Fourier transform infra-red spectroscopic studies of water molecules sorbed in solid polymers

Hiroshi Kusanagi* **and Seiichi Yukawa**
Unitika Research Laboratories Inc., 23 Kozakura, Uji, Kyoto 611, Japan
(Received 22 November 1993; revised 24 May 1994)

Water structures in polymeric matrices were studied using Fourier transform infra-red (*FT*i.r.) spectroscopy. The infra-red spectra of water sorbed in many polymers imply systematic changes. As the polymer becomes more hydrophilic, among the three bands corresponding to the normal vibrational modes of an isolated water molecule the ν_a(OH) and ν_s(OH) bands gradually shift to lower frequencies, while the $\delta(\angle$HOH) band moves to a higher frequency. Using these shifts, we have deduced the heat of water sorption for several hydrophobic polymers. Moreover, it has been found that the atom with the largest electronegativity in the polymers increases the bending frequency shift, $\Delta\delta(\angle$HOH), more than the stretching frequency shifts, $\Delta\nu_a$(OH) and $\Delta\nu_s$(OH). Eventually, it was concluded that water molecules sorbed in solid polymers, in almost all cases (for both hydrophilic and hydrophobic materials), form either strong or weak hydrogen bonds with particular site atoms in the polymers. Various water structures in these polymeric matrices were discussed in terms of the *FT*i.r. data that were obtained.

(Keywords: sorbed water; solid polymers; *FT*i.r. spectroscopy)

INTRODUCTION

Synthetic polymers, such as polyesters, polyamides, polyolefins, etc., are widely used materials in our everyday lives, in the form of fibres, films, and plastics. It is now hard to imagine a world with none of these polymers at all[1]. The changes in their physical structures and properties, as a result of water uptake from the air often attracts our attention, and in particular in the field of high technology, such changes may present a problem, even if hydrophobic polymers are used. For example, when poly(methyl methacrylate) (PMMA) is used as the optical disk substrate in videodisks, computer memory units, and so on[2], bending of the disk caused by moisture sorption ($\sim$0.4 wt%) soon after melt moulding is a troublesome problem in the production process. Strict humidity control in the factory must be achieved for the control of quality in production. For the solution to these problems, a basic understanding of the water-sorption phenomenon in polymer materials is of fundamental importance. Nevertheless, the nature and structure of water molecules in solid polymers, especially in high-performance hydrophobic polymers, are even now still poorly understood[3,4].

The purpose of this paper is to study the intermolecular interactions between various solid polymers and the water molecules which have been sorbed in them, thereby aiming to clarify the water structures in solid polymer matrices and also the molecular mechanisms in polymer–water sorption phenomena.

Infra-red (i.r.) spectroscopy is a basically important technique for the structural study of materials at the molecular level and this is currently an area of rapid development. This technique has long been used as a structural probe of water phases[6,7]. We report here on its application to systems composed of water molecules and various hydrophobic and hydrophilic polymers. In particular, the recently developed high-sensitive Fourier transform infra-red (*FT*i.r.) spectrometer is a powerful tool for studying systems containing high-performance hydrophobic polymers, which although they absorb little water still show the detrimental physical property changes described above.

A new aspect for water structures in synthetic polymers may be a useful way to clarify liquid water itself and also the various water structures which occur in biopolymers.

EXPERIMENTAL

Preparation of samples for FT*i.r. measurements*

Commercially available polymers were largely used in this study. The polymer pellet was melted, pressed between two stainless steel plates using an aluminium spacer, and then quenched in cold water. The film thickness was controlled depending on the water content of each polymer. For example, films with thicknesses of 100 and 6 μm were used for hydrophobic poly(ethylene terephthalate) (PET) and hydrophilic nylon-6 (N6), respectively.

