

Dielectric Relaxations in Poly(vinyl Alcohol)

KEN-ICHI SHIDA* and YASAKU WADA,

*Department of Applied Physics, Faculty of Engineering, University of Tokyo,
Bunkyo-ku, Tokyo, Japan*

Synopsis

Dielectric constant and loss of poly(vinyl alcohol) films of different stereoregularity and crystallinity are measured at frequencies from 30 cps to 3 Mcps in the temperature range from -50 to 25°C . The relaxation strength of local mode relaxation is higher for atactic and syndiotactic samples than for isotactic samples when compared at zero crystallinity. This behavior is reasonably explained in terms of interchain hydrogen bonds in the former and intrachain hydrogen bonds in the latter. Dielectric constant and loss of the crystal aggregate of atactic poly(vinyl alcohol) are measured at temperatures from -50 to 140°C . The relaxation strength of the crystalline relaxation is in good agreement with the theory in which the relaxation is attributed to torsional vibration of crystalline chains. The weak loss peak at low temperatures which almost agrees with the local mode relaxation of bulk samples in the frequency-temperature position is ascribed to the surface disorder of single crystals.

Introduction

Molecular motion in a variety of polymers has been investigated by making measurements of the temperature and/or frequency dependence of dynamic mechanical properties, dielectric properties, and nuclear magnetic resonance absorption. Such measurements are useful for studying molecular mobility in solid-state polymers and have been done by several authors¹⁻⁴ for poly(vinyl alcohol) (PVA).

According to the dynamic mechanical study by Takayanagi and his co-workers,¹ PVA exhibits three relaxations in the same manner as other crystalline polymers; crystalline, primary, and local mode relaxations in the order of descending temperature. The crystalline relaxation is attributed by one of the present authors (Wada) and his co-workers^{5,6} to torsional vibration of crystalline chains. The primary relaxation and local mode relaxation⁷ are ascribed to segmental and torsional motion of amorphous chains, respectively. Since PVA has polar side groups in its chain, relaxations are expected in dielectric behavior too, and in fact, the dielectric primary relaxation and local mode relaxation have been reported for atactic,² syndiotactic, and isotactic samples.⁴

The molecular conformation of PVA has been revealed by x-ray and infrared studies^{8,9} of its crystalline phase. Syndiotactic PVA and the

* Present address: Kurashiki Rayon Co. Ltd., Tamashima Works, Tamashima, Okayama, Japan.

atactic polymer take a planar zigzag conformation with predominantly interchain hydrogen bonds, whereas isotactic PVA has a similar conformation but intrachain hydrogen bonds predominate. Takayanagi and his co-workers⁴ compared the primary relaxations of syndiotactic and isotactic samples and explained the difference, assuming the nature of hydrogen bonds to be essentially similar in the amorphous phase and the crystalline phase.

Behavior of the local mode relaxation which comes from torsional vibration of amorphous segments should also reflect the situation of hydrogen bonds. The first purpose of the present study is to compare the dielectric local mode relaxation among samples of different stereoregularity.

As is well known, single crystals of syndiotactic and atactic PVA can be prepared by precipitation from a dilute solution.¹⁰ The second purpose of this study is to observe the dielectric crystalline relaxation for single crystals and to discuss the behavior on the basis of the theory of crystalline relaxation.

As reported by Wada and his co-workers,^{11,12} single crystals of polymers exhibit the local mode relaxation, probably owing to surface disorder of crystals. The data have been reported for polyethylene in mechanical measurement and for polyoxymethylene in mechanical and dielectric measurements. This problem will also be treated in this paper for PVA crystals.

Experimental

Six kinds of PVA samples as listed in Table I were used in this experiment. Samples A-1 and S-1 were films cast from dilute solutions of atactic and syndiotactic polymers, respectively. The solvent was water for the atactic sample and a water-methanol mixture for the syndiotactic sample.

