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Infrared, Raman and INS studies of poly-ethylene oxide oligomers

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HIGHLIGHTS

- InfraRed and Raman spectroscopy and inelastic neutron scattering on polyethylene oxide.
- The D-LAM spectral contribution depends on the polymerization degree.
- The results show an oligomer–polymer transition.

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ABSTRACT

In the present paper the experimental findings obtained by different spectroscopic techniques on water mixtures of a protein model system, i.e. PolyEthylene Oxide (PEO), are reported. By increasing the polymerization degree m, the D-LAM spectral contribution shows a behavior of the centre frequency and of linewidth which tends to reach a constant value. Also the intramolecular OH stretching contribution, by increasing m, shows a shift which tends to flatten for polymers with molecular weight higher than $M_w = 600$. These results can be connected with the oligomer–polymer transition, at $m = 13$. When in aqueous solutions the D-LAM frequency increases towards the value corresponding to that of the crystal phase; similarly one observes also a sharpening of the D-LAM spectral contribution. These evidences suggest the presence of a more ordered conformation of PEO in water in respect to the melt phase.

1. Introduction

In the last years Poly(Ethylene Oxide), PEO for short, has received an increasing attention both from the academic and from the applicative point of view.

As far as the academic interest is concerned, thanks to the simplicity of its structure and its solubility in water [1,2], it furnishes a precious model system [3] for investigating the interaction mechanisms of water with hydrophilic surfaces [4] and macromolecules. In addition it allows miming the primary, secondary and tertiary structure of biopolymers such as DNA.

The wide range of commercially available m values makes PEO an ideal system for investigating the role of the polymerization degree in determining the polymer properties. The chemical structure, $H{-}(O{-}CH_2{-}CH_2)_m{-}OH$, of this synthetic polymer includes two terminal groups, H and OH, which play an important role in short compounds. The hydrophobic ethylene units and the hydrophilic oxygens, which alternate along the chain, are responsible for its amphoteric character [5]. The similarity of the ether oxygens spacing (2.88 Å) with that of the oxygens in water (2.85 Å) could explain the polymer solubility in water [6], which persists in all proportions at temperatures lower than the boiling point of water. Above this point it presents a miscibility gap that, by diminishing the polymerization degree, m, shifts towards greater temperatures and vanishes [7] for $m < 48$. PEO is commercially available in an extremely broad molecular weight (M_w) range. PEO with $m < 150$ is generally called Poly(Ethylene Glycol), or PEG. Many experimental techniques have been employed in order to characterize the conformation of PEO in the crystalline and in the molten state. In the isolated ethylene glycol (EG) molecule, the basic entity of PEO, many equilibrium configurations can be obtained by rotation of the two CH_2OH groups around the C–C axis.

Crystalline PEO is retained to present a helical conformation that contains seven structural units $CH_2{-}CH_2{-}O$ with two helical turns per fiber identity period (19.3 Å) [8,9]. The structure of this polymer, in the melt or in solution, has continued to intrigue investigators over the years. Pursuit of understanding has led various theoretical studies to quite different results, while vibrational spectroscopy has been revealed to be difficult to apply with confidence, when a broad distribution of a large variety of conformations is involved. It has become clear, however, that a strongly disordered conformation is favored in the molten state, while in aqueous solution the *tgt* conformation is stabilized, due to hydrogen bonds between the ether-oxygen chain and water molecules [10,11].

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As far as the applications are concerned, lower-molecular-weight are used as solvents in oral liquids and soft capsules, whereas solid variants are used as ointment bases, tablet binders, film coatings, and lubricants. Thanks to its low toxicity it is used in a variety of products. The polymer is used as a lubricating coating for various surfaces in aqueous and non-aqueous environments, it is the basis of many skin creams and lubricants and is used in a number of toothpastes as a dispersant. PEG is also used as an anti-foaming agent in food.

The purpose of the present work is to show how the joint employment of spectroscopic techniques, i.e. InfraRed (IR) spectroscopy, Raman scattering and Inelastic Neutron Scattering (INS), furnishes complementary information on the structural properties of PEO, both in the melt and in solution. In particular, the analyses of the D-LAM (acronym for disordered longitudinal acoustic mode) spectral contribution, of the intramolecular OH stretching spectra allow to characterize the dependence of the polymer structural parameters on the polymerization degree, on the solvent content and on temperature.

2. Experimental setup and sample preparation

High purity samples, purchased from Aldrich-Chemie, of Ethylene Glycol (EG) and PEO with average M_w of 106, 200, 300, 400, 600, 900, 1000, 1540, 3400 Da, both in melt and in aqueous solution at different concentrations were analyzed. Fig. 1 shows the molecular structure of PEO. m represents the polymerization degree whereas M_w the molecular weight.

The solutions were freshly prepared and slowly filtered with 0.22 μm PTFE filters. As far as Raman measurement are concerned, polarized (I_{VV}) and depolarized (I_{VH}) spectra were obtained in a 90° scattering geometry in the (−40 °C to 80 °C) temperature range.

