The hydrogen bond interaction dynamics in polyvinylphenol: Studied by Born-Oppenheimer molecular dynamics

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ABSTRACT

In this letter, we present the results of the study of the hydrogen bond network of Poly(4-vinylphenol) (PVPh) by using Born-Oppenheimer molecular dynamics. The polymeric structure and IR spectra of PVPh result from the presence of hydrogen bonds between the hydroxyl group. The presented study focuses on the analysis of changes in the network of conjugated hydrogen bonds observed in Poly(4-vinylphenol). The hydroxyl groups form conjugated hydrogen bonds in separate domains. The *ab initio* molecular dynamics gave us a possibility to understand the stabilization role of the hydrogen bond in the polymer material. Additionally, the quantization of nuclear motion has been performed.

1. Introduction

Nowadays, a variety of polymers surround us: the main part of the used goods is made from a polymer material. Million tons of synthetic polymer are produced each year. However, responsible management of our planet's resources requires paying attention to biodegradable polymers as environment-friendly materials [1,2]. A good example of biodegradable polymers: polyhydroxybutyrate is commonly used in the industry [3]. On the other hand, many synthetic polymers, for example, styrene are hard to degrade and reuse.

Polymers play a pivotal role as one of the essential resources in multiple fields, such as materials, energy, information technology as well as medicine [4–6]. Therefore, it is highly desirable to understand and control complex polymer structures, their intermolecular interactions, and their dispersibility [7–9]. However rational design of the new materialrequires an understanding of the intermolecular (interchain) interactions. It should be stressed that the design of the polymer material with desired properties involves the modeling of the polymer structure and further the strength, orientation, and/or network of the interchain interactions, hydrogen bonds in particular. The crystal structures and physical properties of polymers have been investigated by using various spectroscopic and X-ray diffraction methods, such as infrared (IR) [10], near-IR (NIR) [11], Raman [12,13], terahertz

[13,14], far-ultraviolet (FUV) [15] and wide-angle X-ray diffraction (WAXD) [16]. It should be pointed out that many other methods allow us to analyze hydrogen bonds, e.g. the Bader theory, the Energy Decomposition Analysis (EDA), and other methods that require fragmentation [17–18]. However, the vibrational analysis gave us crucial information about observed hydrogen bonds [15,16,19,20]. Nevertheless, while the size and complexity of systems increase, IR and Raman spectra of such systems become more difficult to analyze. Therefore, the theoretical methods have been used as an effective tool for understanding IR and Raman spectra of polymers and analysis of intermolecular interactions in polymers. The combination of the theoretical and experimental investigation gives us the possibility to perform a detailed study about the strength of interaction and the dynamic character of the interaction network.

Molecular dynamics, in particular Born-Oppenheimer molecular dynamics (BOMD), is a powerful tool for the analysis of intermolecular interactions, especially hydrogen bonds. A broad and detailed description of molecular dynamics has been presented in several monographs [21–22] and review papers [23–25]. The main assumption of adiabatic molecular dynamics is describe the motion of nuclei along the potential energy surface. The Born-Oppenheimer approximation makes it possible to treat the motion of nuclei and electrons independently. The molecular dynamics method is based on the integration of the classical equation of

motion [26,27]. This approach provides information about the electron structure using quantum chemistry methods in the same way as in static calculations. The potential energy surface (PES) calculated by ab initio methods is essential, for systems where there is a possibility of breaking and forming chemical bonds e.g.: systems with strong hydrogen bonds [28–29]. This methodology provides an accurate description of the system's dynamics and allows taking into account structural changes as well as the anharmonicity of nuclei motions. Vibrational spectra calculated as an average along the trajectory is more accurate than the one obtained from static calculations. Another important feature that distinguishes BOMD from some other theoretical methods is the possibility to precisely describe proton motions. It should be emphasized that the dynamics of proton motion in hydrogen bonds are determined by the complex nature of the interactions occurring in the studied system. These interactions are responsible for the complex structure of infrared and Raman spectra of polymeric systems[30,31].

