Influences of Polymer Conformation on Acetalization Reaction of Poly(vinyl alcohol): Langevin Dynamics and DFT Approaches

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In this work we studied changes in poly(vinyl alcohol) (PVA) conformations with respect to the polymer concentrations, using Langevin dynamics at 300 ± 10 K. Constructed polymer chain consisted of 90 units and the friction coefficient of the solvent (water) was set to 55 ps^{-1}. We also turned to quantum mechanical calculations, using B3LYP/6-31+G* level of theory in order to investigate the association via hydrogen bonds (H-bonds) between two OH-groups of PVA and between OH-group and water. It was demonstrated that in dilute solutions PVA macromolecules tend to shrink and form more dense coils by comparison with polymers in more concentrated solutions, where two or more chains overlap, entangle and associate via intermolecular hydrogen bonding. We also established that H-bonds between OH-groups and water molecules were less stable than those between two not adjacent OH-groups of one or various chains. The obtained data allowed us to consider that in the case of low PVA concentrations, the distances between parts of one chain tend to decrease that leads to the polymer conformation favorable for the intramolecular cross-linking when the acetalization of PVA takes place. As far as the cross-linking occurs within the coil, the resulting product should loss it flexibility. We assumed that the mass-transfer in this system may be slower than the subsequent chemical reaction, so the acetalization of partially modified PVA may proceed with essential retardation.

Key words: poly(vinyl alcohol), acetalization, polymer conformation, hydrogen bond

Introduction

The preparation of functional polymers by chemical modification has become a very important technique. Due to the similarities between the reactions of organic macromolecules and their small molecule analogs, this approach opens a way by which the properties of the well known polymers can be modified to make them suitable for various specific uses [1]. Among them are acetals of poly(vinyl alcohol) (PVA), obtained by acid catalyzed modification of PVA with various aldehydes [2]. Acetals of PVA are important industrial products that find application in the aviation and automobile industries as well as in various biomedical fields [3, 4].

Accessibility and reactivity of the functional groups in the linear polymers have been studied in details in numerous works [1, 5-7]. It was established that number of factors can affect the reactivity of the functional groups on the polymer chain. Among them are conformational and preferential solvent effects. Aqueous solutions of PVA at different concentrations were prepared using glutaraldehyde as a cross-linker [4] and the influence of intra-molecular cyclization on the cross-linking processes and the structure of the formed compounds was studied. The sol-gel distribution *versus* PVA concentrations was also evaluated, revealing that the fraction of intra-molecular cyclization decreased linearly with increasing PVA concentration within the measured concentration range. The fraction of intra-molecular cyclization calculated from the straight-line plot increased up to 100% when the PVA concentration decreased to ~1.1 wt%. The calculated value was consistent with the experimental results as the authors did not detect the bulk gel in dilute PVA solutions (<1.1 wt%) and the solution became turbid. In another study, Gebber et al. [8] investigated PVA cross-linking in dilute solution and characterized the reaction product by viscometry and gel permeation chromatography. It was established that the intra-molecularly cross-linked isolated PVA molecules are smaller than the initial polymer molecules and their size decreases with increasing degree of cross-linking. Ahmad et al. [9] determined various thermodynamic parameters of aqueous PVA solutions. It was found that in water the uncoiling and orientation of macromolecules prevailed, the system became more ordered in the course of flow and the entropy of activation was negative. It is also known [4] that in less dilute solutions several chains tend to overlap and entangle. So the higher PVA concentration is the stronger entanglement effect is. According to the listed researches, one can resume that properties of the prepared products depend on the initial polymer concentration. In one`s turn polymer concentrations can affect the conformational changes of the macromolecules and hence the functional groups reactivity. So in this work we studied conformations of PVA chains *versus* polymer concentrations *via* Langevin dynamics in order to investigate the OH-groups accessibility and reactivity. We also studied various types of associations of OH-groups in PVA-Water system, using quantum-mechanic (QM) methods.

