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SOME ASPECTS OF THERMODYNAMIC PROPERTIES OF ETHYLENIMINE AND ETHYLENE GLYCOL LINEAR POLYMERS

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ABSTRACT The two biopolymers, namely polyethy-lenimine (PEI) and polyethylene glycol (PEG) in linear configurations, with a different range of polymerization, containing between 3 and 25 repeat units, have been studied by means of 3 functions of state: enthalpy, entropy and Gibbs free energy in standard conditions, using density functional (DFT) calculations. The preliminary data show that the stability of the two polymers decreases with the increasing of their degree of polymerization, namely with the increasing of their chain length.

Key words: *Thermodynamics, functions of state, biopolymers, PEI, PEG.*

INTRODUCTION

Polyethylenimine (PEI) or polyaziridine and polyethylene glycol (PEG) also known as polyethylene oxide (PEO) are two polymers with a similar structure:

$$\underset{\text{PEI}}{\text{H-(NH – CH}_2\text{–CH}_2)_n\text{–NH}_2} \qquad \underset{\text{PEG}}{\text{H–(O–CH}_2\text{–CH}_2)_n\text{–OH}}$$

Both contain ethylene groups -CH_2CH_2-, separating the ether (-O-), respectively secondary amine (-NH-) groups. Both can exist in linear forms, as presented in the formulas above or branched forms. PEI can also present dendrimeric forms [1], while for PEG there are also starPEGs and combPEGs. For the beginning, here only

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the linear forms will be considered. The name PEG is used mainly for oligomers and polymers with low degrees of polymerization, n (e.g. under 400-500) [2], while PEO is referred for higher degrees of polymerization which can attend some hundreds of thousands (molar weight as high as 10^7g/mol). Likewise, PEI of various polymerization degrees, from oligomers to polymers with molar weight of about 10^6 is used [3]. The basic amine groups in PEI can be easily protonated, conferring a polycationic character to the polymer [4, 5].

Both polymers have multiple utilizations [6]. PEGs have biological and medical applications, e.g. as encapsulating agents for drug delivery [7], for coating gene therapy vectors against inactivation by the immune system [8].

PEI is also a multipurpose polymer used in adhesives, cosmetics, detergents, in the cellulose and paper industry [9, 10]. Much attention is paid to its use as carbon dioxide absorbent [11]. In biology, it is used as transfection agent for DNA [12]

For crystallized PEG oligomers (up to n= 48) secondary helical structures were observed [2]. For polymers above the glass transition temperature and in solution, the polymer theory predicts a random coil configuration. The molecular configurations of PEG (n= 27) and PEO were simulated and analyzed in water solution [13] using Charmm c33b2 program [14]. For liquid PEG molecular dynamics simulations were performed using various force fields [15], and with the OPLS-AA force field its hydrogen-bond structure was discussed [16]. All atom molecular dynamics simulation was also used to study the role of PEG in drug delivery [17]. Calculations of this type were also applied for the study of intercalated in clay [18]. Some thermodynamic properties for liquid PEG were studied from its volume [19].

PEI was as well studied theoretically, especially for its action as a proton acceptor, a real "proton sponge" in acidic medium [20]. For linear chains of PEI in solution, molecular dynamic simulations [20] showed that in basic medium (high pH) the chain presents a coil configuration, while in strong acidic conditions (low pH) the chains are elongated. The thermodynamics of CO_2 adsorption on PEI was also investigated [21]. Molecular dynamics and Monte Carlo simulations were used to study the protonation behavior of PEI in solution [22], and the modelling of CO_2 adsorption on PEI was achieved [23].

Some quantum chemical calculations for PEI and PEG were also realized. The mechanism for the electrochemical polymerization of diethylenetriamine (the dimer, n = 2 in the series of PEI) to linear PEI was studied by ab initio quantum chemical calculations at the Hartree–Fock level with Gaussian 98W of standard reaction free enthalpies, finding that the formation of linear PEI is more probable as that of branched PEI [24]. A similar investigation was made for the electrochemical polymerization mechanism of p-phenylenediamine [25]. The monomer of PEI, EDA (ethylenediamine, n = 1) was studied along with different other aliphatic diamines by ab initio (at Hartree-Fock level) and density functional calculations, giving an insight on the thermodynamics of their protonation [26]. For linear PEI and linear polypropylenimine (n = 1…5), ab initio and quantum-mechanical calculations at diverse levels were compared by computing their vibrational frequencies and intensities after geometry optimization [27].

