

Proton Magnetic Resonance Investigation of the Orientation of Hydrogen Bonds in Nylon 66, Poly(vinyl Alcohol), and Cotton Yarn

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Synopsis

Directional dependence of the PMR-narrow-band in oriented fibers of nylon 66, poly(vinyl alcohol), and cotton has been investigated to study the orientation of hydrogen bonds in the unit cell. Filaments of oriented fibers were conditioned to 75% relative humidity, then aligned together axially and packed in a teflon tube. The teflon tube was suspended in the NMR probe in such a manner that the fiber axis was horizontal and could be rotated to a desired angle with respect to the magnetic field. Variation of the narrow-band line width as a function of the angle between the fiber axis and the magnetic field-direction shows a minimum at 0° orientation for nylon 66 and PVA, but in the case of cotton it shows a minimum at about 80° orientation. This indicates that in the case of nylon 66 and PVA, hydrogen bonds are oriented nearly perpendicular to the chain axis, but in the case of cotton fiber, H bonds are oriented nearly parallel to the chain axis. This would suggest that nylon 66 and PVA have interchain hydrogen bonding, but the hydrogen bonds contributing to directional dependence, in the case of cotton fiber, are intrachain. The interchain hydrogen bonds between the lateral chains, if they exist, must be random and, therefore, do not contribute to directional dependence. The interchain H bonds between central and corner chains are probably oriented in such a way that the horizontal component of p - p vectors have nearly the same orientation in the unit cell as the p - p vectors of the intrachain hydrogen bonds.

Introduction

Hydrogen bonding has been a subject of interest for a long time. It is now known that hydrogen bonding plays an important role in biological as well as other systems. Studies of hydrogen bonding in nylon 66 have been carried out by x-ray and infrared methods.¹⁻⁵ Hydrogen bonding in poly(vinyl alcohol) has been studied by several workers.⁶⁻¹¹ There is a lot of controversy about the hydrogen-bonding scheme in cellulose I.¹²⁻¹⁵ Berendsen¹⁶ has studied collagen hydration by NMR.

In the present work, the directional dependence of the PMR narrow band in oriented fibers of nylon 66, poly(vinyl alcohol), and cotton has been studied, to investigate the orientation of proton-proton vectors involved in hydrogen bonding. This, in other words, would give information about the orientation of hydrogen bonds in the unit cell.

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Experimental

The specimens of nylon 66, poly(vinyl alcohol), and cotton used in this experiment were oriented fibers in the form of a high-tenacity multifilament yarn. Filaments, 1 cm. long, were cut and aligned axially. The axially aligned filaments were packed in a Teflon tube about 1 cm. in length and about $1/2$ cm. in diameter. The samples were conditioned to 75% R.H. in a desiccator, at room temperature. The Teflon tube containing the sample was suspended in the NMR probe so that the fiber axis was horizontal and could be rotated to the desired angle with respect to the direction of the constant magnetic field, H_0 . The error in the axial alignment of the filaments plus the error in angular setting was about $\pm 5^\circ$. Conditioning of the specimen was done for about 4 weeks, until saturation was achieved. The PMR narrow band was recorded for different axial orientations of the specimen. The broad band, in this case, was ignored because it is a contribution from the protons in the polymer unit cell, which are strongly coupled. The narrow band is of interest here because it represents contributions from protons in the hydrogen bonds and the protons in the water molecules trapped in the lattice which are relatively free.

A dual-purpose Varian NMR instrument was used with a variable radio-frequency oscillator. The proton resonance was studied at 14.9 MHz. The following spectrometer settings were used: radiofrequency field H_1 , 0.006 gauss; modulation field, 0.1 gauss; sweep field, 0.04 gauss/min.; response, 3, which corresponds to 3 sec. To register a small variation in the line width it is important to have a very stable magnetic field. Even a slight drift is likely to spoil the experiment.