Measurements

The infra-red spectra of water sorbed in the polymers were measured by using the subtraction method as

---

* To whom correspondence should be addressed

0032-3861/94/26/5637-04

follows. The film, held in a *FT*i.r. sample holder was conditioned at a relative humidity (r.h.) of 65% for 96 h. After transforming this film into the spectrometer (Nicolet Model 7199), a first spectrum was measured immediately at 25°C. Then, after drying the film completely in a flow of N_2 gas, second, third, etc. measurements were carried out until no further spectral changes could be seen. The difference spectrum is obtained by a computer subtraction between the first and final spectra. All films used in the present study, including the hydrophilic polymers, were dried in a flow of N_2 gas.

RESULTS AND DISCUSSION

Wavenumber shifts of the $\nu(OH)$ band of H_2O in polymers

For water molecules sorbed in polymers the i.r. spectra could be clearly obtained by the *FT*i.r. subtraction procedure. The i.r. spectra were measured for many polymers, including hydrophobic materials, and a number of these are shown in *Figure 1*, and compared with that of liquid water. A distinct feature is the variety of shapes of the i.r. spectra, which range from the broad band shapes similar to that of liquid water to the sharp band shapes of hydrophobic polymers. For example, the i.r. spectrum of water sorbed in hydrophobic poly(vinylidene fluoride) (PVDF) shows the well-resolved stretching bands, $\nu_a(OH)$ (antisymmetric) and $\nu_s(OH)$ (symmetric), and one bending band, $\delta(\angle HOH)$, corresponding to the normal vibrational modes of an isolated H_2O molecule[8]. As the polymer becomes more hydrophilic (moving downwards in *Figure 1*), the $\nu_a(OH)$ and $\nu_s(OH)$ bands gradually shift to lower frequencies, while the $\delta(\angle HOH)$ band moves to a higher frequency. This situation may indicate that a H_2O molecule associates itself with a particular site i.e. a polar atom or group (X) in the polymer and also that its interaction becomes stronger with increasing polymer hydrophilicity.

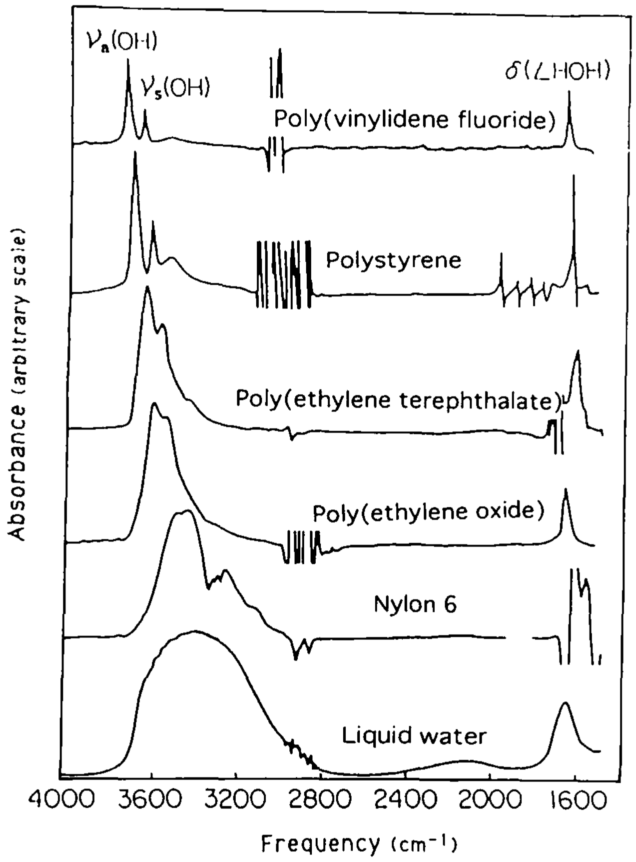

Figure 1 *FT*i.r. spectra of various solid polymers containing sorbed water, at a r.h. of 65%

