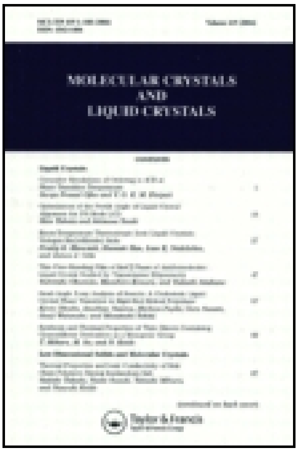

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Conformational Studies of Poly(Ethylene Oxide) in Crystalline, Molten, and Solution Phase

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Conformational Studies of Poly(Ethylene Oxide) in Crystalline, Molten, and Solution Phase

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Abstract Raman scattering measurements were performed on Poly(Ethylene Oxide) both in the crystalline and molten phases and in aqueous solution. The spectral features of the molten state are shown to be largely different from those of the solid phase. Such a difference indicates of a loss of order and an evolution towards a far more disordered conformation. This indication is supported by the analysis of the D-LAM (acronym for Disordered Longitudinal Acoustic Mode) band for the polymeric aqueous solutions. What emerges is that, by increasing the water content, the center frequency of this mode increases (over 10 cm^{-1}) and shifts towards values corresponding to the crystal ones. In order to investigate the role played by the interactive OH end groups, the CH_3 terminated species corresponding to the same degree of polymerization, are therewith examined.

Keywords polymers; Raman scattering; D-LAM

INTRODUCTION

Recent years have seen substantial progress towards the determination of polymer size and shape persistence. This is mainly due to the possibility of demonstrating the correlation between chemical structure, order phenomena and performance in applications concerning advanced or developing technologies. In this frame, Poly(Ethylene Oxide) (PEO) has received a growing attention not only from the applicative point of view. The simplicity of its structure and the unusual solubilty in water [1,2], in fact, make it a precious model system [3] for studying the interaction mechanisms of water with hydrophilic surfaces [4] and macromolecules. The chemical structure of this synthetic polymer, H-(O-CH_2-CH_2)$_m$-OH, 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 oxygen spacing (2.88 Å) with that of the oxygens in water (2.85 Å), could explain the polymer solubility in water [5, 6], which persists in all proportions at temperatures lower than the boiling point of water [2]. Above this point, it presents a miscibility gap that, by diminishing the polymerization degree, *m*, shifts towards greater temperatures and vanishes [7] for $m<48$.

A wide variety of experimental techniques has been employed to investigate the conformation of PEO in the crystalline and 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. IR and Raman measurements and computer simulation studies [8] reveal, also in the liquid phase, the existence of an intra-molecular H-bond which makes the *gauche* conformation the most energetically favoured. In addition, the OH interacting groups promote links among adjacent chains [8], via hydrogen bonding, giving rise to a lot of transient species. Crystalline PEO is retained to present a helical conformation containing seven structural units CH_2-CH_2-O with two helical turns per fibre identity period (19.3 Å) [9, 10]. The structure of this polymer in the melt or in solution has continued to intrigue investigators over the years. Notwithstanding several theoretical studies has led to quite different results, it is commonly ascertained today that a strongly disordered conformation is favoured in the molten state, while in aqueous solution the *tgt* conformation is stabilized, due to hydrogen bonds between the ether-oxygens chain and water molecules [7, 11].

The purpose of the present work is to show how the analysis of the Raman D-LAM (acronym for Disordered Longitudinal Acoustic Mode) spectral contribution, can provide information on the solvent content dependence of the polymer structural parameters and on the role played by the interactive OH end groups.

EXPERIMENTAL SET-UP

We examined: i) high purity Aldrich-Chemie samples of EG and PEO with average M_w of 600 Da (PEO 600), both in melt and in aqueous solution at different concentrations; and ii) the CH_3 terminated species corresponding to the same polymerization degree. The solutions were freshly prepared and slowly filtered with 0.22 μm PTFE filters.

