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Effects of the Cross-Linking Structure on the Water Sorption Ability of Poly(vinyl carboxylate)

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Water sorption behavior of four kinds of polymerized vinyl carboxylate, i. e., vinyl benzoate, vinyl methacrylate, vinyl crotonate, and vinyl cinnamate was investigated. The dielectric measurement and quartz crystal microbalance technique were adopted for this purpose. The polymers were hydrophobic and the water sorption ability was enhanced by cross-linking. The dielectric constant of sorbed water was small compared with that of liquid water and the value slightly increased with increasing the amount of sorbed water. The orientation polarization of sorbed water also slightly increased with increasing the amount of sorbed water. It was proved that the cross-linking structure affected the water sorption behavior of the polymer.

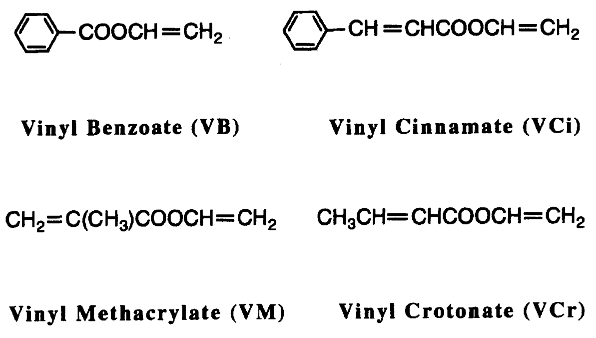
Water sorption behaviors in various polymer films are currently being investigated owing to their theoretical and practical significance. Methyl methacrylate or dimethacrylate networks have been used for a variety of products as chemical sensors, dental materials, optically transparent components, lenses for solar energy systems, etc. These applications depend wholly or largely on water sorption behavior. Many studies were motivated by the large effect of water on mechanical properties, swelling, glass transition temperature, etc. However, the water sorption of a glassy polymer at a given temperature, based on its structure, has not been properly understood. One of the most important factors that affects the sorption ability of the polymer seems to be the hydrophilicity of constituent groups of the polymer. In attempting to understand the origins of differences in hydrophilic character, the relative numbers of atoms present in each polymer that might be expected to form hydrogen bonds with water molecule require consideration. Pauling's simple hypothesis, that one molecule of water is sorbed per designated polar group, works only for undenatured globular proteins.[1,2] More general treatments, based on thermodynamics of mixing and on cohesion parameters, are inadequate for glassy polymers.[3] Additional factors must be considered, for example those which relate to molecular packing. In the case of a polymer that has no strong polar group, the sorption sites of water molecules seem to be the free spaces around the polar nature of the polymer. The contributions of functional groups to van der Waals volumes is quite different and the packing density seems to be dependent on the chemical structure of the polymer.[4] Molecular weight is one of factors which affect the packing density.[5,6] Further in respect of molecular packing, cross-linking produced a marked increase in water sorption in copolymers of methyl methacrylate and dimethacrylate.[7—11] The morphology of the materials may vary with the level of the cross-linking and the water sorption may be dependent on the morphology. It would be interesting to study the morphology of the materials to seek an explanation of this phenomenon. To characterize the sorption and diffusion behavior of water in polymer films, gravimetric methods have been used. In identifying the states of molecules sorbed in various substances, some researchers have adopted the measurement of the apparent dielectric constant.[12—17] Especially when water vapor is the sorbate, dielectric measurements are believed to be an effective means of identifying the macroscopic or microscopic state of the water, because of its strong polarity.

In this study, the state of sorbed water in polymer films was investigeted with dielectric measurement and quartz crystal microbalance (QCM) techniques. The effects of the degree of cross-linking and the chemical structure on the sorption behavior are discussed.

Experimental

Materials. Vinyl benzoate (VB), vinyl cinnamate (VCi), vinyl methacrylate (VM), and vinyl crotonate (VCr) (Shinetsu Sakusan Vinyl Co.) were used as starting monomers. The molecular structures are shown in Fig. 1. While VB has one double bond, the others have two double bonds and the possibility to form a cross-linked film. Further, these monomers have a slightly different side group. These differences in the chemical structure of monomers are expected to form different chemical polymer structures.