TABLE I
Poly(vinyl Alcohol) Samples

Sample code	Stereo-regularity	Form	Density at 25°C., g./cc.	Crystallinity, %
A-1	Atactic	Film	1.291	30.6
A-2	Atactic	Film	1.305	51.1
S-1	Syndiotactic	Film	1.297	38.4
S-2	Syndiotactic	Film	1.315	62.4
I	Isotactic	Film	1.316	Low
C	Atactic	Crystal aggregate	—	Very high

The films were dried first in air and then in vacuum. The degree of polymerization of PVA was 1700 in both cases. Samples A-2 and S-2 were prepared by annealing A-1 and S-1, respectively, in a silicone oil bath at 180°C. for 30 min.

The isotactic sample I which had been prepared from poly(vinyl benzyl ether) was supplied through the courtesy of Prof. H. Tadokoro of Osaka University.

The thickness of the above five samples ranged from 10 to 30 μ . The density was measured with a density gradient tube of benzene-carbon tetrachloride mixtures. The crystallinity X_c of atactic and syndiotactic samples was calculated from the density ρ by eq. (1):¹³

$$1/\rho = X_c/1.345 + (1 - X_c)/1.269 \quad (1)$$

The crystallinity of sample I was found from x-ray diffraction to be relatively low but the exact estimation was impossible. In what follows the crystallinity of sample I is assumed tentatively to be 10%, but this estimation is not significant in conclusions.

Sample C was an aggregate of crystals precipitated from a 0.05% solution of atactic PVA (degree of polymerization = 1700) in triethylene glycol. The precipitation occurred in the course of slow cooling from 180–165°C. The cooling rate was 1°C./30 min. An optical micrograph of the sample is shown in Figure 1. Clusters of two or more crystals are found in abundance.¹⁰

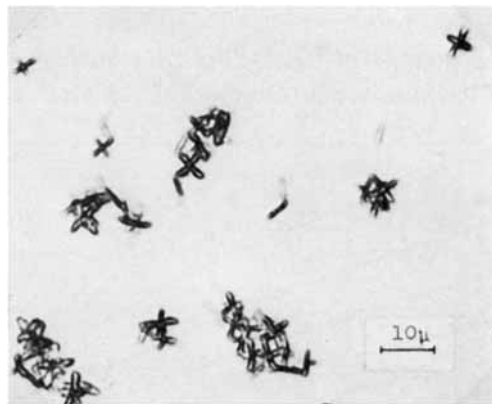


Fig. 1. Optical micrograph of single crystals of atactic PVA (sample C).

For dielectric measurements silver electrodes were vacuum-deposited on both surfaces of the PVA films. Sample C was packed between two metal electrodes 175 μ apart. The packing density was 21% by volume. The construction of the cell for temperature control of the sample capacitor was described elsewhere.⁵ Care was always taken to eliminate the effect of moisture as well as possible. All the samples were kept in a desiccator over P_2O_5 prior to measurements. The cell was filled with dry nitrogen gas.

The capacitance and conductance of the sample capacitor were measured with a transformer bridge in the frequency range from 30 c/s to 3 Mc/s. The dielectric constant ϵ' and loss ϵ'' were calculated by the usual procedure. In the case of sample C, observed values of ϵ' and ϵ'' are only apparent

values, the true values being ten times larger as estimated from the equation,

$$\log \epsilon = v_1 \log \epsilon_1 + v_2 \log \epsilon_2 \quad (2)$$

where ϵ is the dielectric constant or loss of the powder system, ϵ_1 and ϵ_2 the dielectric constants of the powder itself and air, respectively, and v_1 and v_2 are volume fractions.

Local Mode Relaxation of PVA Films

The local mode relaxation (low temperature relaxation) was observed for five samples from A-1 to I as illustrated in Figures 2-6. The upswing of ϵ'' at low frequencies comes from primary relaxation and dc conduction loss. The relaxation strength $\Delta\epsilon$ of the local mode relaxation was estimated at each temperature from the Cole-Cole plot.