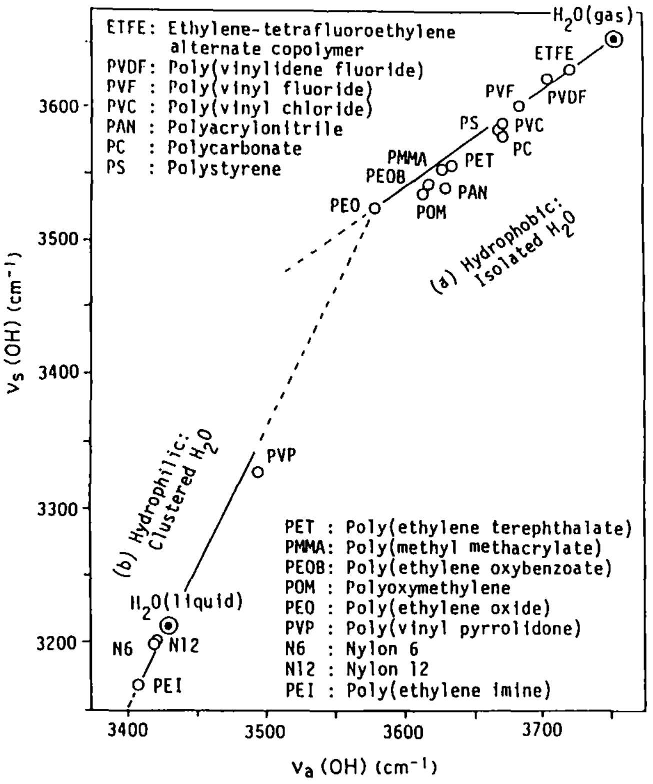

Figure 2 The relationship between the $\nu_a(OH)$ and $\nu_s(OH)$ stretching frequencies of sorbed water molecules in various solid polymers

In order to consider this point in greater detail, we have plotted the $\nu_s(OH)$ frequencies against those of $\nu_a(OH)$ for various polymers and these are shown in *Figure 2*. There is a definite correlation between the $\nu_a(OH)$ and $\nu_s(OH)$ data points, which are distributed between two regions representing the gaseous and liquid state of water. The sorbed water in hydrophobic polymers gives the data points with higher frequencies, which extend towards that of the (gaseous state) water, with their points lying on a straight line (a) over a very wide range. On the other hand, values for the hydrophilic polymers lie on another line (b), with a different slope, extrapolating to the value for liquid water. Poly(ethylene oxide) (PEO) is located at the crossing point of these two lines and this polymer shows unique behaviour as both an amphiphilic and biocompatible molecule[9,10]. The lowering of the OH stretching frequency by hydrogen bond formation is well known[11]. By using the values for the difference in frequency, we can deduce the heat of water sorption for various synthetic polymers and these are shown in *Table 1*. For hydrophilic polymers, we are reminded of the large heats of sorption ($\Delta E = 28 \sim 41\ \mathrm{kJ\,mol^{-1}}$) resulting from the strong hydrogen bond formation between the strong polar atoms or groups in these polymers and the water molecules, comparable to that of liquid water ($\Delta E = 38.5\ \mathrm{kJ\,mol^{-1}}$)[12]. Moreover, a striking feature is the fact that the $\nu_a(OH)$ frequencies of the hydrophobic polymers are spread over such a wide range

Table 1 Frequency shifts, heats of hydrogen bond formation and water affinity parameters (*WAP*s) for water sorption in various synthetic polymers