Simulation details

All calculations of quantum-mechanics (QM) were performed using the Spartan® `08 Version 1.2.0. The geometries of the monomers and dimers were fully optimized using density functional theory (DFT) [10, 11] of the B3LYP [12-14] hybrid exchange functional with the 6-31+G* basis set. The vibrational frequencies were evaluated at the same level of theory and scaled by a constant factor equal to 0.9614

[15] for zero-point energy (ZPE) corrections. The frequencies were assigned with respect to normal mode vibrations. The complexation energies (E_n) of all clusters were calculated using the same methodology. The change in binding energy, ΔE of each complex was calculated as follows:

$$\Delta E = E_{complex} - \{E_1 + E_2\}, \qquad (1)$$

here, $E_{complex}$, represents total energy of any considered complex, formed by individual molecules, with total energies E_1 and E_2 respectively.

Langevin dynamics simulations at 300 ± 10 K were carried out using HyperChem® Professional 8.0 (HyperChem). Friction coefficient, Υ, ps^{-1} of the solvent (water) was calculated from equation (2):

$$\Upsilon = 6\pi\eta a/m \qquad (2)$$

where m is the particle`s mass; η is the solvent viscosity; a is the radius of the hydrodynamic particle. With respect to the value, obtained from equation (2), Υ for water at room temperature was set to 55 ps^{-1}. The step size was set to 0.001 ps. The total simulation time was between 4 and 8 ns, depending on the equilibration.

In order to specify the H-bonds parameters, equilibrium conformations were then optimized using Amber99 force field and Polak-Ribiere algorithm. RMS gradient value was set to 0.001 (kcal/(Å mol).

Results and Discussion

It is well known that PVA has highly polar hydroxyl groups tend to form inter- and intramolecular associations *via* H-bonding [16]. Furthermore, OH-group of alcohols can become interconnected with water molecules or polar molecules of another solvent by HB [17-20]. Preliminary we turn to quantum-mechanic QM methods in order to calculate the H-bonds parameters of the examined systems. On the basis of the literature data on alcohol association, three types of association must be considered: (i) intra-molecular H-bonds, which involve two consecutive OH groups in the chain; (ii) inter-molecular H-bonds, which involve repeat units of different chains; and (iii) H-bonds between OH groups and solvent molecules. perform this task while keeping the models computationally manageable [21,22] 2,4-pentanediol and 2,4,6-heptanetriol were selected as models for PVA. Complexes with different type of association, involving mentioned molecules, are presented in Figure 1. The optimized structural parameters of the listed complexes such as H-bond length, D (Å); interaction energies, ΔE (kJ mol^{-1}); and vibrational frequencies (cm^{-1}) are summarized in Table 1.

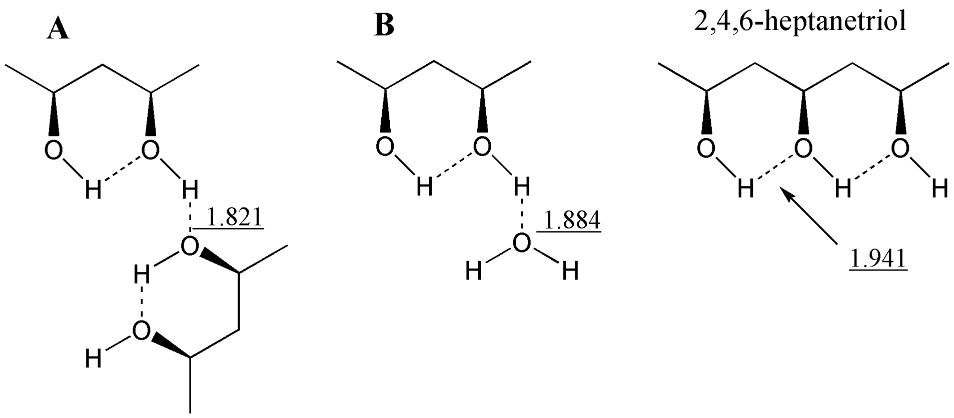

Figure 1. Models of PVA with different type of association. Hydrogen bonds lengths (Å) were calculated after full optimization of listed complexes with B3LYP/6-31+G* level of theory. H-bonds donated with dashed lines.

Table 1. Geometric, energetic and frequency parameters of the single molecules and hydrogen bonded complexes shown in Figure 1. All parameters were obtained after full optimization of all compounds using B3LYP/6-31+G* level of theory.