Procedure. Sandwich-type devices were prepared for the measurement of dielectric properties according to the following procedure. Monomers were initially polymerized with a small amount of benzoyl peroxide (BPO) until they had an appropriate viscosity. In addition, graded amounts of BPO were added to prepolymerized monomer, followed



Vinyl Benzoate (VB)   Vinyl Cinnamate (VCi)

$CH_2{=}C(CH_3)COOCH{=}CH_2$ $CH_3CH{=}CHCOOCH{=}CH_2$

Vinyl Methacrylate (VM)   Vinyl Crotonate (VCr)

Fig. 1. Chemical structure of vinyl carboxylate.

by spin coating (about 2—3 μm in thickness) on a glass substrate that had a platinum electrode deposited by the RF sputtering technique. The thin film on the substrate was heated under various conditions. The upper gold electrode was prepared by the vacuum evaporation technique. The area of electrode was 2×4 mm. A schematic diagram of the device is shown in Fig. 2. A thin polymer film was also formed on a quartz crystal oscillating element (4 MHz) with a silver electrode for measuring water content.

Measurement. To examine the effects of sorbed water on the dielectric characteristics of the film, the devices were placed in a thermostated vessel in which water vapor pressure was controlled by mixing dry and wet air. The electrical properties were measured using a LCZ meter (YHP 4274A, 4276A, 4277A) at various frequencies. The amount of sorbed water was calculated from the variation in oscillating frequency of the QCM with universal counter (ADVANTEST, TR5822). To characterize the sorption behavior in polymer film, the gravimetric method has been used. The QCM technique has been widely used to measure the mass change at the molecular level. The QCM is an instrument for accurately measuring the mass change and is useful for observation of sorption change *in situ* in a thin film. The principle of the quartz crystal microbalance is based on changes Δf in the fundamental oscillation frequency f_0 upon mass changes on the crystal surface. The linear relationship between the mass added onto the crystal surface and the change in its frequency can be derived from the Sauerbrey equation,[18,19]

$$\Delta f = C f_0{}^2 \Delta m / A$$

where C is a constant, A is the surface area (cm^2) of crystal, and Δm is the mass change (g). The film thickness was measured with a mechanical surface-roughness analyzer (Tokyo Seimitsu, Surfcom 703A).

Results and Discussion

Effects of Polymerizaton Condition on the Dielectric Relaxation Behavior of the Film. To examine the effects of cross-linking structure of the polymer on the water sorption behavior, it was necessary to discover the relationship between the polymerization condition and the chemical structure of the prepared film. The dielectric relaxation measurement was adopted for this purpose. It is known that the dielectric relaxation of a polymer arises from the segment motion of the main chan and the side chain. If the polymerization and/or cross-linking reaction proceeds and the film becomes rigid, the segment motion of the main chain seems to be depressed. Consequently, the value of the dielectric loss is lowered. For all samples, dielectric relaxation behavior was affected by the polymerization temperature, t_p, and atmosphere as well as by the BPO content. As the polymerization proceeded, the relaxation peak became lower and shifted to a higher temperature. In any case, the dielectric relaxation peak of the film polymerized in a nitrogen atmosphere was observed at a higher temperature compared with that in air. The peak height was also lowered by polymerizing in nitrogen. Effects of the polymerization temperature and the amount of BPO added to the prepolymerized monomer on the value of $\tan\delta$ and the temperature at maximum $\tan\delta$, $t_{\max}$, are summarized in Table 1. Addition of 4 milligrams of BPO per gram of prepolymerized monomer was effective to make the polymerization proceed. The effects of polymerization temperature were more complicated. Although the optimum polymerization temperature for obtaining film with the lowest value of $\tan\delta$ depended on the monomers used, the heat treatment in two stages was effective It seems that the heat treatment at a lower temperature is related to the polymerization and that at a higher temperature it is related to the acceleration of polymerization and the removal of the residual monomers. The $\tan\delta$ vs. temperature relationships measured for the optimum films at 10 kHz are shown in Fig. 3. Especially, for the films obtained by polymerizing VM or VCr, the peak-height was very small. This behavior may be related to the cross-linking structure of VM and VCr because these compounds have two double bonds. Although VCi also has two double bonds, it is known that the cyclization is likely to occur in preference to the cross-linking reaction. Consequently, the dielectric relaxation peak did not decrease upon polymerization. It is natural that a linear polymer, VB, has a larger dielectric relaxation. Although we could not measure the degree of cross-linking directly, the order of the value of $\tan\delta$ seemed to be equivalent to the order of the degree of cross-linking, that is, the polymer with higher degree of cross-linking structure showed a lower value of $\tan\delta$.