For PEG (n = 1-5, 10, 20, 30), quantum chemical calculations using DFT, ab initio Hartree-Fock and semiempirical PM3 were used to calculate HMO and LUMO energies and quantities related to these, and adsorption energy on Al surface were evaluated, for correlations with the inhibitor effect of these compounds on the corrosion of Al [28]. The vibrational spectrum of polyethylene was compared with the spectrum of PEG, obtained using Gaussian [29]. The influence of intramolecular hydrogen bonds in PEG (n = 2-5) was studied by DFT calculations and MD simulations [30]. Quantum chemical calculations for PEG (n = 1-5) were also used to calculate saturation vapor pressures, after selecting the lowest energy conformers [31].

Here we test the capacity of quantum chemical computation to characterize the stability of polymeric molecules by calculation of thermodynamic quantities.

THEORETICAL DETAILS

Fully extended PEI and PEG molecules with different degrees of polymerization were used as initial configurations for our investigations, using the Gaussian 09W package [32] at the DFT PBEPBE 6-311G (d,p) level of theory. The studied molecules have been built using Gauss View 5.0. Thermodynamic quantities at standard temperature (298 K) have been calculated using the thermochemistry output from Gaussian, as obtained in the program by using the equations of Statistical Thermodynamics. These calculations were made for all the terms of the two polymer homologous series, from n = 3 to 20.

RESULTS AND DISCUSSION

The structures of the linear polymers with different degrees of polymerization, n, are presented in Fig. 1 for PEI, with n = 5 …15 mers (structure units) and Fig. 2 for PEG, with n = 5…15 mers.

Some of the calculated Gibbs free energy (G) values expressed in kcal/mol and enthropy (S) values in cal/(mol.K) units for different PEI molecules [n = 5…15] are given in Table 1 and the similar quantities for PEG [n = 5…15] in Table 2. They were obtained by reporting the thermodynamic quantities given by the DFT calculations to the number of mers, n. They are therefore average molar quantities, per mole of unit of structure (mer). Of course, the thermodynamic values for the different mers are not the same along the polymer chain. In particular, the two terminal mers differ from the inner ones by a hydrogen atom and thus have lower energies, but their effect on the total energies decreases with increasing n values

The Gibbs free energy was calculated because it is a measure of the thermodynamic stability of the molecules. The lower the value of this quantity, the more stable the compound. The negative values suggest a thermodynamic stability. The values are lower for the PEG molecules as compared with the corresponding PEI molecules, due to the presence in the former of the more electronegative oxygen atoms, replacing the NH groups of PEI.

The entropy values are small, as expected given the restriction imposed on the configurations of the molecules: fully extended configurations as found in solid state. They are the same for the two series of molecules, in the limits of the used model

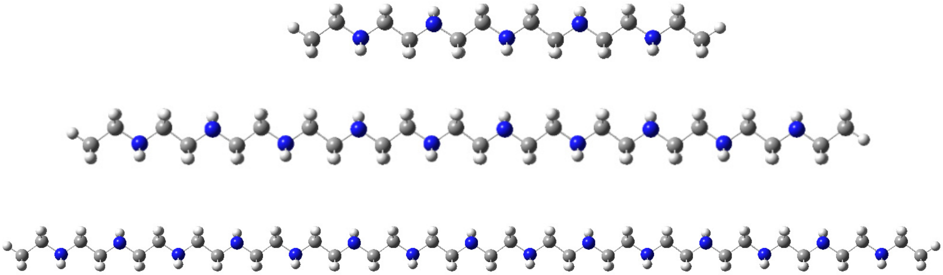

Fig. 1. PEI containing 5, 10 and 15 mers. Gray circles represents the carbon atoms, blue circles the nitrogen atoms, and the smaller circles – the hydrogen atoms

In Fig. 3, the values of the molar Gibbs free energy in kcal/mol are represented against the number of mers for PEI (n from 3 to 20) and in Fig. 4 for PEG (n from 3 to 20). From both figures 3 and 4, an analogous increase of the Gibbs free energy per mole of mers with the degree of polymerization, n, is observed. That means a slightly decreasing stability for the higher polymers. It is a logarithmic variation, faster for the lower terms of the polymer homologous series but slowing down for the higher terms, where the stability becomes practically constant up from 15-20 mers.