Model	D, Å	ΔE, kJ mol^{-1}	V. F.*, cm^{-1}
2-butanol	-	-	3611
2,4-pentanediol	1.964	-	3535
2,4,6-heptanetriol	1.941	-	3510
A	1.821	-36.3	3363
B	1.884	-29.4	3466

* Vibrational frequencies (O-H stretching)

Thus, the first cluster (A) simulates inter-molecular H-bond formation that can occur between two isolated OH-groups of two different polymer chains or between two not consecutive OH-groups of the same chain when the polymer conformation is favorable for their interaction. B-cluster represents interactions between OH-groups and water molecules. 2,4,6-Heptanetriol simulates intra-molecular association *via* H-bond of two adjacent OH-groups.

Observing the calculated H-bonds lengths it can be said that D increases in the following order: A<B<2,4,6-heptanetriol<2,4-pentanediol. Together with calculated interaction energies (for A, ΔE = -36.3 kJ mol^{-1}; for B, ΔE = -29.4 kJ mol^{-1}), this data indicate A-complex should exhibit more stability comparing to all other models.

Since the IR spectroscopy was proclaimed to be one of the most powerful tools for investigating the H-bond strength [23], we turn our look to calculated IR spectra in order to prove the previous assumptions. The involvement of an O-H group in H-bond formation weakens the bond, resulting in bond elongation and lowered O-H stretching/vibrational frequencies [24]. The calculated IR spectra of several models are shown in Figure 2 and the wave numbers are listed in Table 1.

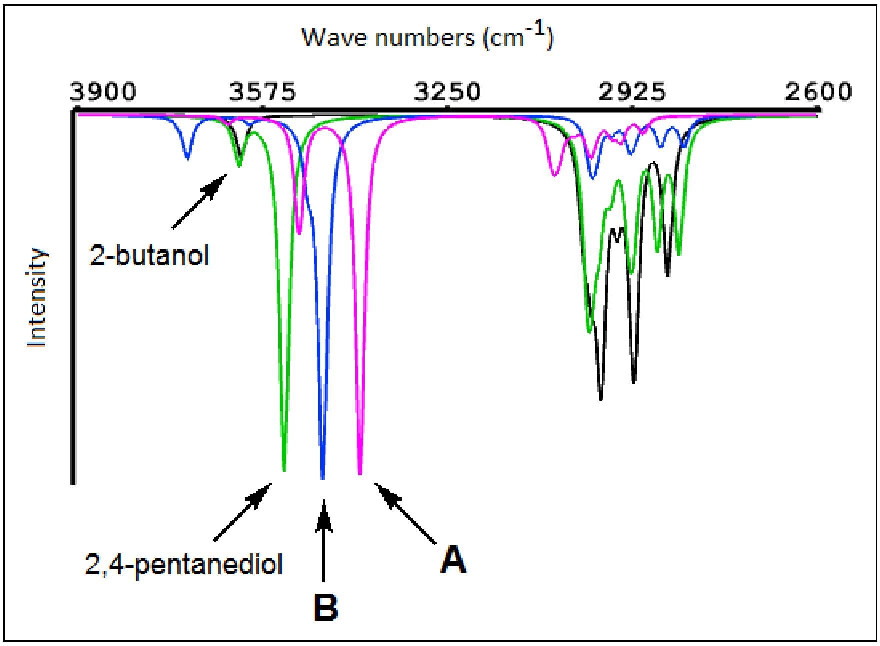

Figure 2. Calculated IR spectra of 2-butanol (black), 2,4-pentanediol (green) and dimers: B (blue) and A (purple) (Figure 1). Wave numbers scaled by a constant factor equal to 0.9614.

It was found that O-H stretching frequency of a single 2-butanol and a single 2,4-pentanediol arises at 3611 and 3535 cm^{-1} respectively. Figure 2 and Table 1 illustrate that the expected frequencies of the H-bonded OH-groups in A (3363 cm^{-1}) and B (3466 cm^{-1}) are red shifted. Such tendency indicates that H-bond strength decreases in the following order: A<B<2,4,6-heptanetriol<2,4-pentanediol and confirms the above conclusions based of the H-bond length and interaction energies. It points that inter-molecular association *via* H-bonds should be more stable than intra-molecular association or association of the OH-groups with water.

In order to investigate the conformations of PVA macromolecules in dilute solution (when the simulation process involves only one isolated chain) and in more concentrated one (when at list two chains interact) Langevin dynamics approach was used. Langevin dynamics simulates the effect of molecular collisions and the resulting dissipation of energy that occur in real solvents, without explicitly including solvent molecules. Atomistic PVA model with 90 basic vinyl alcohol units (n = $-CH_2$-CHOH-) was constructed. Figure 3 shows typical equilibrium snapshots for the folding process of a single PVA chain. Total energies for each conformation are also present.