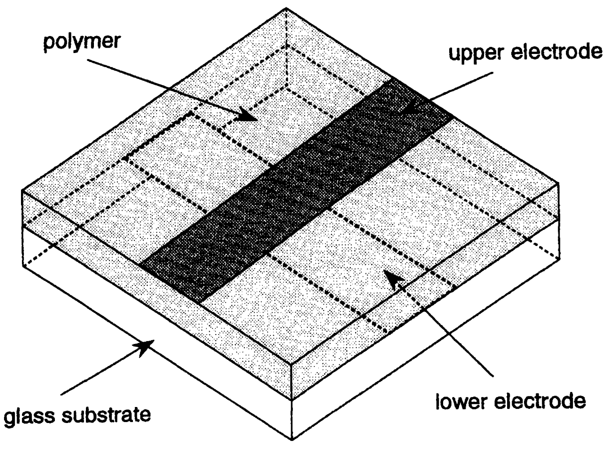


Fig. 2. Schematic diagram of the device for the dielectric measurement.

Change in film thickness with heat treatment was examined for VM. Results are shown as shrinkage percentage in Table 1. It can be observed that the film shrinks as the value of $\tan\delta$ becomes lower. This is due to the proceeding of the cross-linking reaction and is consistent with the interpretation of the results of dielectric relaxation behavior. The measurement of the dielectric relaxation may be considered as a reliable indication of the degree of cross-linking.

Water Sorption Behavior of the Polymerized

Table 1. Polymerizing Condition and Some Properties of the Present Films

Monomer	Sample No.	t_p °C	BPO $\mathrm{mg\,g^{-1}}$	$\tan\delta\times10^3$	t_{max} °C	Schrinkage %
VB	1	90 (1 h)	1	136.0	120	
	2	70 (1 h)	1	48.6	90	
	3	70 (1 h)	4	55.2	90	4.0
VM	4	120 (1 h)	1	27.2	115	
	5	120 (1 h)	4	21.3	115	11.3
	6	70 (1 h)—120 (1 h)	1	23.0	120	
	7	70 (1 h)—120 (1 h)	4	21.1	135	15.1
	8	90 (1 h)	1	78.1	120	
VCr	9	70 (1 h)—120 (1 h)	1	47.7	135	
	10	70 (1 h)—120 (1 h)	4	17.5	155	
VCi	11	90 (0.5 h)—160 (1 h)	1	165.5	210	
	12	90 (0.5 h)—160 (1 h)	4	146.1	215	

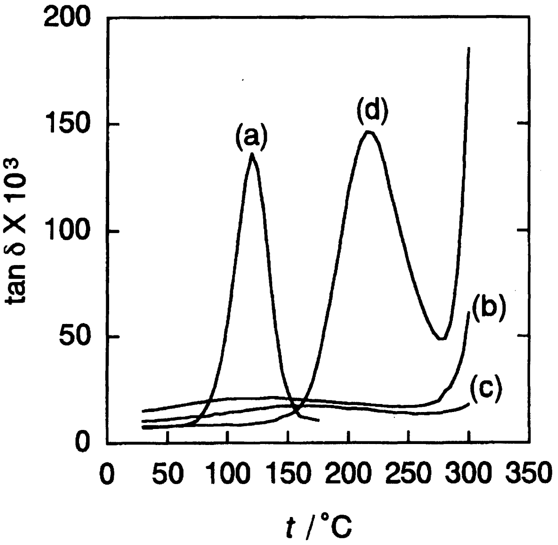


Fig. 3. Dependence of $\tan\delta$ on temperature measured at 10 kHz. (a) poly-VB (Sample No. 1), (b) poly-VM (No. 7), (c) poly-VCr (No. 10), and (d) poly-VCi (No. 12).

