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Influence of the Grafting Ratio on the Conformations of Poly(ethylene oxide) Chains Grafted on Silica

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ABSTRACT: ESR spectroscopy of labeled grafted poly(ethylene oxide) chains has been used to estimate the ratio of the population of free end segments in solution to that of adsorbed ones on a silica surface as a function of temperature. The influence of the grafting ratio is investigated. Grafted molecules of molecular weight 1000 with grafting ratios of 0.17 and 0.37 molecule/nm² are in contact with benzene. The measured values are consistent with a flat conformation of the chains and some longer dangling tails.

Introduction

Grafted polymers, owing to their numerous potential applications, now give rise to a large number of studies, both theoretical^{1,2} and experimental.³⁻⁹

In the present investigation, the configuration of poly(ethylene oxide) (PEO) chains grafted on silica is examined by the spin-labeling technique. A nitroxide-type free radical is fixed at the free end of some chains. The electronic paramagnetic resonance signal is then split into two parts: a spectrum with a broad line width, characteristic of immobilized end segment adsorbed on the surface, and narrow lines characteristic of mobile end segments in solution. The measurement of the ratio of the fast to slow populations allows then comparisons with the theoretical models for the concentration profile.

Here in particular the influence of the grafting ratio on the configurations of low molecular weight chains is examined and some characteristic features of the tail behavior are discussed.

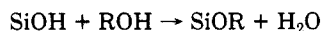
Experimental Section

Silica. The solid support was pyrogenic, nonporous Aerosil 300 silica from Degussa. The particles have a diameter of about 10 nm, a specific area, measured by nitrogen adsorption, of 200 m²/g, and 3.3 silanol groups per nm². The silica was dehydrated by heating at 300 °C under vacuum for 3 h.

Oligomers and Polymers. Mono-, di-, tri-, and tetraethylene glycols from Fluka were used without purification. Poly(ethylene oxides) (PEO) were supplied by Merck and are designated PEO 400 (number of repeating units $N = 9$) and the PEO 1000 ($N = 23$).

All compounds were dried at 70 °C under vacuum for 3 h.

Grafting. The grafting reaction is the direct esterification of the silanol groups by the hydroxyl end groups of the compound.



The silica was dispersed in an excess of PEO, carefully degassed, and heated at 230 °C for 16 h under a nitrogen atmosphere. The reaction product was then dispersed in acetone, filtered, and solvent extracted for 1 day. The grafted silica was dried at 60 °C under vacuum. The grafting ratios were determined by pyrolysis weight loss at 700 °C (Table I).

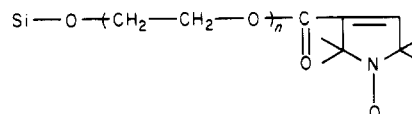
According to Howard and McConnell¹⁰ and Couper and Eley,¹¹ who observed PEO in very flat conformations, the area occupied by a monomer unit is about 20 Å. The different grafting ratios were obtained by using two different synthesis temperatures, 113 and 160 °C.

Spin Labeling. The bonding reaction of the free radical nitroxide, 3-carboxy-2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl, was the same as previously described^{5,6,9} for short chains and was the direct esterification of the label for PEO 1000. After labeling, the grafting ratios were measured once more by pyrolysis and were found to

Table I
Grafting Ratios of PEO 1000 Measured by Pyrolysis

sample	grafting ratio
PEO 1000 ($N = 23$) grafted on Aerosil at 113 °C	9.4% in weight or 0.27 molecule/nm ²
after spin labeling	5.7% in weight or 0.17 molecule/nm ² or 0.04 molecule/a ²
PEO 1000 ($N = 23$) grafted on Aerosil at 160 °C	17.7% in weight or 0.53 molecule/nm ²
after spin labeling	12.6% in weight or 0.37 molecule/nm ² or 0.09 molecule/a ²

be somewhat lower (Table I). The labeled molecules have the following chemical formula:



About 1% of the chains were labeled, but the signal was strong enough to allow the measurements.