FTIR absorption spectra were recorded by a spectrometer Vertex 80 V of Bruker Optics. PEO samples were placed between a pair of CaF_2 windows separated with a 25 μm Teflon spacer. Absorbance method was chosen for spectrum collection. For each spectrum 64 interferograms were collected and co-added by Fourier transformed employing a Happ-Genzel apodization function to generate a spectrum with a spectral resolution of 4 cm^{-1}. Each measure was performed under vacuum in order to eliminate minor spectral contributions due to residual water vapor. However, a smoothing correction for atmospheric water background was performed. IR spectra were baseline corrected and area normalized. In particular, vector normalization was used, calculating the average value of the spectrum and subtracting from the spectrum decreasing the mid-spectrum. The sum of the squares of all values was calculated, and the spectrum was divided by the square root of this sum. The automatic baseline scattering correction function was used to subtract baselines from spectra, which allows getting spectra with band edges of up to the theoretical baseline.Raman spectra were recorded by a spectrometer HORIBA Jobin–Yvon T64000, working with a He-Ne laser with a mean source power of 60 mW at a wavelength of $\lambda = 632.8$ nm. The samples were sealed in optical quartz cells. The spectral range covered was 100–1600 cm^{-1}, with an instrumental resolution from 0.2 to 4 cm^{-1}, depending on the examined spectral range. The scattered photons were automatically normalized for the incoming beam intensity in order to ensure good data reproducibility. The optical purity of the samples ensured to collect data with quite good signal-to-noise ratio and with high reproducibility. However rough data were processed before the analysis by a multiresolution wavelet approach. The spectra at different resolutions were subsequently numerically matched and corrected for the density ρ, for the refractive index n and for local field effects. These corrections correspond to a normalization of the intensity by the factor $n\rho^{-1}(n^2+2)^{-4}$, with $n(T)$ and $\rho(T)$ taken from the literature. One of the spectral information which matters most in this study is the isotropic scattering intensities, calculated from the parallel and perpendicular components of the scattered light. In an ordinary (non-resonant) Raman effect, for linearly polarized excitations, the depolarization ratio $\rho = I_{VH}/I_{VV}$, which as well known varies in the range $0 \leqslant \rho \leqslant 3/4$, being nearly equal to 3/4 for fully depolarized bands, has been also evaluated.

Vibrational spectra of Inelastic Neutron Scattering (INS) on EG and PEGs at different degrees of polymerization, namely 4, 9, 13, corresponding to PEG 200, PEG 400 and PEG 600 (200, 400 and 600 being the molecular weights) have been collected by the indirect geometry time-of-flight (t.o.f.) spectrometer TOSCA at the ISIS Pulse Neutron Facility (DRAL, UK) in the energy range 0–4000 cm^{-1} (0–500 meV). TOSCA's resolution (in the whole energy range of interest, the instrument provides very good energy resolution, about $\Delta E/E \approx 1.5$–2%, which is comparable with optical techniques such as IR and Raman spectroscopies), combined with the high intensity of the ISIS source, allows to perform the study of the dynamics with high accuracy, reducing the background noise/signal ratio down to negligible for strongly scattering samples. For the data treatment a small amount of flat background from the empty-cell measured at similar conditions was subtracted from the measured data [12,13]. The measured INS data were transferred to the dynamical structure factor $S(Q, \omega)$ vs energy transfer by using a standard data treatment program. For what concerns the Debye–Waller factor that strongly influences the spectral intensity, its effect is reduced by collecting the INS spectra at low temperature. The multiple scattering contribution has been minimized by using a thin sample in order to obtain a scattering transmission from the sample $\geqslant$90%. For all the investigated hydrogenated samples, the measurement time was 12 h for each run. For the sample preparation, thin walled aluminum cells have been used. The samples were cooled to 17 K by a liquid helium cryostat.

In this work a Multiresolution Wavelet Transformation (MWT) to suppress noise interference while minimally distorting Raman, IR and INS spectral features, is used (performed). Previous methods used to eliminate fluorescence background include Spline fit subtraction (SFS), fast-Fourier transformation (FFT) high-pass and low-pass filtering, and Savitzky–Golay (SG) smoothing and derivation extraction algorithms. Although each of these have proven to

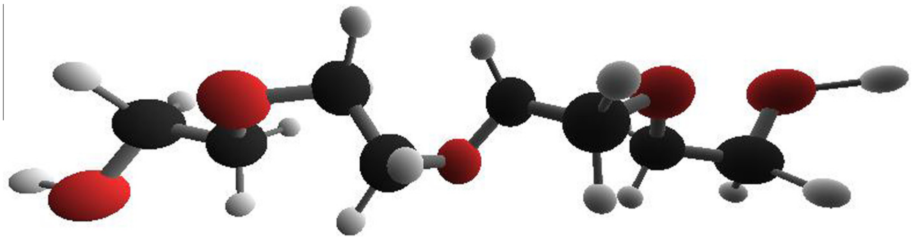

Fig. 1. 3D molecular structure of PEO.