Table 2. The Values of W_g and W_m Measured at $p/p_0=0.81$ and 30 °C

Monomer	No.[a)]	$W_g/\mathrm{mg\,g^{-1}}$	W_m
VB	1	4.9	0.02
	2	6.1	0.04
VM	4	28.1	0.08
	6	30.1	0.09
	7	37.4	0.10
VCr	9	12.8	0.04
	10	20.9	0.06
VCi	11	13.3	0.07
	12	14.4	0.07

a) Sample No. is reffered to Table 1.

Vinyl Carboxylate Thin Films. The amount of sorbed water was measured for these polymer thin films as a function of relative vapor pressure, p/p_0. The effects of polymerization conditions on the amount of sorbed water were observed to be significant. The water content of the films W_g, which was based on grams of sorbed water per one gram of dry polymer, measured at $p/p_0=0.81$ and 30 °C is summarized in Table 2. It should be noted that the sorption ability increased with proceeding of the cross-linking reaction for each polymers. Sorption isotherms measured at 30 °C for the films are shown in Fig. 4. All the curves are almost linear. These polymers were hydrophobic and W_g depended on the polymer species. The differences of sorption ability seems to be derived from the differences of the structure of the films as well as the differences of the side groups of the polymer. It has been reported that the saturation value of water gain of copolymers of MMA with dimethacrylate monomers increases with increasing degrees of cross-linking.[7—10] The behavior can be interpreted in terms of an increase in the concentration of the hydrophilic groups by introducing the hydrophilic cross-linking agent. In the case of this system, the effects of hydrophilicity of the cross-linking agent need not be considered because this monomer can cross-link by itself. Kalachandra et al.[11] measured the water sorption ability and compared the water uptake with the contact angle for water in glycol dimethacrylate and methyl methacrylate polymers. The weight per cent oxygen content (WPO), which is indicative of the hydrophilic character of these materials, was calculated and correlated with weight percent water uptake. The linear relationship between the WPO and the percentage water uptake was observed in a series of four glycol dimethacrylate and eight linear methyl

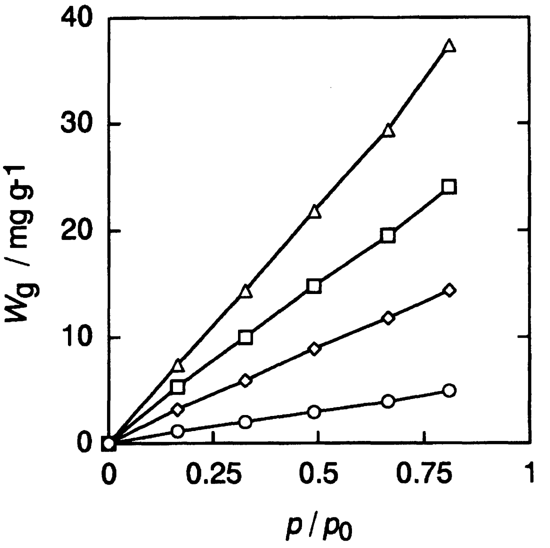


Fig. 4. Sorption isotherms measured at 30 °C. ○) poly-VB (Sample No. 1), △) poly-VM (No. 7), □) poly-VCr (No. 10), and ◇) poly-VCi (No. 12).