Results and Discussion

Figures 1, 2, and 3 show the variation of line width as a function of the angle between the fiber axis and the magnetic field direction, for nylon 66, poly(vinyl alcohol), and cotton, respectively. Nylon 66 and PVA specimens show minima at about 0° orientation of the fiber axis with respect to the magnetic field direction, and the cotton fiber shows a minimum at about 80° orientation. To determine the orientation of the proton-proton vector with respect to the chain-axis we use the relation,¹⁷

$$\Delta H = I(3\mu/r^3)[3 \cos^2 \delta \cos^2 (\Phi - \Phi_I) - 1] \quad (1)$$

where δ is the angle which the p - p vector makes with the plane, Φ is the angle between an arbitrary axis in the plane and magnetic field, Φ_I is the angle between the projection of p - p vector in the plane and an arbitrary zero line. In our case δ is nearly zero, and the arbitrary axis coincides with the chain axis, which is also the fiber axis. Therefore $\cos \theta = \cos \delta \cos(\Phi - \Phi_I)$ and eq. (1) reduces to:

$$\Delta H = \pm(3\mu/r^3)[3 \cos^2 \theta - 1] \quad (2)$$

where θ is the angle between the internuclear vector and the external magnetic field.

If the $p-p$ vector were parallel with the chain axis, then the minima would fall at about 55° . In the case of nylon 66 and PVA, the minima

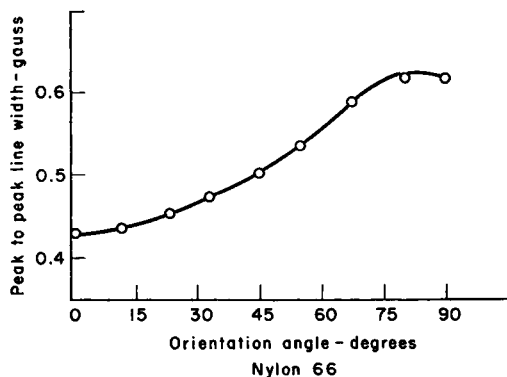


Fig. 1. Peak-to-peak line width vs. orientation angle for nylon 66.

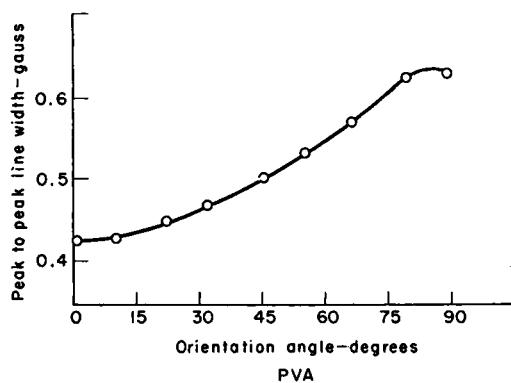


Fig. 2. Peak-to-peak line width vs. orientation angle for PVA.

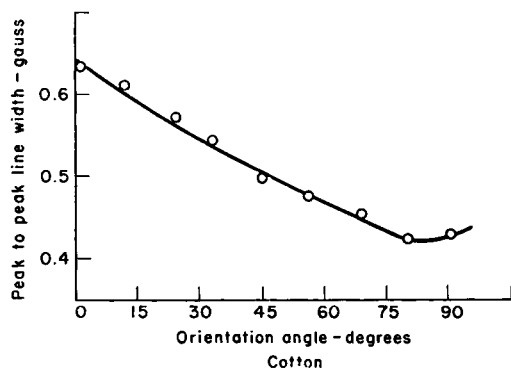


Fig. 3. Peak-to-peak line width vs. orientation angle for cotton yarn.

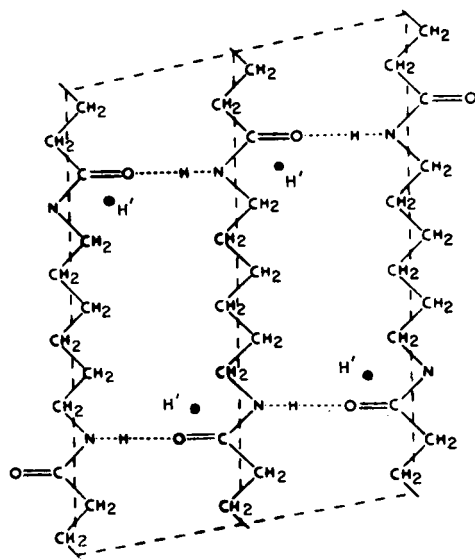


Fig. 4. Unit cell for nylon 66, showing hydrogen bonding and approximate positions of proton-proton ($\text{H-H}'$) vectors involved.