The molecular nature of the local mode relaxation has been concluded by Wada and his co-workers¹⁴ to be essentially the same as that of the crystalline relaxation. The difference exists only in the phase involved. According to the theory of Okano¹⁵ and Hayakawa,¹⁶ $\Delta\epsilon$ for polar vinyl polymers with a planar zigzag chain is given by

$$\Delta\epsilon = (4\pi/3)N_{\text{dip}}\mu^2[(1/2g) - (1/2g_0)](E/E') \quad (3)$$

where N_{dip} is the number of dipoles per unit volume, g_0 the interchain force constant for the torsional displacement of a unit, i.e., a CH_2 or $\text{CH}(\text{OH})$

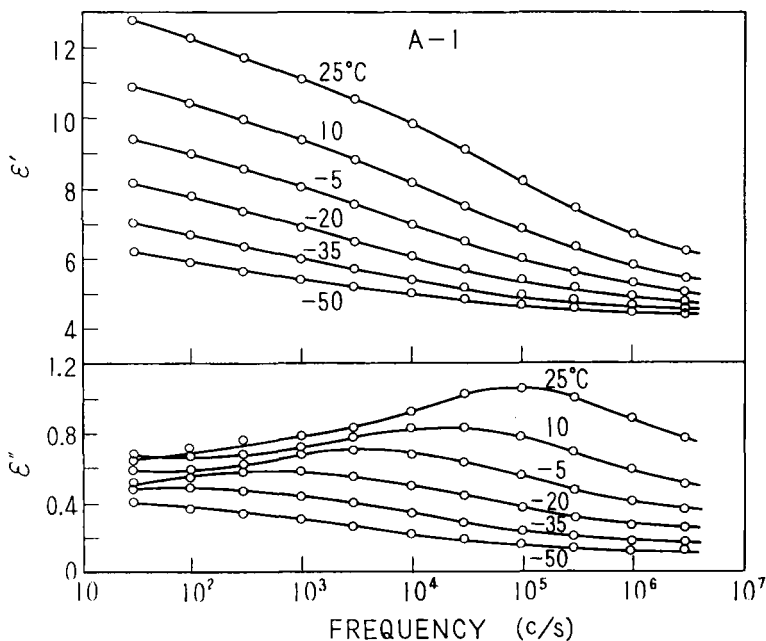


Fig. 2. Dielectric constant and loss of atactic PVA film (sample A-1).

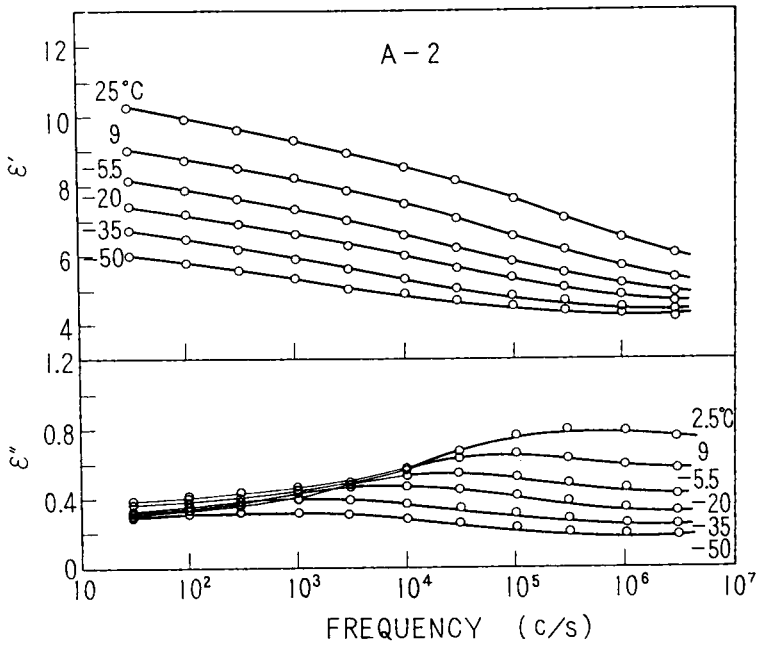


Fig. 3. Dielectric constant and loss of atactic PVA film (sample A-2).