It is also important to point out the time cost of the MD calculation: it is approximately equal to the cost of the "static" ab initio calculation multiplied by the number of trajectory steps. Long trajectories are advantageous for spectroscopic studies, especially in the low-frequency range, which is characteristic of slow motions. Note that the time step is an important parameter for molecular dynamics calculations. A decreasing time step in the numerically calculated trajectory leads to more accurate results. Nevertheless, the computational cost increases with the number of steps. In practice, the maximum number of time steps is determined by the period of the vibration with the highest energy.

Poly(4-vinylphenol) (PVPh) is often compared to polystyrene due to structural similarities: poly(4-vinylphenol) contains a hydroxyl group in the *para* position of the phenyl ring additionally (Fig. 1a). Recent research proved the presence of medium-strong interchain hydrogen bonds in PVPh structure [19,20,32]. These interactions can serve as donors forming hydrogen bonds with other polymers. PVPh is frequently investigated as a component capable of promoting miscibility in various polymer blends: in particular, with poly(vinyl methyl ketone) by Bourara et al. [32], poly(methyl methacrylate) by Ozaki et al. [19,20] or poly (vinylpyrrolidone) by Kuo et al. [33]. The especially interesting is blended polyvinylphenol with biodegradable polymers that may change the properties and stability of polymers [41]. This may be explained by computational enzymology [42].

The aim of this work is to take an insight into the nature of interchain interactions in PVPh structure by means of theoretical methods. We present the results of ab initio BOMD calculations performed for the 4-chains model of PVPh. Fig. 1 depicts the considered model of PVPh. This presented model and applied method allow us to consider hydrogen bond interaction while describing details of electron structures. The emphasishas been put on the reconstruction of the vibrational bands of the hydrogen-bonded functional group. We have also discussed the dynamics effects and conjugation between hydrogen bonds as well as chain position fluctuation along with MD simulations.

2. Computational details

The *Born-Oppenheimer* molecular dynamics (BOMD) simulations were carried out for the model system of polyvinylphenol polymer (PVPh). The studied system contains four chains. The structure of each chain has been extracted from the crystal structure. The one chain contains 32 monomers contracted syndiotactic polymer. After MD simulation some of the monomers reorients and the finished structure has been atactic. It should be pointed out that atactic conformation is a standard polystyrene structure. The computational cell is illustrated by parameters: $a = b = c = 80$ Å, $\alpha = \gamma = \beta = 90°$. Fig. 1 and 2 illustrate the considered model system.

The MD simulations were carried out using the Born-Oppenheimer approach in the Quickstep scheme [34–35]. The temperature was set to 300 K and the MD time step was set to 1 fs. The total simulation time was c.a. 110 ps each (110 000 steps). The Pade functional was used as the exchange-correlation functional with the Grimme's dispersion correction (D3) [36–37]. A mix of DZVP basis sets and plane waves (cutoff = 250 Ry) was used. The trajectory was visualized and analyzed by the VMD software [38] and many tools were created for performed analyses.

The interactions between polymer chains in the model system were analyzed between one selected chain and the rest of the systems (three chains). Snapshot structures of the trajectory were extracted every 1000 steps (equivalent to 1 ps), yielding 100 distinct structures to represent a variety of possible conformers. For each of the extracted snapshot structures, a one-dimensional (1D) proton potential function was obtained by stepwise displacement of one hydrogen-bonded proton along the hydrogen vector parallel to the pertinent O—H line. The corresponding internal coordinate (x) was defined as the distance between hydrogen and oxygen atoms. The scan typically covered the × range from 0.6 Å to 2.45 Å. The hydrogen was displaced along the distance steps of 0.05 Å. Having acquired the potentials, the vibrational energy levels and proton wave functions were obtained by solving the vibrational Schrödinger equation for each individual potential [43,44].

3. Results and discussion

The experimental spectra have been published and analyzed by Ozaki *et al.* [19,20]. However, the origin of the limited number of hydrogen bonds observed in PVPh polymer was an open question. Theoretical spectra of the model structure of PVPh have been presented in Fig. 3. The high-frequency region in the power spectra has a rich structure. This region, between 2000 cm^{-1} and 3000 cm^{-1}, reflects hydrogen bonds. The highest region reflects the stretching modes of non-interacted groups. Let us discuss the stretching mode region carefully: firstly the experimental data then the computational results. The experimental spectrum of PVPh shows an intense first band between 2800 cm^{-1} and 3050 cm^{-1}the maximum is at 2920 cm^{-1}. The half-width of this band has been assigned as ca. 150 cm^{-1}. It should be pointed out that this band has two additional maxima with low intensity before and after the intense central maximum. Further, the next band occurs between 3150 cm^{-1} and 3260 cm^{-1}, with a maximum of 3350 cm^{-1}.