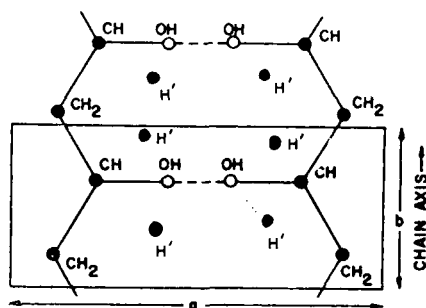


Fig. 5. Unit cell for PVA, showing hydrogen bonding and approximate positions of proton-proton vectors ($\text{H-H}'$) involved.

fall at about 0° , which would mean that the proton-proton vector makes an angle of about 55° with the chain axis. If the $p-p$ vector makes an angle of 125° which is supplementary, then it would also satisfy the condition for a minimum at 0° .

Figures 4 and 5 show the hydrogen bonding and approximate positions of proton-proton vectors involved for nylon 66 and poly(vinyl alcohol). $\text{H-H}'$ vectors in both these cases make approximately a 55° angle, within experimental error. In polymers where hydrogen bonding is interchain and is perpendicular to the chain axis, proton-proton vectors will be oriented as in PVA or nylon 66, and ΔH will show a minimum at about 0° . In cases where hydrogen bonding is not perpendicular to the chain axis the minima will fall at some other angle. The approximate angle subtended

by the hydrogen bond to the chain axis can be determined by this method. In nylon 66, there is a lateral shift of the adjacent chains which enables the hydrogen bonds to be perpendicular to the chain axis. The hydrogen bonds in PVA are also perpendicular to the chain axis, therefore, we observe a similar directional dependence in these cases.

For cotton fiber, the minimum of ΔH falls at 80° . This would mean that proton-proton vector makes a 25° angle with the chain axis. Figure 6 shows the intrachain hydrogen bonding scheme proposed by Liang and Marchessault for cellulose I. If we assume that the hydrogen bonding for cotton fiber would be similar to that of cellulose I, then the proton-proton vector involved in interchain hydrogen bonding would subtend an angle of about 25° with the chain axis, as observed experimentally.

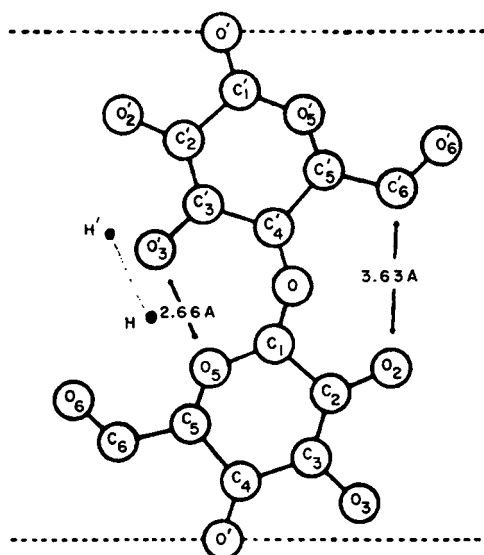


Fig. 6. Unit cell for cellulose I, showing intrachain hydrogen bonding and the approximate position of proton-proton ($H-H'$) vectors involved.

The proton-proton vectors involved in interchain hydrogen bonding between the corner and central chain probably subtend an angle of about 25° with the chain axis, so as to contribute to the directional dependence in the same manner as the $p-p$ vector for intrachain hydrogen bonding or a supplementary angle.

Hydrogen bonding between adjacent chains does not contribute to the observed directional dependence. This suggests that either there is no hydrogen bonding between the adjacent chains or it is so random that it does not contribute to directional dependence. It is possible that the water molecules trapped between the adjacent chains are random.

Intrachain hydrogen bonding seems to be more predominant in case of cotton fiber than interchain hydrogen bonding. Hydrogen bonding is

nearly parallel to the chain axis. In case of nylon 66 and PVA, hydrogen bonding is interchain and is perpendicular to the chain axis.