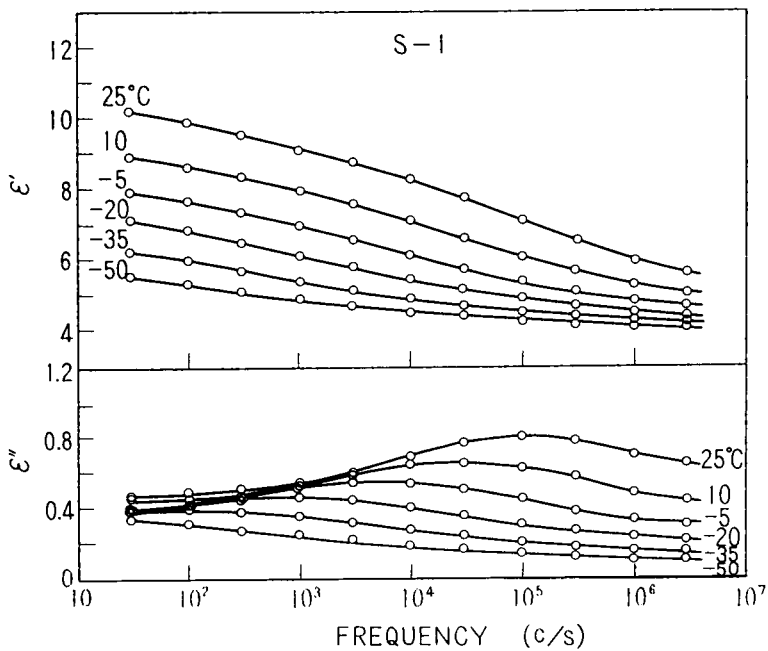


Fig. 4. Dielectric constant and loss of syndiotactic PVA film (sample S-1).

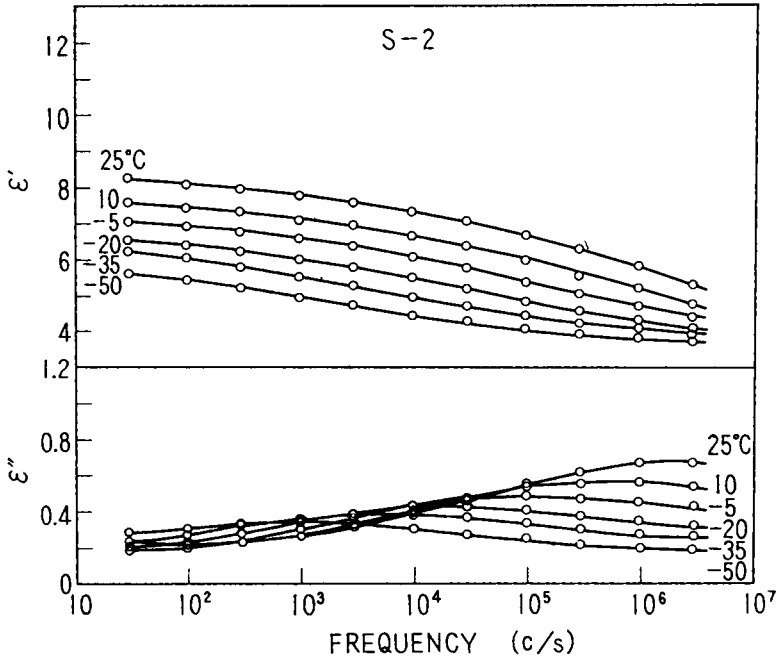


Fig. 5. Dielectric constant and loss of syndiotactic PVA film (sample S-2).