The theoretical results are mainly in line with experimental data. The first band in the high-frequency region occurs between 2800 cm^{-1} and 3000 cm^{-1} and has two maxima 2920 cm^{-1} and 2985 cm^{-1}. The next band ranges between 3000 cm^{-1} and 3200 cm^{-1} with the maximum at 3090 cm^{-1}. The third band starts around 3300 cm^{-1} and finishes around 3600 cm^{-1}, with the maximum at 3450 cm^{-1}. In the last band with an
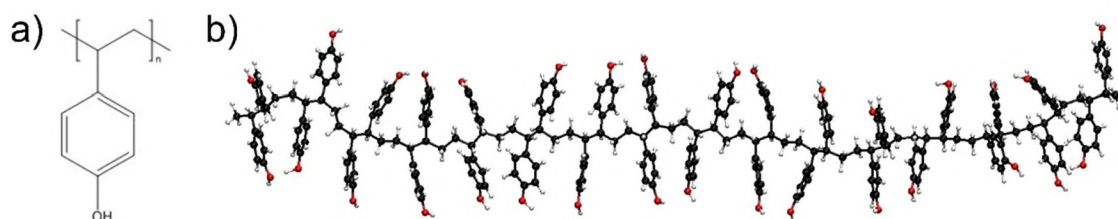

Fig. 1. Panels: a) shows the chemical structure of Poly(4-vinylphenol), b) depicts the chain model of PVPh.
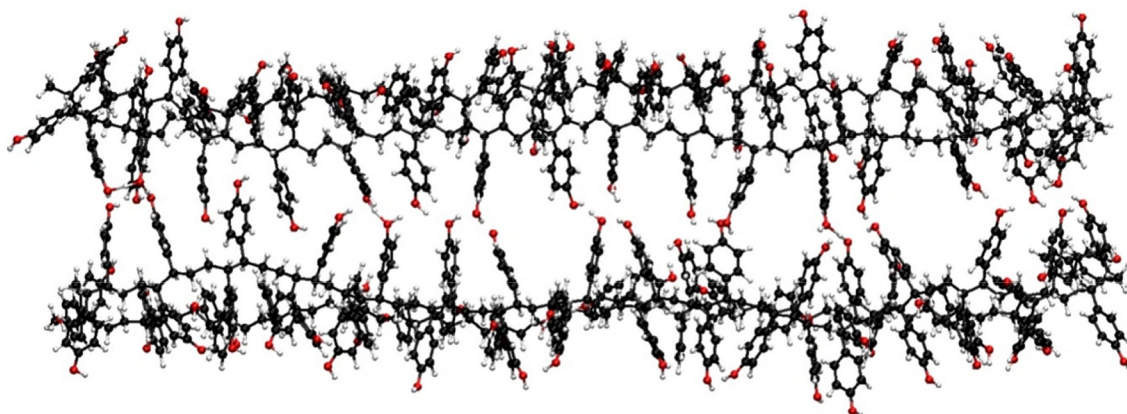
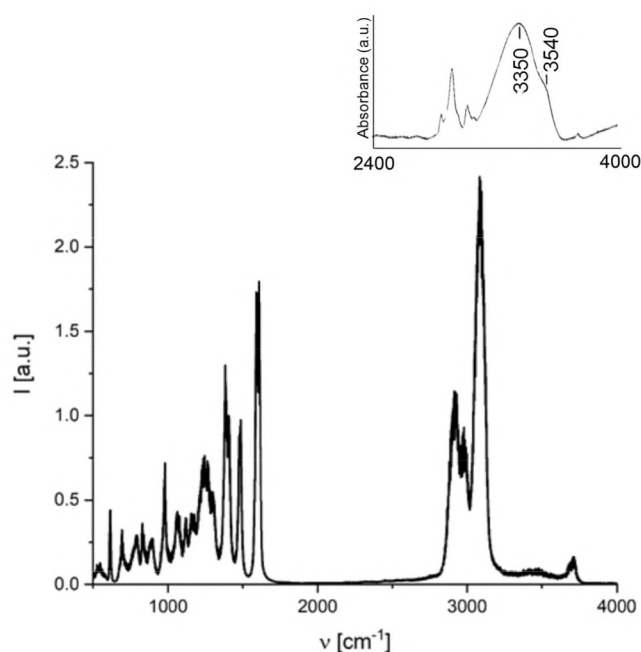**Fig. 2.** The computational cell of the four-chain model of the PVPh.