methacrylate monomers. The increased water uptake of polymer compared with monomers was attributed to the microvoids present in the polymer matrix. However, the effects of the cross-linking degree were not considered. We estimated another measure of water content W_m instead of W_g on the basis of the mole ratio of sorbed water molecule to oxygen atom in each monomer molecule. Results are shown in Table 2. Poly-VM had the largest W_m (0.10 mole water/mole oxygen atom) and decreased in the order of poly-VCr (0.07), poly-VCi (0.07), and poly-VB (0.04) at $p/p_0=0.8$. The value of W_m of the cross-linked polymers was greater than that of linear polymers. There were also some differences among the cross-linked polymers. The orders of W_m may be related to the cross-linking degree. The packing density change of the films with the formation of cross-linking structure should be taken into consideration. In the case of hydrophobic polymer without strong sorption sites, the free space around the polar site is likely to be a sorption site. Cross-linked films prepared by polymerizing monomers with short chains seem to have highly strained chain conformations which prevent close chain packing. That leads to an increase in free spaces. Now, it must be noted that the film shrinks as the cross-linking reaction proceeds, as shown in Table 1. The data seems to be in conflict with our explanation. However, the conflict may be resolved by the following explanation. A water molecule may be encompassed by a sphere of diameter about 3 Å, small enough to fit into typical microvoids or spaces that comprise the structural free volume. The volume, which was decreased by cross-linking reaction, seemed to be large compared with the adsorbate molecule (H_2O molecule in this case) and such a larger volume acted as dead volume for sorption in a hydrophobic polymer measured gravimetrically or electrically. Consequently, the apparent reduction of volume in Table 1 was independent of results of the measurement of sorption ability. The free space we now consider as the sorption site is a molecular size in which the water molecule and polar site of polymer can interact. The space must affect the sorption behavior of the hydrophobic polymer. As mentioned above, the cross-linking reaction proceeds easily for VM and a lot of free space seems to exist. This explanation agreed with the order of water content.

Effects of the Sorbed Water on the Dielectric Properties. Water has a large value of ε compared with other liquids or solids. Consequently, the sorption of water in the polymer affects the apparent dielectric constant of the polymers very much. The electrical capacitance of present polymers was measured as a function of the relative vapor pressure at 100 kHz. The electrical capacitance increased almost linearly with increases in the relative vapor pressure. The value of C_{90}/C_0 (since the capacitance is affected by the film thickness, we adopted the ratio of capacitance at $p/p_0=0.9$ to that capacitance at $p/p_0=0$ for comparison) are shown in Table 3. Dependence of the C_{90}/C_0 on W_g was examined and is shown in Fig. 5. The C_{90}/C_0 increases linearly with an increase in W_g in the low sorption region, followed by curvature upward. Irrespective of the difference of polymer species and of the degree of cross-linking, the C_{90}/C_0 depended only on W_g. The dielectric constant of the sorbed water was estimated by applying Kurosaki's equation[12)]

$$\varepsilon_s = \varepsilon_p + (\varepsilon_w - \varepsilon_p)/V, \tag{1}$$

where ε_w, ε_p, and ε_s are the dielectric constants of the sorbed water, the dried polymer (about 2.6), and the

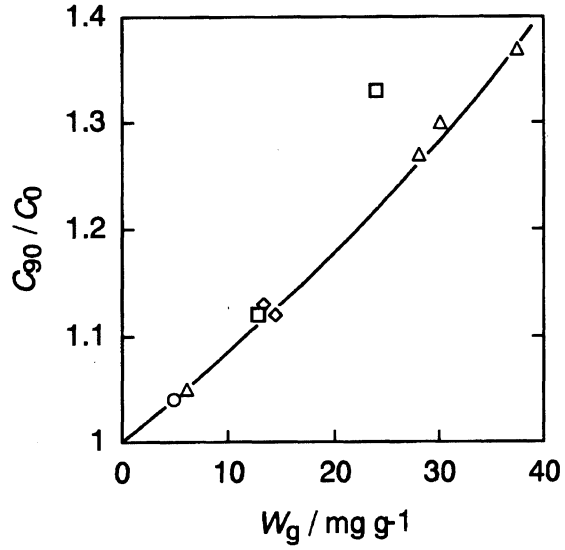


Fig. 5. Dependence of the C_{90}/C_0 on the amount of sorbed water measured for film with various cross-linking degree at 100 kHz and 30 °C. ○) poly-VB, △) poly-VM, □) poly-VCr, and ◇) poly-VCi.