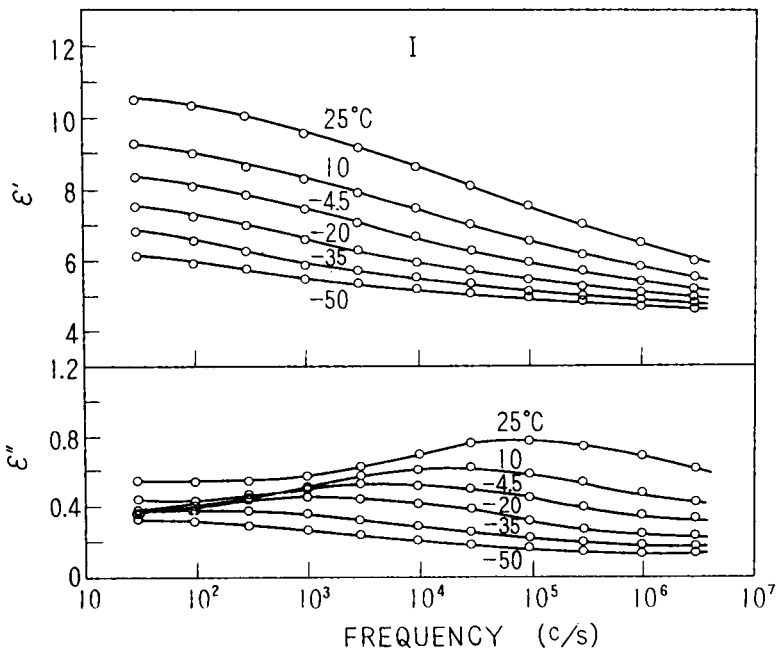


Fig. 6. Dielectric constant and loss of isotactic PVA film (sample I).

group, and E/E' the ratio of local field to macroscopic field. For the isotactic chain, μ represents the dipole moment perpendicular to the chain axis. For the syndiotactic chain, on the other hand, μ stands for the component in the zigzag plane of the moment perpendicular to the chain axis, because the vertical component to the zigzag plane changes its direction alternately along the chain and hence contributes to $\Delta\epsilon$ only to a negligible extent.

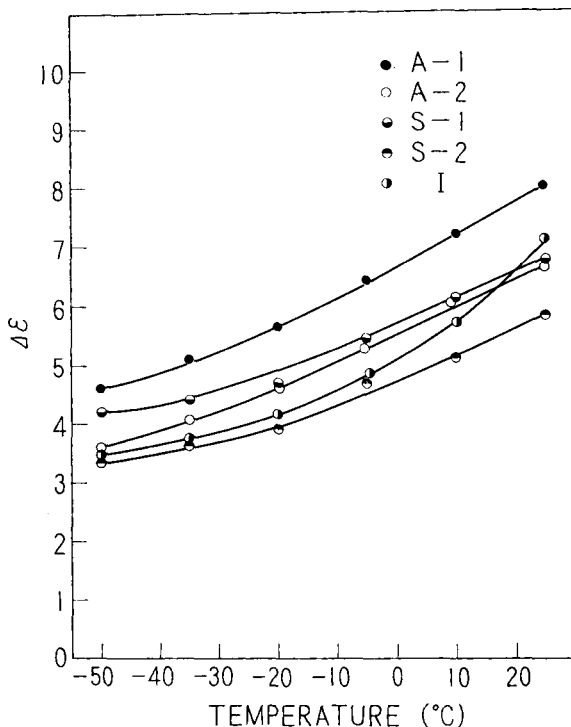


Fig. 7. Relaxation strength of local mode relaxation of PVA as a function of temperature.

The interchain force constant g_0 is reduced to g as a time average owing to the large amplitude vibration (incoherent lattice vibration as called by Peterlin^{17,18}) which occurs in the temperature range of relaxation. According to Peterlin and his co-workers,^{17,18} g is related to g_0 by

$$g = g_0 \exp \{ - 2S^2 \} \quad (4)$$

In this equation, S^2 is the mean-square fluctuation of torsional displacement of chain units and is approximated¹⁶ by

$$S^2 = NkT/6f \quad (5)$$

where N is the number of units in a segment (in case of a crystal, a segment corresponds to the long period), k is the Boltzmann constant, T the absolute