Samples. The grafted silica was put in contact with benzene, a good solvent of PEO. The well-known Flory interaction parameter between solvent and polymer is $\chi = 0.2$ at 25 °C.¹² The tubes were sealed under vacuum after repeated freeze-pump-thaw cycles.

ESR Spectroscopy. The ESR spectra were recorded on a Varian E-4 spectrometer at X-band. The temperature controller was an E-257 Varian. Each time, 10 min was allowed for thermal equilibration of the sample.

Our method of analysis of the spectra has been described previously^{6,9} and is shown in Figure 1. At high temperatures (above 50 °C) the spectrum consists of three narrow lines due to the fast motion of the label. Such a spectrum is explained by the Kivelson theory.¹³ The faster is the motion, the narrower are the lines. This motional narrowing is well-known in magnetic resonance and occurs in our case when the rotational correlation time is less than 3×10^{-9} s.

Toward the low temperatures (below -40 °C) the spectrum has a shape influenced by the anisotropic part of the Hamiltonian, not wholly averaged in the slow-tumbling region. The spectrum is explained by the more comprehensive Freed theory.¹⁴ In the most interesting region the spectra of grafted labeled PEO appear as a superposition of the two types of lines described before; they have already been reported for other grafted⁵⁻⁷ and physically adsorbed polymers.¹⁵⁻¹⁷

The analysis of these two-state spectra proceeds in the following way: the fast-motion spectrum is calculated on a HP 9825 computer using the Kivelson theory. Then it is superimposed on the experimental spectrum, focusing attention on the high- and low-field lines. After two integrations of the simulated and the

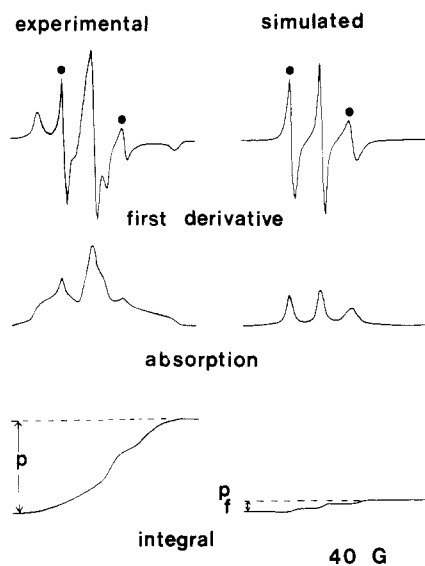


Figure 1. Method of analysis of the EPR spectra: the fast-motion theoretical spectrum is adjusted on the experimental spectrum and the integrals give the respective populations.

experimental spectra, one obtains the populations of fast and slow labels.

Our purpose was to illustrate the main features of the phenomena, and we do not claim extreme precision.

Results and Discussion

Predictions on the Concentration Profile. As a theoretical reference point, we shall take a simple random walk model on a cubic lattice, which is not dependent on the detailed chemical structure of the chain. There are several criticisms that can be made against this model. It is suitable for very long chains, but ours are a little too short. Moreover, when the grafting ratio is low, the self-consistent approach is not very successful and when most of the segments are in close contact with the surface, the calculated configurations are only roughly correct. Indeed this approach is rather macroscopic and does not take into account fluctuations of concentration² but it has the advantage of being tractable. Therefore we shall not try to obtain an exact numerical agreement between theory and experiment but instead compare the main features of the phenomena.

However, it is important to have a well-defined model in order to explain the meaning of the measurements.

