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Effects of isotopic substitution on the conformational properties of polymeric aqueous solutions

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Abstract

This work deals with a side-by-side comparison between the PEO conformational properties in H_2O and D_2O. The gyration radius, evaluated by SANS, the hydrodynamic radius, evaluated by PCS, and the Raman D-LAM band analysis furnish valuable information on the structural arrangement of the molecules. The findings clearly show different behavioural properties of the polymer in H_2O and D_2O. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Isotope substitution; Small angle neutron scattering; Raman scattering; Polymers

1. Introduction

The aim of the present work is to study to what extent the conformational properties of a typical macromolecular system are influenced by the isotopic H↔D substitution in the solvent. We investigated, using three scattering techniques, Poly(Ethylene Oxide) (PEO)[1] aqueous solutions (H_2O and D_2O).

SANS data on D_2O solutions of PEO 3400 were collected on the 30 m instrument of the W.C. Koehler Scattering Center of Oak Ridge National Laboratory (USA). Neutrons had a mean wavelength of 4.75 Å ($\Delta\lambda/\lambda \sim 5\%$) and the momentum transfer was in the range of 0.03–0.38 Å^{-1}. PCS measurements were performed using a BROOKHAVEN BI-2030 correlator. Polarized I_{VV} and depolarized I_{VH} Raman spectra were obtained by a SPEX Ramalog 5 triple monochromator in the 200–400 cm^{-1} spectral range.

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2. Results and discussion

Assuming a random coil conformation for PEO 3400 chains in water, SANS data were analysed using the Debye form factor [2] from which the gyration radius, R_g, can be evaluated. In the low-k region of the spectra the decrease in the intensity with the increase of polymer concentration reflects the contribution of the interactions between polymer coils. In the high-k region, the magnitudes of the scattered intensities rank in the opposite order with increasing polymer concentration. Following normalisation of the spectra by sample concentration, (see Fig. 1) the similarity of the differential scattering cross-section at high-k indicates that each polymer coil acts as an independent scatterer. The nonlinear decrease with increasing concentration observed for the evaluated apparent R_g values, may be due to the combined effects of possible changes in the three-dimensional structure and, at high concentration, to the interparticle interaction of PEO coils [3]. As a consequence, it is expected that SANS spectra furnish reliable values of R_g only in the most dilute solutions. From PCS data, we evaluated the hydrodynamic radius R_H for PEO 3400/H_2O and D_2O solutions in the temperature range 278–353 K. What emerges from the comparison is that, in heavy water, R_H reveals a different behaviour, both in the
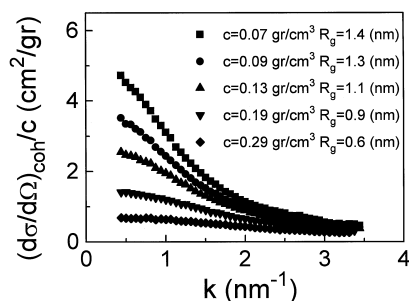
Fig. 1. Coherent differential scattering cross-section normalized to concentration at $T = 313$ K.
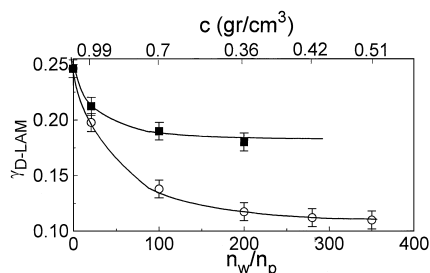

Fig. 2. Concentration dependence of the D-LAM width ($\gamma_{\text{D-LAM}}$) for the PEO 3400/H_2O solutions (open circles) and for the PEO 3400/D_2O solutions (closed squares) at 333 K. The lines are guides for the eye.

magnitude and in the temperature dependence since the whole behaviour in D_2O shifted towards lower temperatures with respect to those in H_2O.

The study of the Raman D-LAM band, a strongly polarized band representing the lowest frequency intra-chain collective mode [4], confirms the previous result. The log-normal distribution function, used to fit the D-LAM band, directly furnish the band center frequency, $\omega_{\text{D-LAM}}$ and the width of the distribution, $\gamma_{\text{D-LAM}}$, the latter being reported in Fig. 2 as a function of n_w/n_p (n_D/n_p) ratio (n_w), (n_D), and (n_p) are the number of water and polymer molecules, respectively. As can be seen in PEO/D_2O solution the asymptotic values of $\gamma_{\text{D-LAM}}$ and $\omega_{\text{D-LAM}}$ are lower and higher, respectively, than the corresponding ones in H_2O. These findings indicate that the addition of water molecules makes PEO conformation more ordered in H_2O than in D_2O, when a full hydration is reached. This behaviour suggests the existence of a stronger structuring effect.

In view of these results what emerges is that the isotopic substitution gives rise to different conformational arrangements of PEO chains and their temperature dependence in the two solvents. This occurrence can be related to the net result of different causes, connected with the polymer hydration shells (depending on the bond strength between solvent and polymer and on the similarity of the ether oxygen spacing (2.88 Å) with that of the oxygens in light water (2.85 Å)) and with the network in the bulk solvent, stronger in D_2O than in H_2O.

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