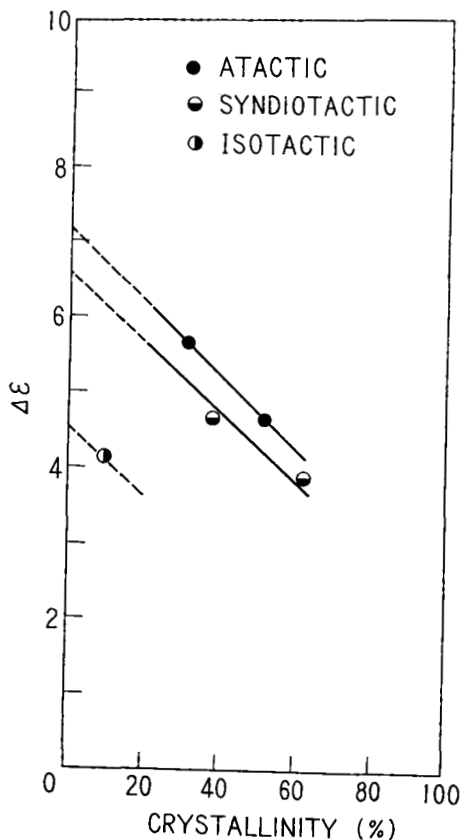


Fig. 8. Relaxation strength of local mode relaxation of PVA at -20°C . plotted against crystallinity.

temperature, and f the intrachain force constant of the C—C bond. (E/E') in eq. (3) is replaced by Onsager's expression,

$$E/E' = [(n^2 + 2)/3]^2 \left[\frac{3\epsilon'}{(2\epsilon' + n^2)} \right] \quad (6)$$

where n is the refractive index.

Since g_0 and hence g in eq. (3) decrease with increasing temperature on account of thermal expansion and furthermore the increase of S^2 with temperature also favors the decrease in g , $\Delta\epsilon$ is expected to increase with increasing temperature. Figure 7 shows $\Delta\epsilon$ plotted against temperature for five samples. $\Delta\epsilon$ increases with increasing temperature as predicted by the theory.

Figure 8 gives $\Delta\epsilon$ as a function of crystallinity for various stereoregularities. When extrapolated to zero crystallinity, $\Delta\epsilon$ of the atactic and syndiotactic samples is appreciably larger than that for the isotactic one. Similar behavior was observed also by Takayanagi.⁴

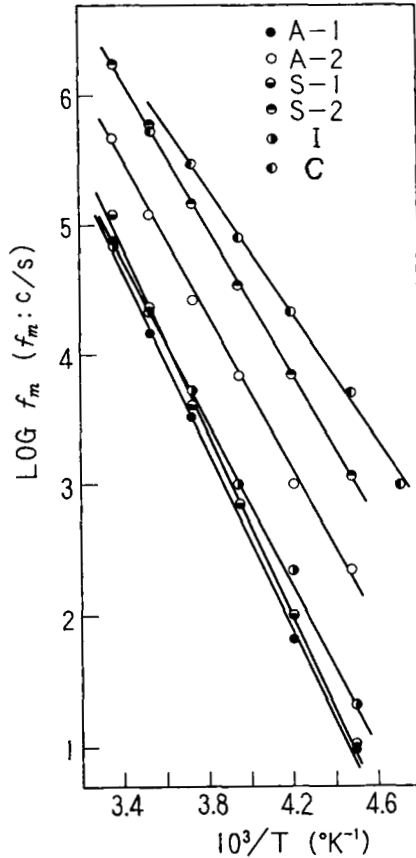


Fig. 9. Logarithm of loss maximum frequency of local mode relaxation of PVA plotted against reciprocal absolute temperature.

As described in the first section of this paper, conformations of PVA chains were studied by measurements of x-ray diffraction and infrared spectra. The conformations have been confirmed for crystalline chains, but it may be safely assumed that amorphous chain segments which contribute to the local mode relaxation have the same conformations for the most part. According to these studies, the isotactic chain has predominantly intrachain hydrogen bonds and μ is estimated at 0.76 D. Two types of interchain hydrogen bonds are possible in syndiotactic chains, one between chains in the same unit cell (A type) and the other between chains in neighboring cells (B type).⁸ The value of μ is nearly zero for A-type bonds (the moment is nearly perpendicular to the zigzag plane) and 1.06 D for B-type bonds.