Like Rubin¹⁸ we distinguish the layer parallel to the surface at a distance qa (where a is the length of a monomer unit and q is an integer) by the index q . A mean field theory by Levine¹⁹ then allows the calculation of the unnormalized probability for the n th link being in the q layer $P_q(n)$ by a recurrence formula. The model used is rather similar to the one of Jones and Richmond.²⁰

The measured slow and fast populations are then defined from the density profile $P_q(n)$ by

$$P_f \sim \sum_{q=1}^N P_q(N)$$

$$P_s \sim P_0(N)$$

where N is the number of repeating units of the chain. These expressions are realistic only if we assume that the main hindrance to the motion is due to adsorption. Apparently, the fast isotropic motion of the label results from the motion of a short segment.²¹

Denoting by E the adsorption energy of a monomer unit, by χ the polymer-solvent interaction parameter of the well-known Flory-Huggins theory,²² and by S the grafting

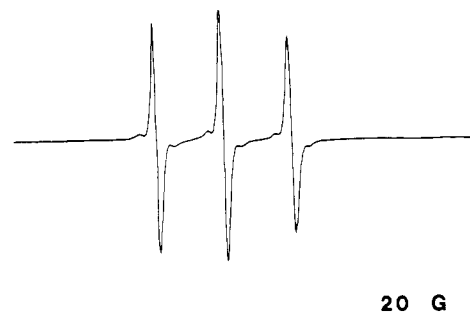


Figure 2. Spectrum of PEO 1000 grafted on silica with a high grafting ratio ($S = 0.37$ molecule/nm² or $S = 0.09$ molecule/ \AA^2) at 22 °C in C₆H₆.



Figure 3. Spectrum of the PEO 1000 grafted on silica with a low grafting ratio ($S = 0.17$ molecule/nm² or $S = 0.04$ molecule/ \AA^2) at 22 °C in C₆H₆.

ratio in molecules for an a^2 area, the following predictions can be made from the simplest theories. For an ideal isolated chain the calculated concentration profile is an exponential decay (see, for example, ref 23):

$$P_q(n) \sim \exp(-(E/kT)q)$$

Such a behavior leads to the law

$$P_f/P_s \sim \exp(-E/kT)$$

For interacting chains, however, the profile is more complicated but still decreases exponentially at great distance from the solid.^{19,20} An additional factor appears, containing the quantity $NS(1 - 2\chi)$. When the segment density on the surface increases, the chain spreads out in solution.

The influence of the major physical parameters, temperature, molecular weight, grafting ratio, and solvent quality, are thus characterized from a theoretical point of view, and the predictions can be compared with the experimental results, at least qualitatively.^{6,9} As our chains are labeled on the end segment, our aim is to test the behavior of the tail in this flat conformation and to compare it with the model described here.

Influence of the Grafting Ratio. The effect of the grafting ratio is shown in Figures 2 and 3 for PEO 1000 ($N = 23$) on silica in contact with benzene, a good solvent. The spectrum at room temperature for the sample with the lower grafting ratio is clearly a composite, whereas the fast population only remains detectable when the grafting ratio is multiplied by a factor of 2. Quantitatively, in the region where the spectra are composite, the ratio of fast to slow population as a function of the inverse of absolute temperature fits a vant Hoff type of law (Figure 4) (uncorrected for the specific adsorption of the label)

$$\ln(P_f/P_s) = -A/T + B$$

The values of A and B are given in Table II. When this result is compared with the theoretical predictions, the meaning of the parameters A and B is clear: A is an

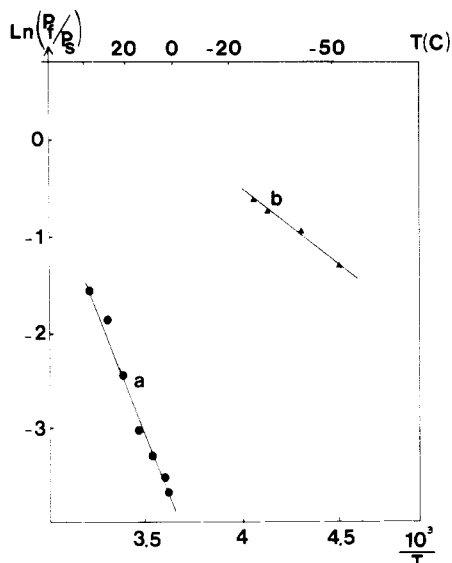


Figure 4. Evolution with temperature of the ratio of the two populations of labels (fast to slow) for PEO 1000 grafted on silica in C_6H_6 with grafting ratio $S = 0.17$ molecule/nm² or $S = 0.04$ molecule/a² (●) and $S = 0.37$ molecule/nm² or $S = 0.09$ molecule/a² (▲).