Conclusion

The directional dependence of the narrow line of the PMR spectra for nylon 66, poly(vinyl alcohol), and cotton fiber indicates that in the cases of nylon 66 and PVA, hydrogen bonding is oriented nearly perpendicular to the chain axis. In the case of cotton yarn, hydrogen bonding is oriented nearly parallel to the chain axis. This would suggest that nylon 66 and PVA have interchain hydrogen bonding. The hydrogen bonds which contribute to directional dependence, in the case of cotton fiber are intrachain hydrogen bonds. If there is interchain hydrogen bonding present, it would be between the corner and central chain. Interchain hydrogen bonding between the lateral chains is not detectable, if such hydrogen bonds exist, they would have random orientations and would therefore not contribute to directional dependence. The water molecules trapped between the lateral chains are oriented randomly.

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Résumé

La dépendance de la bande étroite de résonance nucléaire magnétique en fonction de la direction dans des fibres orientées de nylon 66, d'alcool polyvinylique et de coton a été étudiée en vue d'étudier l'orientation des hydrogènes dans la cellule unitaire. Les filaments des fibres orientées avaient été conditionnées à 75% d'humidité relative, ensuite alignées entre elles axialement et emballées dans un tube en téflon. Le tube en téflon était suspendu à un porte-objet NMR de façon que l'axe de la fibre soit horizontal et puisse être tourné à un angle désiré par rapport au champ magnétique. La variation de la largeur de la raie étroite en fonction de l'angle entre l'axe de la fibre et la direction du champ magnétique montrait un minimum à une orientation de 0° pour le nylon 66 et le PVA, mais dans le cas du coton, il montrait un minimum à une orientation d'environ

80°. Ceci indique que dans le cas du nylon 66 et du PVA les liaisons hydrogènes sont orientées environ perpendiculairement par rapport à l'axe de la chaîne, mais dans le cas de la fibre de coton, les liaisons hydrogènes sont orientées environ parallèlement à cet axe de la chaîne. Ceci suggérerait que le nylon 66 et le PVA ont des liaisons hydrogènes intercaténaires, mais que les liens hydrogènes contribuant à la dépendance en fonction de la direction dans le cas de la fibre de coton sont intramoléculaires. Les liaisons hydrogènes intramoléculaires entre les chaînes latérales, si elles existent, doivent être statistiques et donc ne contribuent pas à la dépendance en fonction de la direction. Les liaisons hydrogènes intermoléculaires entre les chaînes centrales et celles sur les côtés sont probablement orientées de telle façon que le composant horizontal du vecteur $p-p$ ait approximativement la même orientation dans la cellule unitaire que le vecteur $p-p$ dans les liaisons hydrogènes intramoléculaires.

Zusammenfassung

Die Richtungsabhängigkeit der Schmalband-PMR in orientierten Nylon 66-, Polyvinylalkohol- und Baumwollfasern wurde zur Bestimmung der Orientierung der Wasserstoffbindungen in der Elementarzelle untersucht. Fäden aus orientierten Fasern wurden auf 75% r.F. konditioniert, axial ausgerichtet und in ein Teflonrohr gepackt. Das Teflonrohr wurde so im Probenraum des NMR-Geräts aufgehängt, dass die Faserachse horizontal lag und gegen das magnetische Feld um einen gewünschten Winkel gedreht werden konnte. Die Abhängigkeit der Schmalbandlinienbreite vom Winkel zwischen Faserachse und Magnetfeldrichtung zeigt ein Minimum bei 0°-Orientierung für Nylon 66 und PVA, im Falle der Baumwolle jedoch ein solches bei 80°-Orientierung. Im Fall von Nylon 66 und PVA sind daher die Wasserstoffbindungen nahezu senkrecht zur Kettenachse orientiert, im Falle der Baumwollfaser aber parallel. Das würde dafür sprechen, dass Nylon 66 und PVA Wasserstoffbindungen zwischen den Ketten besitzen, während die zur Richtungsabhängigkeit beitragenden Wasserstoffbindungen im Falle der Baumwollfaser innerhalb der Ketten liegen. Die Wasserstoffbindungen zwischen Seitenketten müssen, falls sie vorhanden sind, ungeordnet sein und tragen daher nicht zur Richtungsabhängigkeit bei. Die H-Bindungen zwischen zentralen und an den Ecken liegenden Ketten sind wahrscheinlich so orientiert, dass die Horizontalkomponente des $p-p$ -Vektors nahezu die gleiche Orientierung in der Elementarzelle besitzt wie der $p-p$ -Vektor der Wasserstoffbindungen innerhalb der Ketten.

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