.

Discussion

Three steps can be distinguished in the association of end-functionalized polymers. Above a certain concentration the polymers associate into well-defined small aggregates containing a single multiplet of end groups. This step bears close analogy to micelle formation of classical surfactants. At a higher concentration these "micelles" can bridge if the polymers are functionalized at both ends. As a consequence, aggregates are formed with increasing size and polydispersity as the concentration increases. This second step can be described in terms of an open association model. When the aggregates fill up the whole space, a transient network is formed, possibly described by the percolation model. Sometimes instead of a space-filling network a phase separation occurs between a polymer rich transient gel phase and solvent rich phase. In telechelic ionomers the three steps are clearly distinguished and occur at well-separated concentrations.[13] Our previous study of PEO end-capped with dodecyl groups using light scattering and viscometry measurements showed that the first two steps occur simultaneously for the higher molar mass samples.

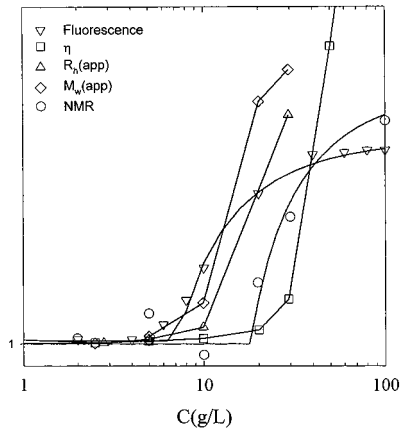

Figure 3. Comparison of the concentration dependence of the experimental signal from different techniques for α,ω PEO20: apparent molar mass from SLS (◇); apparent hydrodynamic radius from DLS (△); viscosity (□); ratio of the third to the first pyrene fluorescence peak (▽) and chemical shift from NMR (○). In each case, the signal is normalized by the signal from unfunctionalized PEO20.

Different experimental techniques are sensitive to different steps in the association. NMR and fluorescence spectroscopy are sensitive only to the first step, i.e., the association of end-group into multiplets. Static and dynamic light scattering measure the increase of the average molar mass and size, respectively. However, the effect of interactions dominates the signal at concentrations above the overlap concentration (C^*). These techniques are thus sensitive to the first two steps if they are well separated and occur below C^*. Viscometry is sensitive mainly to the third step, i.e., the formation of a transient gel.

For the α,ω POE35 and α,ω POE20, we observe a relatively good agreement between the different techniques. However, for the α,ω POE10 a smooth transition is observed both in SLS and NMR. The value of cmc from SLS measurements given in the table corresponds to the concentration where the molar mass and the hydrodynamic radius start to increase. The value from NMR measurements results from the fit shown in Figure 2 and is probably overestimated. The much lower value found in fluorescence measurements could be due to an influence of the pyrene probe.

In Figure 3 we compare the concentration dependence of the experimental signal from the five different techniques mentioned above for the same sample (α,ω PEO20). The signal is normalized by that of the unfunctionalized sample. The increase occurs at approximately the same concentration for all techniques, which are sensitive to the initial association. The increase of the viscosity marks the formation of a transient gel (C_{gel}). The small difference between the cmc and C_{gel} can be explained by the fact that the cmc is close to C^* for the sample investigated (see table).

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