Table II
Experimental Values of the A and B Parameters
Characterizing the Evolution of the Two Populations with
Temperature

sample	A , kJ	A , eV	B
PEO 1000, $S = 0.17$ molecule/nm ²	40	0.45	15.5
PEO 1000, $S = 0.37$ molecule/nm ²	12	0.14	6.0

adsorption energy and B an entropic term. The values are rather high, indicating a strong adsorbing surface.

When the grafting ratio increases, the fraction of labels mobile in solution at a given temperature increases. Indeed at low grafting ratio, the chains have a flat conformation on the surface. When the grafting ratio increases, the chains spread out in solution: they do interact, repel each other, and adopt a more extended configuration. This evolution is qualitatively in agreement with the theoretical model.

Moreover, when the segment density on the surface increases the slope A of the experimental law decreases. This tendency is confirmed by earlier studies on the influence of the chain length.⁹ The surface sites appear more active when the chain coverage is lower, and therefore the adsorption energy of the end segment is greater.

Tail Length. It is now important to know what is the mean number of links in a dangling tail in solution. For this discussion we shall focus our attention on the sample with the lower grafting ratio, $S = 0.04$ molecule/a², in the vicinity of the room temperature, where the influence of the solvent is well-known ($\chi = 0.2$).

With an experimental value of $\ln(P_f/P_s) = -2$ at 22 °C, the chains should adopt a very flat conformation, and in particular the tails should be very short. On Figure 5 are reported the spectra of short grafted molecules: $N = 1, 2, 3, 4$, and 9 at room temperature. These spectra are very different from that for $N = 23$; as the line width of the fast-population spectrum depends on the mobility of the label, it can be concluded that the tails for $N = 23$ must consist of at least 4–9 repeating units. It appears that the few tails are rather long and much longer than is predicted by the theory used here.

This result must be compared with SANS measurements by Cosgrove³ which give the concentration profile of ad-

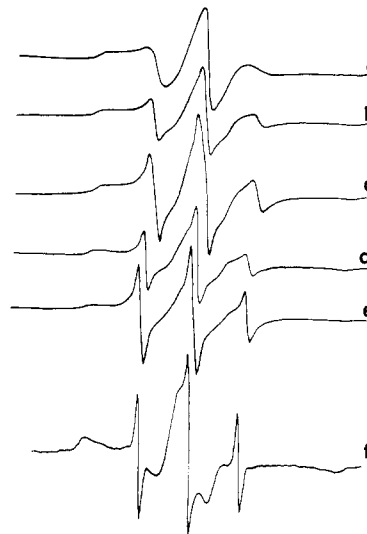


Figure 5. Comparison of the spectra of the oligomers at 15 °C and of PEO 1000 at 22 °C in C_6H_6 . The line widths corresponding to fast population decrease with the length of the oligomers.

sorbed molecules on lattices. These authors found a profile consisting of two parts: one with a fast decay due to the loops near the surface and a second extending far into solution, due mainly to the tail contribution. For their ellipsometric data Kawaguchi and Takahashi^{24,25} find the same result.

From the theory of Scheutjens and Fleer²⁶ such a behavior is predicted and also supported by our results.

Conclusion

Experimental evidence of the influence of the grafting ratio on the configuration of poly(ethylene oxide) chains has been provided by the spin-labeling technique. The behavior of tails and of loops appears very different. The tails appear rather long even for a flat conformation of the chains. This behavior was not predicted by the model used but is in agreement with the results of other authors. It constitutes a contribution to our understanding of the conformation of polymer chains at the solid-liquid interface.