polymer at a certain relative vapor pressure, respectively. V is the volume fraction of sorbed water calculated from the amount of sorbed water assuming that the density of the polymers is 1.2 and that of water vapor is unity. The results are summarized in Table 3. The dielectric constant is less than that of liquid water, which is 76.6 at 30 °C, and also smaller compared with that of cellulose derivatives.[20,21)] The dielectric constant of sorbed water on cellulose derivatives had a larger value when the number of sorbed water molecules per monomer became more than unity. We have explained this behavior as the formation of clusters of sorbed water molecules. The value of the dielectric constant on these polymers is equivalent to the previously reported polymethyl methacrylate and cross-linked polyimide,[21,22)] which are too hydrophobic to form clusters. The dielectric constant became slightly larger with increases in the relative vapor pressure. This indicates that the interaction between water molecules becomes slightly larger and the sorbed water molecule begins to associate with increases in the amount of sorbed water. Further the polarization of sorbed water was estimated. A modified Kirkwood's equation[16)] for the dielectric constant, ε_0 of a binary system is expressed as

$$(\varepsilon_0 - 1)(2\varepsilon_0 + 1)/9\varepsilon_0 = 4N_1(\alpha_1 + g_1\mu_1^2/3kT)/3 + 4N_2(\alpha_2 + g_2{\mu_2}^2/3kT)/3, \quad (2)$$

where N_1 and N_2 are the number of molecules per unit volume, α_1 and α_2 are the polarizabilities, μ_1 and μ_2 are the dipole moments for the two constituents, respectively, k is the Boltzmann constant, T is the absolute temperature, and g, the correlation parameter, is a measure of the local ordering of the dipole. It has a value of unity if fixing the position of one dipole does not influence the positions of the rest of the dipoles at all. On the other hand, if fixing one dipole tends to make the neighboring dipoles line up in a parallel direction, the correlation parameter will be greater than unity and is close to 3 for bulk water. Similarly, if fixing one dipole tends to line up the neighbors in an antiparallel direction, the correlation parameter will be less than unity. Potentially, valuable information is available about the state of sorbed water by studying dielectric properties as a function of temperature, frequency, and concentration.

Table 3. The Value of C_{90}/C_0 Measured at 100 kHz and 30 °C and the Value of ε_w Estimated at p/p_0= 0.8, 1 kHz and 30 °C

Monomer	No.[a)]	C_{90}/C_0	ε_w
VB	1	1.04	21.3
	2	1.05	20.4
VM	4	1.27	24.1
	6	1.30	24.9
	7	1.37	25.0
VCr	9	1.12	23.3
	10	1.33	34.5
VCi	11	1.13	24.3
	12	1.12	20.2

a) Sample No. is reffered to Table 1.

By assuming that the number of polymer molecules per unit volume is hardly dependent on the relative vapor pressure, Eq. 2 can be rewritten as

$$(\varepsilon_0 - 1)(2\varepsilon_0 + 1)/9\varepsilon_0 = (\varepsilon_p - 1)(2\varepsilon_p + 1)/9\varepsilon_p 4N_w(\alpha_w + g_w\mu_w^2/3kT)/3, \quad (3)$$

where ε_p is the dielectric constant of polymer in a dry atmosphere and the subscript w, indicated the component of sorbed water.

For an a. c. electrical field, Eq. 4 is used instead of Eq. 3

$$(\varepsilon - 1)(2\varepsilon + 1)/9\varepsilon = (\varepsilon_p - 1)(2\varepsilon_p + 1)/9\varepsilon_p + 4N_w(\alpha_w + P(\omega))/3, \quad (4)$$

where $P(\omega)$ indicates the polarization term caused by the orientation of dipole and depends on the applied frequency. When $\omega = \infty$, Eq. 4 is rewritten as

$$(\varepsilon - 1)(2\varepsilon + 1)/9\varepsilon = (\varepsilon_p - 1)(2\varepsilon_p + 1)/9\varepsilon_p + 4N_w\alpha_w/3. \quad (5)$$

In this case, the dipole moment is zero or becomes ineffective. Consequently, the value of $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ measured in the higher frequencies gives the value of the polarizability term and is scarcely dependent on the