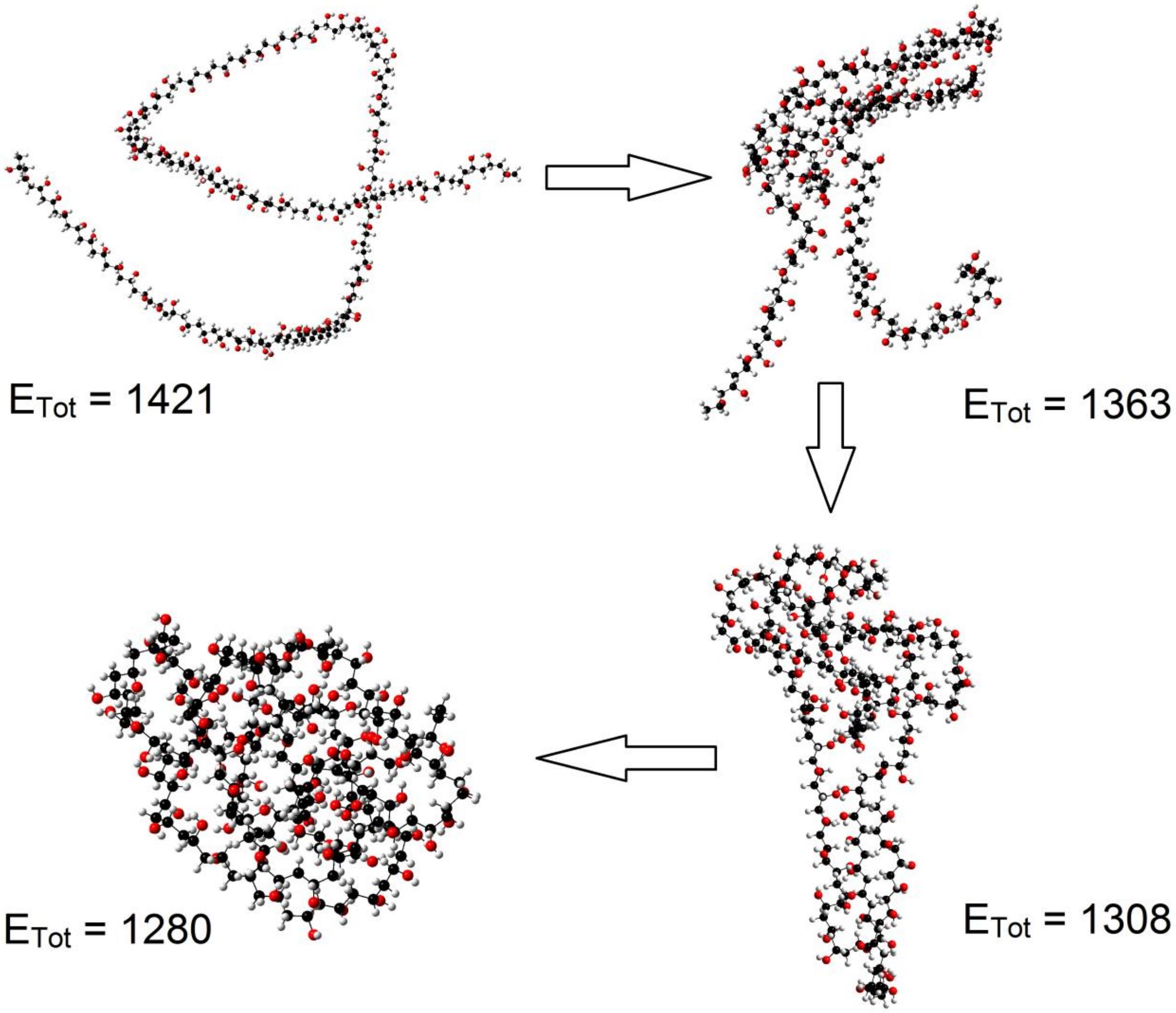

Figure 3. Snapshots displaying folding process for a single PVA chain (n = 90). Total energies, E_{Tot} (kcal mol^{-1}) are present for each conformation.