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Studies of Chain-Extended Morphology in Polyethylene by Vibrational Spectroscopy

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ABSTRACT: Investigations of the 39-cm⁻¹ band observed at low temperatures in the far-infrared region suggest that this band is characteristic of chain-extended polyethylene (CEPE). In the process of chain extension via the hexagonal phase, partial disclinations (long chain twists) and gauche bond defects are most certainly introduced. During the transition from the hexagonal to the orthorhombic phase upon cooling, these defects can be "frozen in" and activate the spectroscopically inactive modes of the PE chain and lattice by a lowering of the molecular symmetry in the vicinity of the defect. This mechanism is believed to be the origin of the IR band at 39 cm⁻¹. Spectroscopic studies do not support the assignment of this band to the monoclinic phase known to be present in mechanically processed PE.

Introduction

When chain-extended polyethylene was first reported by Wunderlich and Arakawa,¹ it attracted much attention because of its novel morphological structure and potential for enhanced mechanical stiffness. Recently, it has been suggested^{2,3} that the intermediate hexagonal phase⁴ which exists at high temperature and pressure plays an important role in the formation of this chain-extended morphology. Crystallization of PE via this hexagonal phase proceeds very rapidly with a large lamellar growth rate resulting in lamellar thicknesses in the 2000–7000 Å range.³ Unfortunately, in this thickness range, many of the standard characterization methods (SAXS, IR, and Raman) are ineffective, and hence most of the useful information on CEPE has been provided by thermal analysis and electron microscopy.³ Recently, a low-frequency Raman-active longitudinal acoustical mode (LAM) has been observed⁵ in CEPE by Fabry-Perot interferometry, and thus this technique shows considerable promise as a future characterization method.

An interesting study of CEPE in the far-infrared region has been reported by Frank et al.⁶ in which a distinctive feature at 39 cm⁻¹ was observed below 170 K. Although intermolecular vibrations of the crystalline lattice are generally found in this region, the usual characteristic temperature-dependent frequency shift associated with lattice modes was not observed for this band, with its position remaining unchanged down to 12 K. The absence of this band in melt- or solution-crystallized PE has added to the apparent intrigue surrounding this mode and led to the suggestion that its origin may be due to the presence of a monoclinic crystalline modification known to be

present^{7,8} in mechanically deformed PE. An alternative explanation attributed this band to the A_u (IR and Raman inactive) c-axis transitory mode⁹ made spectroscopically active by molecular disorder within the crystal, but no attempt to definitely assign this band was made.

It is the purpose of this work to explore the origin of the 39-cm⁻¹ band through a series of spectroscopic measurements obtained at 10 K from samples with varying morphologies prepared with different thermal and mechanical processing histories. These results have been combined with those obtained from DSC measurements and those published previously⁵ using Fabry-Perot interferometry to propose an assignment of this low-frequency band.

Experimental Section

The material used in the preparation of CEPE was that obtained from BASF (Lupolen 6011L) or ICI (Rigidex 50). Both were high-density PE with a weight-average molecular weight near 100 000. They were subjected to high-temperature annealing (498–503 K) while under a pressure of about 5 kbar and were similar to those used in the study of Frank et al.⁶ DSC traces of these CEPE samples gave a peak melting temperature of 142 °C at the deepest minimum. Two considerably weaker minima were observed at 130 and 136 °C and most probably correspond to crystal populations resulting from segregation due to molecular weight and/or branching content.²

The PE used for the deformation studies was Dow LP 51.1-6 high-density polyethylene. Samples were used without further purification. Deformation was induced by simply pressing in a KBr pellet die while higher deformation was achieved by grinding at room temperature either with a mortar and pestle or with a "Wiggle-Bug" grinder followed by cold pressing at 20 000–30 000 psi.

Fourier transform IR spectra were recorded with an IBM IR 98 vacuum interferometer. A high-pressure mercury vapor lamp was used as a source, with detection of the transmitted radiation being provided by either a DTGS pyroelectric crystal fitted with

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