Polymer	Polar site	Frequency, ν_a (cm^{-1})	Shift, $\Delta\nu_a$[a] (cm^{-1})	Heat, ΔE[b,c] ($kJ\,mol^{-1}$)	*WAP*, a[c,d]
H_2O[e]		3756	0	0	0
ETFE	F	3721	35	4.1	0.107
PVDF	F	3705	51	6.0	0.156
PVF	F	3684	72	8.5	0.221
PVC	Cl	3673	83	9.8	0.255
PVDC	Cl	3672	84	9.9	0.258
PC	COO	3672	84	9.9	0.258
PS	π Electron	3670	86	10.1	0.264
PEEK	CO,O	3659	97	11.4	0.298
PET	COO	3635	121	14.3	0.371
PAN	C≡N	3630	126	14.9	0.387
PMLG	COO	3629	127	15.0	0.390
PMMA	COO	3628	128	15.1	0.393
PEOB	COO,O	3618	138	16.3	0.423
POM	O	3614	142	16.8	0.436
PEO	O	3579	177	20.9	0.543
PVP	NCO	3520	236	(27.8)	(0.798)
NOMEX	NHCO	3480	276	(32.6)	(0.848)
H_2O[f]		3430	326	(38.5)	1.0
N12	NHCO	3421	335	(39.8)	(1.028)
N6	NHCO	3418	338	(39.9)	(1.037)
PEI	NH	3408	348	(41.1)	(1.067)

[a] Shift, $\Delta\nu_a = 3756 - \nu_a$

[b] Heat, $\Delta E = \Delta\nu_a \times 0.118$

[c] ( ) = reference data on the clustered H_2O

[d] *WAP* is defined as follows: $a = \Delta\nu_a/(3756 - 3430)$, where 3756 and 3430 are the frequencies for H_2O (gas) and H_2O (liquid), respectively

[e] H_2O (gas)

[f] H_2O (liquid)

[$3721\,cm^{-1}$(ETFE) $-3579\,cm^{-1}$(PEO)]. This gives, after translating the frequency shift into the heat of sorption, $\Delta E = 4$–$21\,kJ\,mol^{-1}$. The lowering of the ν(OH) frequencies increases according to the following order: F < Cl < C (aromatic π-electron) < COO < O < NHCO < NH. From this order, we can presume that the chemical structure of a particular atom or group (X) within a certain polymer essentially decides the frequency shifts.

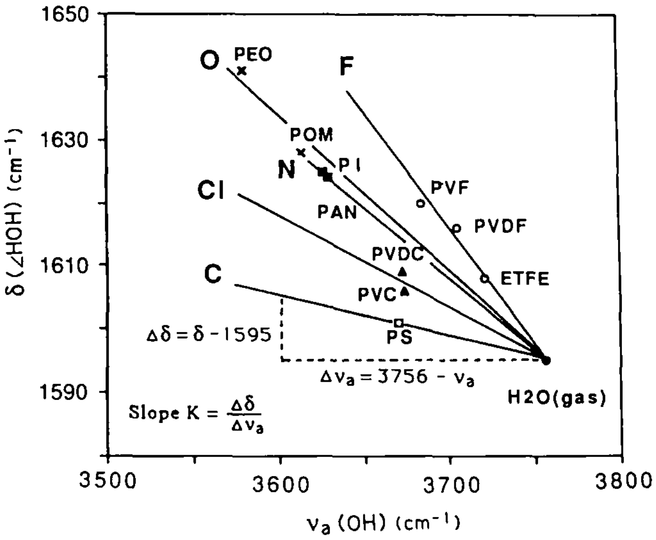

Figure 3 The relationship between the ν_a(OH) stretching and δ (< HOH) bending frequencies of sorbed water molecules (see *Figure 2* for names of polymers used)

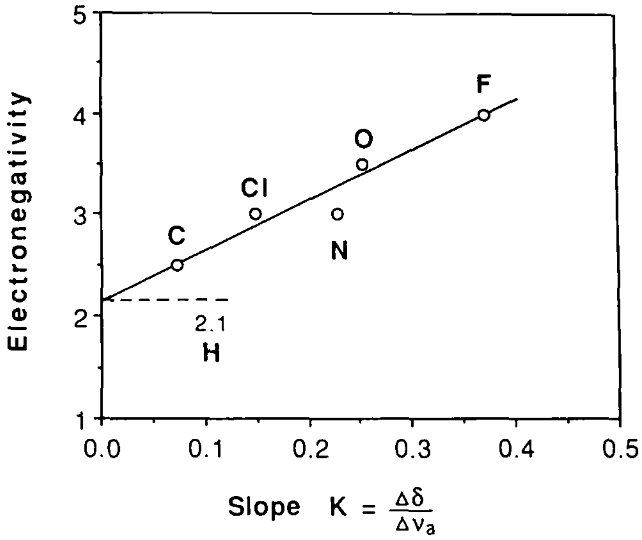

Figure 4 Correlation between the slope *K* (from *Figure 3*) and the electronegativity of various atoms