Polarized and depolarized spectra were obtained by a SPEX Ramalog 5 triple monochromator in a 90° scattering geometry in the -40°C ÷ 80°C temperature range. In order to avoid fluorescence, the 5145 Å line of an Argon laser was chosen. The laser power was mantained at approximately 5 W. The detection apparatus consisted of a photon counting system whose outputs were processed on line by a computer. The scattered photons were automatically normalized to the incoming beam intensity in order to ensure good data reproducibility. The optical purity of the samples ensured the good signal-to-noise ratio and high reproducibility of the collected data. The samples were sealed in optical quartz cells and then mounted in an optical thermostat stabilizing temperature within ±0.1 °C. The spectral range covered was 100 cm^{-1}÷500 cm^{-1}. The isotropic scattering intensities, I_{iso}, were calculated from the parallel, I_{VV}, and perpendicular, I_{VH}, components of the scattered light by using the relationship: $I_{iso} = I_{VV} - 4/3\ I_{VH}$.

RESULTS AND DISCUSSION

As well known, for normally flexible polymers to display liquid crystal characteristics, rod-like or disk-like elements must be incorporated into their chains. In this way, Liquid Crystals Polymers form partially ordered melts, which show attractive mechanical and rheological properties. In this frame, it is of outstanding interest investigating the structural factors, which promote the self-organization in polymeric systems.

In order to characterize the dependence of the polymer structural parameters on solvent content and to investigate the role played by the interactive OH end groups, we have examined high purity samples of EG and PEO 600 in melt and in aqueous solution at different concentrations.

The strongly polarised LAM of polymers is commonly attributed to a complex of contributions representing the polymer skeletal bending and stretching vibrations[12]. According to the elastic rod model, appropriate for crystalline systems, the LAM frequencies are inversely proportional to the rod length, l_K, and directly proportional to the propagating velocity of the longitudinal perturbation:

$$\omega_{LAM} = kv = \frac{n}{l_K}\sqrt{\frac{E}{\rho}} \tag{1}$$

where E and ρ are the elastic modulus and density, respectively, and n is an odd integer (for the selection rules we will be concerned with n=1). In non crystalline systems, the presence of conformational disorder dramatically changes the low-frequency Raman spectrum. The narrow LAM band, characteristic of the crystalline state, is replaced by the much broader polarized band associated to the D-LAM [13]. Eq (1) is usually extended to the evaluation of the D-LAM frequencies in disordered systems. In the latter cases, l_K rather represents the length below which the coil can be treated as rigid (persistence length) [14, 15].

Figure 1 shows the D-LAM contribution in EG and Ethylene Glycol Dymethyl Ether (EGDE), where the active OH sites of EG are substituted by the non-interacting CH_3 groups. Because of the asymmetric profile of the D-LAM contributions, they have been fitted by using the log-normal distribution function:

$$I(\omega) = A\exp\left[-0.5\left(\frac{\ln(\omega/\omega_{D-LAM})}{\gamma_{D-LAM}}\right)^2\right] \tag{2}$$

where A is the amplitude, $\omega_{D\text{-}LAM}$ the band center frequency and $\gamma_{D\text{-}LAM}$ the width of the distribution. The noticeable differences in center frequency and width can be attributed to the different system compressibility and/or to the existence of intermolecular interactions among the EG molecules, which give rise to a distribution of *n*-mers with a greater spatial correlation length. Therefore, the comparison of the spectra obtained in EG and in the less interactive EGDE, evidences the role of the OH terminal groups, which determine an inter-chain connectivity[16,17].

