European Polymer Journal 48 (2012) 391–403

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Intramolecular and intermolecular OH···O and OH···F interactions in perfluoropolyethers with polar end groups: IR spectroscopy and first-principles calculations

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ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 2 November 2011
Accepted 30 November 2011
Available online 8 December 2011

Keywords:
DFT calculations
Hydrogen bonding
Fluoropolymers
Vibrational spectroscopy

ABSTRACT

Perfluoropolyether (PFPE) fluids constitute a class of polymers that fulfil a wide range of requirements for hi-tech applications, due to their pefluorinated backbone. For some of these applications they are requested to bear polar end groups, and the combination of a chemical inert backbone and a reactive end group can produce peculiar conformations and supramolecular structures. The molecular structure and the vibrational properties of the ethoxyl-terminated PFPE FLUOROLINK®E10H in solution are here investigated by means of IR spectroscopy. It is shown that the complex spectral features of the OH-stretching region cannot be explained without a thorough computational study, involving the investigation of the conformational space of an isolated model molecule by means of semi-empirical AM1 calculations and DFT calculations. The most relevant conformers were singled out, showing a high degree of conformational disorder for FLUOROLINK®E10H. Furthermore, it is shown that intra- and intermolecular H-bonding affects significantly the molecular structure and the vibrational spectrum. Several interactions are shown to be relevant, such as OH···F interactions and complexes with residual water. Theoretical values of the absolute intensities of OH stretching IR bands, relevant for the analytical applications, are obtained.

1. Introduction

Since the discovery of polytetrafluoroethylene (PTFE), perfluorinated polymers have been widely known for their superior properties, related to the characteristics of the C–F bonds [1].

Most of these properties, such as high thermal and chemical stability and low glass transition temperature, are shared also by the family of perfluoropolyether (PFPE) fluids: this makes them suitable for advanced applications such as ultrahigh vacuum technologies, advanced lubrication and coating technologies, electronics, etc.; moreover they are used as intermediates in the synthesis of new copolymers. Molecular structure and vibrational properties of several PFPE have been thoroughly investigated in the past [2,3].

The wide range of applications requires the formulation of various classes of PFPE, either completely perfluorinated, or with polar end groups, or even containing different monomers (perfluorinated or nonfluorinated) [4]. In this work we analyze the structural and spectroscopic properties of FLUOROLINK®E10H, a PFPE with a fluorinated backbone and two chain ends formed by a short (hydrogenated) ethoxylic chain, bearing a polar OH group.

Vibrational spectroscopy (IR and Raman) is one of the main techniques for the investigation of the molecular structure and for the characterization of polymers [5], also

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doi:10.1016/j.eurpolymj.2011.11.022

for practical purposes (e.g. production control); this holds even more for perfluorinated polymers, whose characteristics often reduce the usability of other techniques (e.g. NMR). For this reason, a vast literature exists about the IR spectra of these polymers, and several "diagnostic" spectral bands are known and used as markers of various structural features. It is also well known that the presence of hydrogen bonds in a molecular assembly generates peculiar spectral features, which usually allow to determine the ratio between free and associated species [3].

We already found in the past that the combination of these two features, a perfluorinated molecular backbone with polar end groups prone to H-bonding, often produce spectra that cannot be readily interpreted without a detailed ab initio computational modelling: this is for example the case of perfluoropolyamides [7].

Thus, it is not surprising that similar problems arise in the interpretation of the vibrational spectrum of FLUOROLINK®E10H solutions: the higher frequency OH stretching region, usually assigned to "free" molecules (not involved in hydrogen bonding), shows a complex band feature that cannot be explained on the basis of a standard approach.

Here we present a computational investigation on a model molecule, from which we obtain an insight on the intramolecular structure of the polymer and on its relevant intermolecular complexes. This suggests an interpretation of the observed spectroscopic features, which involves subtle effects due to intermolecular and intramolecular interactions such as complexes with water and conformation dependent intramolecular OH···F interactions.

2. Materials and methods

2.1. Experimental details

FLUOROLINK®E10H is a perfluoropolyether with linear structure and characterized by the presence at both ends of an ethoxyilic chain terminated with an –OH group, as reported below:

$$HO-(CH_2-CH_2-O)_n-CH_2-CF_2-O-(CF_2-CF_2-O)_p(CF_2-O)_qCF_2-CH_2-(O-CH_2-CH_2)_n-OH$$
$$(M_n \approx 1600, 1.5 < p/q < 2 \text{ and } 1.5 < n < 2.5)$$

Since this macromer is not soluble in nonpolar solvents, the solutions were made in H-GALDEN®ZT130, a linear PFPE, fully fluorinated except for the end groups which are characterized by a difluoromethylic structure: CF_2H–O–$(CF_2$–CF_2–O$)_p$–$(CF_2$–O$)_q$–CF_2H. Its M_n is 500 as determined by ^{19}F NMR, the p/q ratio is $1.5 < p/q < 2$ and the distribution of the repeating units along the polymeric chain is random. The presence of a quite "acidic" CH groups at the ends of the H-GALDEN®ZT130 chain offers a site suitable for intermolecular links ruled by electrostatic interactions (or even by hydrogen bonding) with solute molecules containing polar groups. Solutions with a concentration of FLUOROLINK®E10H ranging from 0.05–5% w/w were considered.

In order to obtain additional information useful for the vibrational assignment (see Section 3.1), we also synthesized a similar polymer, characterized by a shorter end chain, with only one ($n = 1$) ethoxylic unit; this was as well characterized by means of IR spectroscopy. In the following it will be referred to as 1ET.

IR spectra have been recorded with a Thermo Nicolet Nexus® 870 FTIR instrument, injecting the samples in a liquid cell with CaF_2 windows and fixed optical path-length of 1 mm. The acquisition parameters of IR spectra were 256 scans for each spectrum with a spectral resolution of 2 cm^{-1}.

2.2. Computational details

The conformational space of a model molecule was explored , according to the procedure described in Section 3.2, via the semiempirical AM1 method [8], as done in previous works [9].

Starting from the molecular structures selected by this preliminary computational investigation, further Density Functional Theory (DFT) calculations were performed to predict the IR spectra of the relevant conformers. In addition, we studied the intermolecular effects of hydrogen bonding in suitable model dimers by calculating their IR spectra. For all DFT calculations the hybrid exchange–correlation functional B3LYP [10] and the 6-311++G** basis set were used. In previous papers [7,9] we verified that B3LYP functional (with triple-zeta basis set, with or without diffuse functions) can give a good description of the spectral pattern (i.e. frequency and IR intensities) of fluorinated molecules in different environments, in nice agreement with the experimental data. On this basis, this functional has been chosen also for this work.

In the case of intermolecular complexes, the values of the interaction energies were corrected for the Basis Set Superposition Error (BSSE) according to the Counterpoise (CP) scheme [11]. All the semiempirical AM1 and DFT calculations were carried out by means of the Gaussian03 code [12].

3. Results

3.1. Analysis of IR spectra

In Fig. 1A the experimental IR spectra of FLUOROLINK®E10H solutions with different concentrations of the polymer are shown, in the frequency range associated to