Wavenumber shifts and the electronegativity

Further information is obtained from the bending frequencies of sorbed water. The correlation between the ν_a(OH) and δ(∠HOH) values is shown in *Figure 3*. Three data points obtained for three kinds of polymers containing fluorine (F) atoms lie on a line passing through the point which corresponds to H_2O (gas). The slope of the line (*K*) is defined in *Figure 3* and is evaluated in the same manner for different polymers containing F, Cl, N, O, and C (aromatic π-electron) atoms. For these atoms we have plotted the electronegativity (*EN*) values taken from ref. 12 against the *K* values (see *Figure 4*). A linear relationship is obtained, which shows directly that atoms with large electronegativities increase the bending frequency, $\Delta\delta$, of sorbed H_2O molecules, more than the stretching frequency, $\Delta\nu$. This correlation gives strong evidence that a H_2O molecule is located close to a polar atom or group (X … $(H_2O)_1$), because this molecule has entered into the interaction field created by the polar site (X) so that the three-dimensional structure or force constants of the ν(OH) and δ(∠HOH) frequency modes of the sorbed H_2O molecule are changed. The ethylene–tetrafluoroethylene copolymer, $-(CH_2CH_2-CF_2CF_2)_n-$ (ETFE) is the most hydrophobic polymer to our knowledge in this study, with a sorbed water content of 0.005 wt% at a r.h. of 65%. In fact, the homopolymers of polyethylene and polytetrafluoroethylene, which constitute ETFE, do not form hydrogen bonds with water molecules. However, they often show the existence of small amounts of trapped water in voids employed in the polymers, depending on the processing conditions employed (from *FT*i.r. data).

This means that even in ETFE the fluorine atom can act as the 'hydrogen bond acceptor', and also implies the existence of a hydrogen bond to the covalent fluorine atoms[12] which is more hydrophobic than the aromatic π-electrons of benzene[13]. Of course, this weak interaction is a reflection of the very short correlation time, τ_c, of translational and rotational motion for the sorbed H_2O

molecule in ETFE, which can be detected by n.m.r. spectroscopic measurements[14]. Furthermore, the electronegativity value of 2.1 which is obtained by extrapolation to $K=0$ (reduced to $\Delta\delta=\Delta\nu=0$) corresponds to the value for the hydrogen atom. This means that the water molecule does not adopt the isolated (X ... $(H_2O)_1$) state in polyethylene (PE), as mentioned above.

The variety of water structures in solid polymers

The variety of different structures found for sorbed water in synthetic polymers should help us to explain the existence of the two lines shown in *Figure 2*. The first type is located at the point representing the gaseous state of water, near to the isolated state (X ... $(H_2O)_1$) in hydrophobic polymers. As the site affinity to H_2O molecules within the polymer gradually increases, the corresponding data points move down along the line (a). When the affinity exceeds a critical value (corresponding to the point for PEO), a number of H_2O molecules (greater than two) are attracted to a polar site of the polymer and thus form a water cluster (X... $(H_2O)_n$, where $n=2$–6). As a result, the data points are transfered from line (a) to line (b). This present *FT*i.r. study is the first case in which two clearly distinct states, namely the isolated (X ... $(H_2O)_1$) and clustered (X ... $(H_2O)_n$) states, could be observed in the structures of water sorbed in hydrophobic and hydrophilic polymers, respectively. With respect to the mechanism of water sorption three important factors must be considered: one is the chemical structure of the polymer along with two kinds of intrinsic property of the gaseous water itself. A significant viewpoint for cluster formation of water molecules in these systems is that the affinity of the polar site (X) in the polymers cooperates with both of the self-associating ability of the water and the water activity (relative humidity). However, the water sorption behaviour of all of the polymers belonging to the above mentioned categories is finally governed by the same mechanism, i.e. the variety of water structures in solid polymers originates only from the wide and continuous change of the affinity of the polymer site to water molecules.