As concerns polymeric aqueous solutions, Table 1 evindences that for PEO 600, by increasing the water content, the D-LAM spectral contribution sharpens significantly and its center frequency increases remarkably (over 10 cm^{-1}) shifting towards values corresponding to the crystal ones. These findings confirm that PEO in water tends to assume, relative to the melt case, a more ordered conformation, closer to the crystalline one. The picture that emerges is that adding water molecules, a certain number of these bonds themselves, by H-bond, to the oxigens of the oxirane groups, thus promoting the formation of

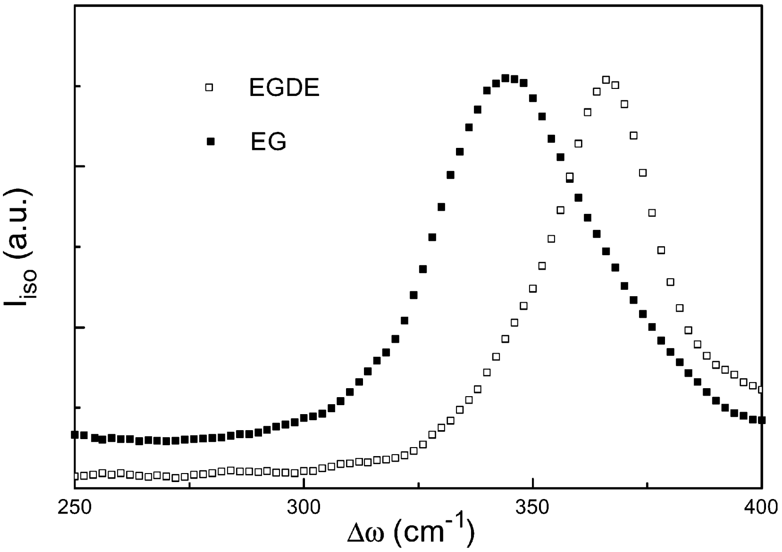

FIGURE 1 D-LAM contribution in EG and EGDE at 45°C.

more rigid hydrated polymeric coils. This gives rise to the $\omega_{D\text{-}LAM}$ increase, and, on a macroscopic scale, to the diminishing of the system compressibility. It is plausible hypothesizing that the compressibility of the polymeric coil is closely connected with the compressibility of the entire system until a full hydration of the polymer chain is reached. A further addition of water molecules, in fact, introduces an amount of bulk water and, as a consequence, the measured system compressibility beyond the hydration values, corresponds to the average value between that of the hydrated polymer and that of bulk water. This hydration process destroys the intermolecular interactions among the polymeric chains and promotes the sharpening of the D-LAM contribution, until only one intense band, corresponding to the *isolated* hydrated polymer coil, is found. In this frame, as above stressed, the amount of water which signals the crossover to the $\omega_{D\text{-}LAM}$ and $\gamma_{D\text{-}LAM}$ plateau values should correspond to the full hydration of the polymer.

n_w	$\omega_{D\text{-}LAM}$ (cm^{-1})	$\gamma_{D\text{-}LAM}$ (cm^{-1})
0	273	0.157
2	275	1.148
10	279	0.137
26	284	0.124
40	284	0.122
60	284	0.122
80	284	0.122
Crystal	284	0.122

TABLE 1 D-LAM center frequency, $\omega_{D\text{-}LAM}$, and width, $\gamma_{D\text{-}LAM}$, of PEO 600 aqueous solutions with different concentration at 45°C. n_w denotes the number of water molecules.

CONCLUDING REMARKS

The primary purposes of this work are characterizing the dependence of the PEO structural parameters on solvent content and investigating the role played by the interactive OH end groups, by analyzing the Raman D-LAM spectral contribution.

As a first result, by increasing the water content, the center frequency of this mode is found to increase (over 10 cm^{-1}) shifting towards values corresponding to the crystal ones. This finding supports the fact that PEO in water tends to assume, relative to the melt case, a more ordered conformation, closer to the crystalline one. In second place, the role played by the interactive OH end groups is evidenced by examining the CH_3 terminated species corresponding to the same degree of polymerization. In the case of EG and EGDE samples, the observed peculiarities can be attributed to the different system compressibility and/or to the existence of intermolecular interactions among the EG molecules which give rise to a distribution of *n*-mers with a greater spatial correlation length.

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