From the obtained data it can be said that in dilute solutions, when all interactions between different polymer chains can be neglected, PVA chain tends to collapse into a globule-like conformation. It can be explained from the OH-group association point of view. As it was shown above the inter-molecular associations between two isolated OH-groups of two different polymer chains or between two not consecutive OH-groups of the same chain were favorable towards lower energy hierarchy, compare to the intra-molecular association and association with water. Such factor directly affects the conformation of PVA. Due to the absence of any other explicit macromolecules in the system the more efficient way for isolated PVA chain for stabilizing the energy in water is to fold, forming strong intermolecular H-bonds within the coil.

As mentioned above the distance between two chains decreases with the increase of PVA concentration until those molecules overlap or interpenetrate. Interactions between macromolecules in more concentrated solutions increase the volumes of the coils and finally unwrap them in order to increase the number of interacting centers between chains. OH-groups of different macromolecules associated *via* H-bonds are consider to be such centers and responsible for stabilizing the new shape. Therefore, interactions between two initially dense coils deform their shape and leads to H-bonds reorganization from inter-molecular within the coil (between two not consecutive OH-groups of the same chain) to inter-molecular between two different chains. Figure 4 shows the initial stage of interaction between two dense coils of PVA.

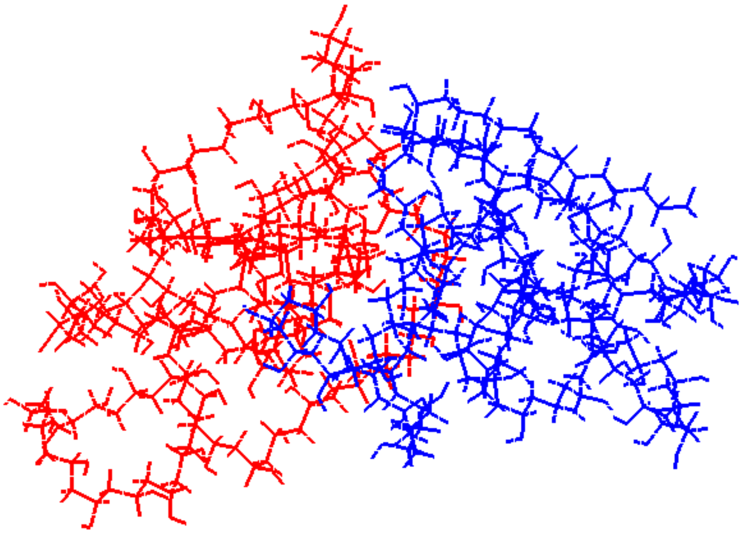

Figure 4. The initial stage of interaction between two PVA coils. E_{Tot} = 2527 kcal mol^{-1}.

According to Tager [25] the distance between two ends of one chain indicates the volume state of any coil. Thus far, the mentioned distance increases with an increase of the volume of the coil. We found that for an isolated coil (Figure 3) the distance was equal to 16.9 and 20.1 Å for the interacted one (Figure 4). Therefore, we can approve that interaction between two macromolecules even in a globule-like mode leads to their unwrapping. Armed with observations made in this work together with literature data on PVA association we suggest the essential differences in kinetics of the acetalization reaction of PVA with aldehydes in dilute compare to concentrate solutions. The conformations of PVA in dilute solutions may lead to more dense coils, hence the distances between various parts of a single chain decrease, resulting in a coil shape favourable for intra-molecular cross-linking. Intra-molecular cross-linking is accompanied by a loss of flexibility of the resulting products due to internal cross-linking, which leads to the shrinking of individual chains. The mass-transfer process in such systems may be slower than the subsequent chemical reaction, so that the rate of diffusion controls the rate of the reaction. As a result, the reaction may proceed with anomalous retardation.

Conclusions

Various parameters of three types of H-bonds formed in PVA-water systems were calculated using quantum-mechanical techniques. According to them inter-molecular association between OH-groups was more stable *versus* intra-molecular association (between two adjacent OH-groups) or association between OH-group and water.

PVA conformations in dilute and concentrated solutions were studied using Langevin dynamics simulations. It was established that in dilute solution PVA chain tend to collapse, folding into a dense coil.

Based on the theoretical investigations it was presumed that in dilute solution of PVA the acetalization reaction may proceed with essential retardation.

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