A clear manifestation of weak hydrogen bond formation between benzene and water molecules (C_6H_6 ... H_2O) is obtained by far i.r. spectroscopy[13]. The polymer system composed of polystyrene (PS) and water molecules is also based on the hydrogen bond character of aromatic rings associated with water molecules: the heat of water sorption, ΔE, of 10.1 kJ mol^{-1} for polystyrene is in agreement with the values of $\geqslant 7.5$ kJ mol^{-1} and 6.8–11.6 kJ mol^{-1} which have been obtained for benzene[13,15]. These data strongly confirm our conclusion that polystyrene, as well as rather more hydrophobic polymers containing atoms such as fluorine, i.e. all polymers located on the line (a) in *Figure 2*, all form weak but definite hydrogen bonds with water molecules by the same mechanism.

Finally, we focus our attention again on the fact that so called hydrophobic polymers exhibit a wide range of ΔE values. For these polymers a measure known as the water affinity parameter (*WAP*), is defined by using the frequency shift of ν_a(OH), measured exactly by *FT*i.r. spectroscopy (see *Table 1*). The reciprocal of the *WAP* parameter represents the hydrophobicity of the polymer, which is similar to the concept of hydrophobicity for amino acids in protein chemistry[16]. We believe that a quantification of the hydrophilicity of synthetic polymers is significant in polymer science as well as in the polymer industry. The 'bending' problem of the optical disk, mentioned above, can be attributed to the rather large water affinity parameter of 0.393 for PMMA. This indicates that polymer engineers should pay attention, not only to the water uptake, but also to the water affinity, of high-performance hydrophobic polymers.

ACKNOWLEDGEMENTS

We are grateful to Professors S. Okamura and H. Kawai of Kyoto University for valuable discussions and suggestions.

REFERENCES

1 Brauman, J. I. *Science* (*Washington, DC*) 1991, **251**, 852
2 Darmstadt, J. H. *Kunststoffe* 1985, **75**, 19
3 Jellinek, H. H. G. 'Water Structure at the Water–Polymer Interface', Plenum, New York, 1972
4 Wiggins, P. M. *Prog. Polym. Sci.* 1988, **13**, 1
5 Stoutland, P. O., Dyer, R. B. and Woodruff, W. H. *Science* (*Washington, DC*) 1992, **257**, 1913
6 Hibben, J. H. *J. Chem. Phys.* 1937, **5**, 166
7 Hemley, R. J., Chen, L. C. and Mao, H. K. *Nature* (*London*) 1989, **338**, 638
8 Herzberg, G. 'Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules', Van Nostrand, New York, 1956, p. 280
9 Bergar Jr, H. and Pizzo, S. V. *Blood* 1988, **71**, 1641
10 Apicella, A., Cappello, B., Del Nobile, M. A., La Rotonda, M. I., Mensitieri, G. and Nicolais, L. *Biomaterials* 1993, **14**, 83
11 Badger, R. M. *J. Chem. Phys.* 1940, **11**, 288
12 Pauling, L. 'The Nature of the Chemical Bond', 3rd. Edn, Cornell University Press, Ithaca, New York, 1960
13 Suzuki, S., Green, P. G., Bumgarner, R. E., Dasgupta, S., Goddard III, W. A. and Blake, G. A. *Science* (*Washington, DC*) 1992, **257**, 942
14 Kusanagi, H., unpublished results
15 Gotch, A. J. and Zwier, T. S. *J. Chem. Phys.* 1922, **96**, 3388
16 Sweet, R. M. and Eisenberg, D. *J. Mol. Biol.* 1984, **171**, 479