Fig. 3. Calculated power spectra of the PVPh polymer model. The top right panel shows the experimental spectra of the high frequency region, adopted from 19.

average intensity range between 3630 cm^{-1} and 3790 cm^{-1}, the pick is situated at 3670 cm^{-1}. The comparison of experimental features of both studied crystals shows the largest differences in intensities, but the position of the band looks reasonably well described after comparing with experimental data.

The analysis of the band component has been based on the calculation of Fourier transformation from the atom position autocorrelation function. The analysis of power spectra allowed us to understand the genesis and discuss separately each band. The selection of hydrogen-bonded groups in PVPh (hydroxyls) allowed us to understand interchain interaction influence on the spectra.

During the molecular dynamics simulations, the hydroxyl group from two different chains creates the hydrogen bond domains containing from 3 to 7 or 8 hydrogen bonds. The longer domains are not preferable because of the steric hindrance. During the 100 ps, each hydrogen bond domains are stable. The one typical hydrogen bond domains has been depicted in Fig. 4. The hydrogen bonded hydroxyl group has been marked by grey sphere. The motion of hydrogen bonds in the investigated domains has been studied by vibrational analyses. The power

spectra have been calculated for the marked grey spheres of hydrogen and oxygen atoms.

Fig. 5 shows the power spectra of the selected HB domain. The most interesting high-frequency region contains two bands. The first broadband range between 2200 cm^{-1} and 3400 cm^{-1} with maximum at 3050 cm^{-1}. The half-width of this band has been assigned as ca. 700 cm^{-1}. The enlargement of this band and intensity indicates the strong hydrogen bonds between hydroxyl groups. The second and the last band range between 3550 cm^{-1} and 3750 cm^{-1} with the pick situated at 3650 cm^{-1}. This band is located in the highest frequency region we may easily associate with the two O-H modes that are not involved in the hydrogen bond interactions. It should be noted, that each hydrogen bond dogman always has at least one O-H group (first or last group in the hydrogen-bonded chains) that does not create any hydrogen bonds.

In the end, we performed an analysis of the interaction energies between the one polymer chain and the three surrounding chains. The analysis of the interaction between molecules can be done in terms of the energy components. The difference between the energy of the whole model system and the sum of energies of fragments gave a good estimation of the interaction energy. Fig. 6 presents values of the interaction energies along the trajectory. Each point corresponds to one structure extracted from the ab initio trajectory. The structures have been taken every 1 ps.

The value of interaction energy spans from −480 kcal/mol to −400 kcal/mol. The fluctuation of these points is around 50 kcal/mol which corresponds to the room temperature of the simulation. It should be stressed that each chain contains 32 monomers with an OH group. In this case, 32 hydrogen bonds can be maximally created. To recalculate the interaction energy for one monomer, the values range between 15 kcal/mol and 12.5 kcal/mol. This results elucidate relatively strong hydrogen bonds between hydroxyl groups in the hydrogen bond domain. However, some of the groups do not create any specific interaction as a proton donors due to the steric effects. A similar effect has been observed previously in the vitamin C crystalas well as nylon 6 polymorphs [39,40].