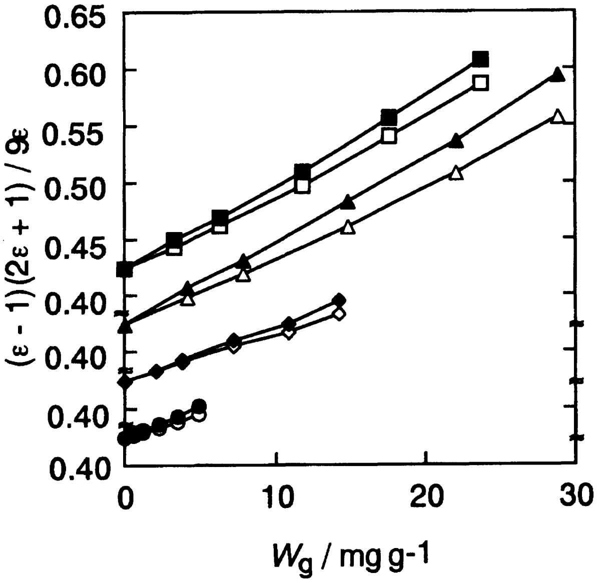


Fig. 6. Dependence of $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ on W_g measured at 30 °C. ○) poly-VB (Sample No. 1), △) poly-VM (No. 7), □) poly-VCr (No. 10), and ◇) poly- VCi (No. 12). Open symbols; 100 kHz and closed symbols; 1 kHz.

Table 4. The Value of ΔP Estimated at 30 °C

	W_g		
	5 mg g^{-1}	10 mg g^{-1}	20 mg g^{-1}
Poly-VB	0.007		
Poly-VM	0.010	0.016	0.027
Poly-VCr	0.007	0.012	0.021
Poly-VCi	0.004	0.007	

distortion polarization caused by the intermolecular interaction. By assuming that the low-frequency limit and high-frequency limit of the dielectric constant correspond to the dielectric constant observed at 1 kHz and 1 MHz, respectively, the degree of the distortion polarization may be estimated. The relationship between $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ and W_g is shown in Fig. 6, in which these results were obtained at 1 kHz and 1 MHz in the humidification process at 30 °C. The value of $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ was affected by the applied frequency and increased monotonically with an increase in W_g. The result is slightly different from that of cellulose derivatives.[20] In the case of cellulose derivatives, the value was scarcely affected by the frequency until the molar ratio of water/monomer unit of cellulose became unity. In the region where the number of the sorbed water per monomer unit of cellulose was less than unity, $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ for the sorbed water increased linearly with the amount of sorbed water then steeply, especially for the measurement at 1 kHz. The difference between $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ values observed at 1 kHz and 1 MHz corresponds to $4N_2P(\omega)/3(=\Delta P)$ and indicates the degree of the orientation of dipoles. As the water molecule is associated with more other water molecules with increasing W_g, the slope of $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ vs. W_g becomes larger and the difference of $(\varepsilon-1)(2\varepsilon+1)/9\varepsilon$ between the two frequencies becomes large. The value of ΔP at certain W_g is shown in Table 4. In the case of these polymers, the difference was very small compared with other polymers.[21] This is due to the small interaction between the polymers and the sorbed water molecules and between water molecules. By considering these results together with the result of estimated dielectric constant of sorbed water, the sorbed water scarcely formed clusters due to the hydrophobic nature and the space limitations of polymers.

Conclusion

Water sorption behavior of four kinds of polymerized vinyl carboxylate, i. e., vinyl benzoate (VB), vinyl methacrylate (VM), vinyl crotonate (VCr), and vinyl cinnamate (VCi) was investigated. Among these monomers, VM and VCr formed a cross-linked structure by polymerization while VB and VCr did not. The difference of the structure of polymer, that is, whether the polymer is cross-linking type or linear type and the difference of the degree of cross-linking, affect the sorption ability. The polymer with highly cross-linked structure had a larger amount of water content. The state of sorbed water estimated with dielectric measurement was almost the same for both cross-linked and linear polymer, irrespective of the difference of degree of cross-linking. The sorbed water molecules scarcely formed clusters, because of the hydrophobic properties and space limitation of the polymer. Consequently, the enhancement of water sorption ability by forming cross-linked structure is attributable to the increase in free space in molecular size around a polar site derived from the highly strained chain conformations.

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