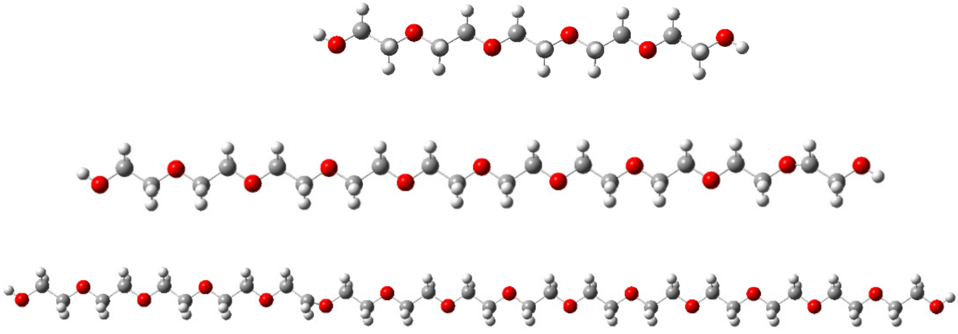

Fig. 2. PEG containing 5, 10, and 15 mers, Gray circles represents the carbon atoms, red circles the oxygen atoms, and the smaller circles – the hydrogen atoms

Table 1. Some G and H values in kcal/mol and S values in cal/molK for PEI

Molecule	G, kcal/mol	H, kcal/mol	S, kcal/mol
PEI5	-150	-143	24
PEI10	-142	-137	18
PEI15	-139	-135	15
PEI20	-138	-134	14

Table 2. Some G and H values in kcal/mol and S values in cal/molK for PEG

Molecule	G, kcal/mol	H, kcal/mol	S, kcal/mol
PEG5	-169	-163	19
PEG10	-161	-157	13
PEG15	-158	-155	11
PEG20	-157	-154	10

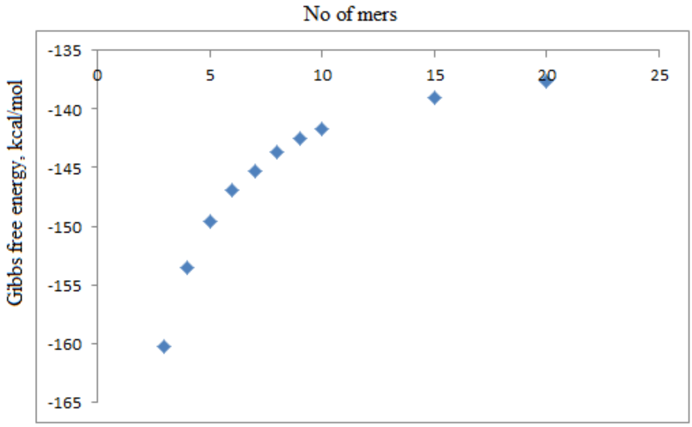

Fig. 3. G in kcal/mol against number of mers for PEI

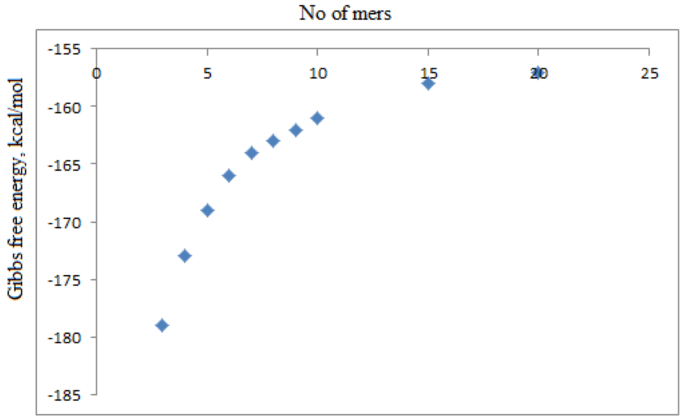

Fig. 4. G in kcal/mol against number of mers for PEG

These results were obtained using fully extended configurations of the polymer molecules. However, the flexibility of the carbon backbone of the molecular chains leads to the random coil conformation of polymers with higher degree of polymerization, in fluid state or in solution. This would increase the entropy of the higher polymers and, in consequence, decrease their free energy, thus showing a higher thermodynamic stability.

Taking into account the intramolecular hydrogen bonds in PEG [30] would also affect the configuration of the molecules, but only for the lowest values of n, since in higher polymers the contribution of free –OH groups becomes negligible.

CONCLUSIONS

Thermodynamic characteristics of PEI and PEG polymers of different degrees of polymerization (up to 20), as estimated from a computational chemistry model, suggest a slight decrease of stability for the first terms of the two polymer homologous series. A more elaborate model, taking into account the flexibility of macromolecule segments for higher degrees of polymerization, should complete these preliminary results.

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