The above statement has been confirmed by the *a posteriori* quantization of nuclear motion. Firstly, the calculation of the one-dimensional (1D) proton potentials corresponding to the instantaneous snapshot structures extracted from the trajectory has been done. We generated one-dimensional proton potentials using one linear pathway (O-H). Fig. 7. shows the solution of the vibrational Schrödinger equation. The band that represented the sum of contours (black line) has three maxima located at 2397 cm^{-1} (highest intensity), 2660 cm^{-1}, and 3371 cm^{-1} (lowest intensity). The maximum at 3371 cm^{-1} origins from the nonbonded hydroxyl group (green line). The theoretical band is red-shifted from the experimental one. However, It should be stressed that molecular dynamics calculations show that only some parts of hydroxyl
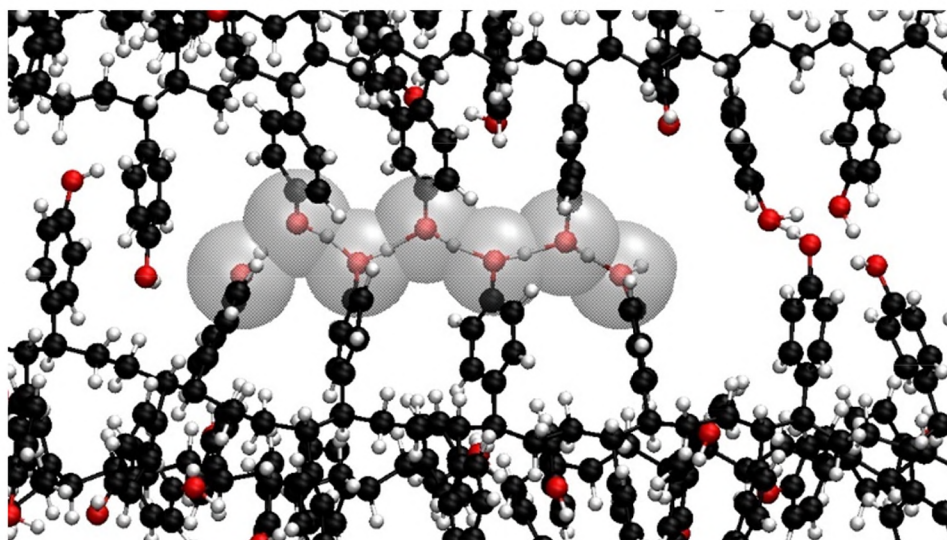
Fig. 4. Hydrogen bond chain between PVPh chains. The grey sphere marked the considered hydrogen bond domain.
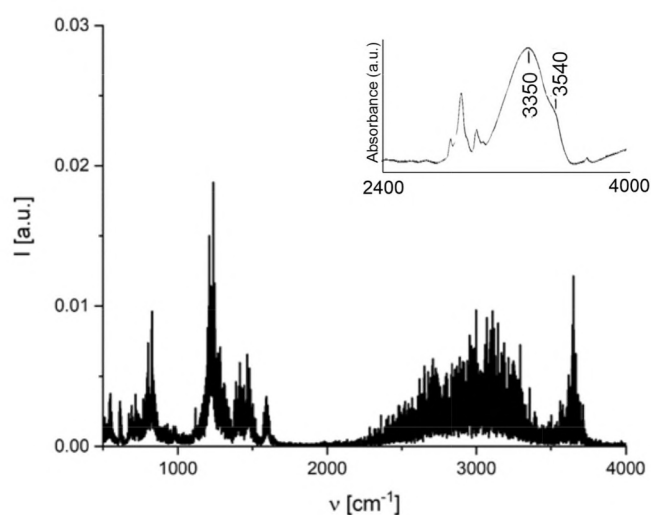

Fig. 5. Power spectra of the sevenOH groups of the PVPh polymer formed HB chains.The top right panel shows the experimental spectra of the high frequency region, adopted from 19.

Fig. 6. Values of interaction energies between one selected PVPh chain and three surrounding PVPh chains along the trajectory.

groups form conjugated hydrogen bonds and we mainly consider the hydroxyl groups from PVPh that form strong hydrogen bond interaction.

4. Conclusions

In this article, we investigate hydrogen bond networks in poly(4-vinylphenol) (PVPh). The used methodology was evaluated by comparing calculated power spectra with the experimental ones. The calculations have been performed for model systems containing four PVPh chains. Positions of calculated bands are in good agreement with the experimental data, which gave us the possibility to discuss and compare studied systems.

Further, we analyzed the hydrogen bond interactions between polymer chains by calculating the power spectra in terms of the chemical group. The analysis of positions and intensities of peaks shows the difference in the strengths of hydrogen bonds. Redshift in the spectrum of the OH stretching mode has been elucidated while a big part of this band was in the high-frequency region. The results show the origin of presence in the IR spectra of non-interacted hydroxyl groups.

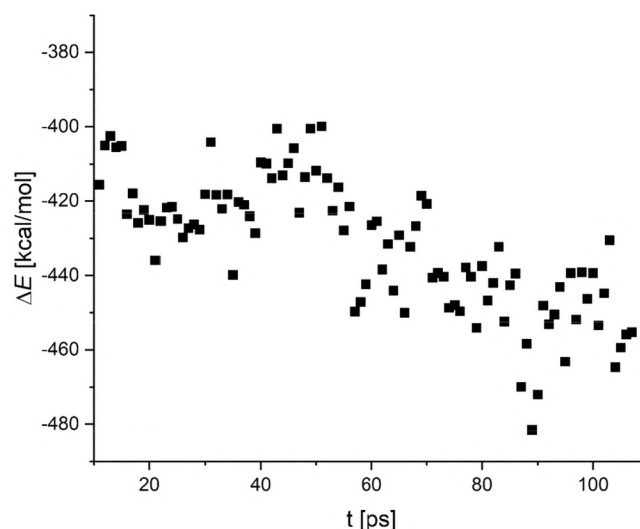In the paper, we analyzed the interaction energy between one

polymer chain and the neighborhood of three polymer chains. The time courses of the interaction energies show that the intermolecular interaction is generally stable in the PVPh model system. The PVPh polymer chains create a separate domain that is not conjugated together. On the one hand, analysis shows the limited number of hydrogen bonds, but on the other hand the created interactions are strong.

The perspective of further analysis should be analysis of the hydrogen bond domains statistics in the bigger model systems. A matter of choice is the selection of the methodology. In this work, we perform quantum (DFT) calculations for 2176 atoms. The statistical analysis of hydrogen bond domains requires huge extensions of the used model and goes toward the force field.

CRediT authorship contribution statement

Mateusz Z. Brela: Investigation, Conceptualization, Methodology, Writing – review & editing. **Yuliia Didovets:** Investigation. **Marek Boczar:** Methodology. **Harumi Sato:** Conceptualization. **Takahito Nakajima:** Writing – review & editing. **Marek J. Wójcik:** Conceptualization, Writing – review & editing.
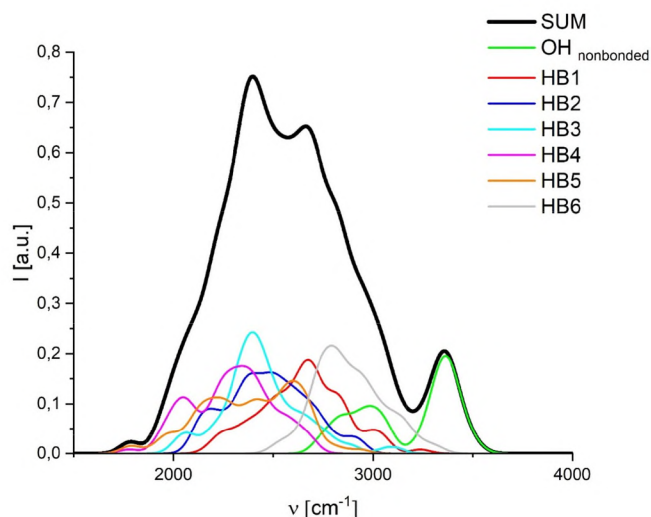
Fig. 7. O—H stretching band contours of the hydrogen-bonded hydroxyl group in PVPh polymer. Each line contours were calculated from individual fundamental vibrational transitions as a superposition of Gaussian functions with a half-width of 50 cm^{-1}. The color line represents the hydroxyl group in the hydrogen bond chains depicted in Fig. 4 (HB1 is the first hydroxyl group in the right part of the selected hydrogen-bonded chain, each hydrogen bond has been numbered respectively from right to left). The black contour represents the sum of seven contours. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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