According to eq. (3), $\Delta\epsilon$ should be proportional to the square of μ . Since $\Delta\epsilon$ is larger for syndiotactic chains than isotactic ones (Fig. 8), it may be concluded the B-type bonds are predominant in the former. If all the

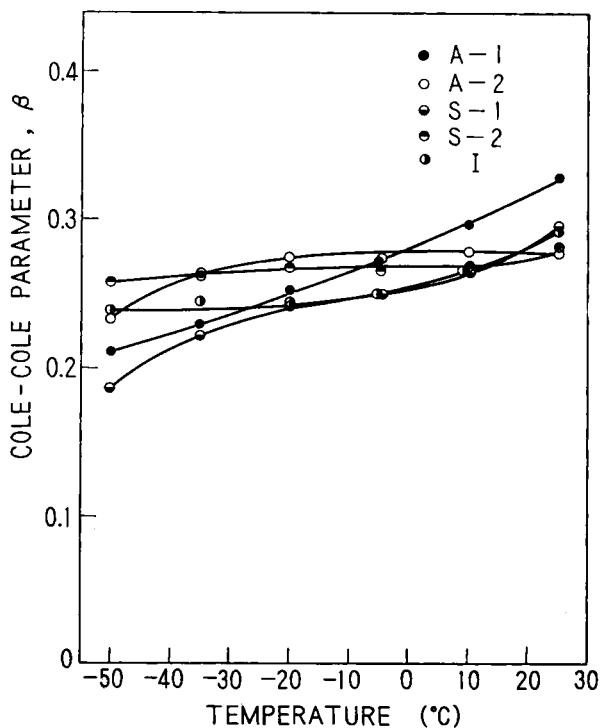


Fig. 10. Cole-Cole parameter of local mode relaxation of PVA.

bonds in syndiotactic chains are assumed to be of the B type, the ratio ($\Delta\epsilon_{\text{synd}}/\Delta\epsilon_{\text{iso}}$) should be equal to $(1.06/0.76)^2 = 1.9$, which agrees roughly with the observed value $(6.6/4.5) = 1.5$. In this comparison, other parameters in eq. (3) are taken as common for reasons which will be described in the following.

Figure 9 represents the logarithm of loss maximum frequency f_m plotted against reciprocal absolute temperature. The slope gives the activation energy as listed in Table II. As readily seen in Figure 9, f_m for a fixed temperature is higher for higher crystallinity. When reduced to an equal crystallinity, f_m and activation energy do not differ so much with stereo-

TABLE II
Activation Energy of Local Mode Relaxation of Poly(vinyl Alcohol)

Sample	Activation energy, kcal./mole
A-1	15.8
A-2	13.7
S-1	16.3
S-2	13.0
I	14.3
C	11.2

regularity. Since f_m is equal to $1/(2\pi\tau)$ (where τ is average relaxation time) and τ is proportional to η/f (where η is the interchain viscosity corresponding to the imaginary part of g as a complex quantity), the similarity in f_m and activation energy indicates the similarity in the nature of interchain interaction for chains of different stereoregularity.

The Cole-Cole parameter β which reflects the width of distribution of relaxation times is plotted against temperature in Figure 10. The value of β increases and hence the distribution is narrowed with increasing temperature for all samples.

The comparison between local mode relaxation and crystalline relaxation will be discussed in the next section.

Crystalline Relaxation in PVA

The primary and crystalline relaxations which are situated at higher temperatures than the local mode relaxation could not be observed in bulk samples because they were masked by the dc conduction loss. For sample C, however, the crystalline relaxation is observed as a shoulder in a doubly logarithmic curve of dielectric loss against frequency as illustrated in Figure 11. The position of the loss peak in the temperature-frequency plane almost agrees with the dynamic mechanical measurement.¹

Separation of the relaxation from the dc conduction loss was carried out by using the Cole-Cole plot.¹¹ An example is represented in Figure 12, where the circular arc represents the relaxation. Since the dc conduction

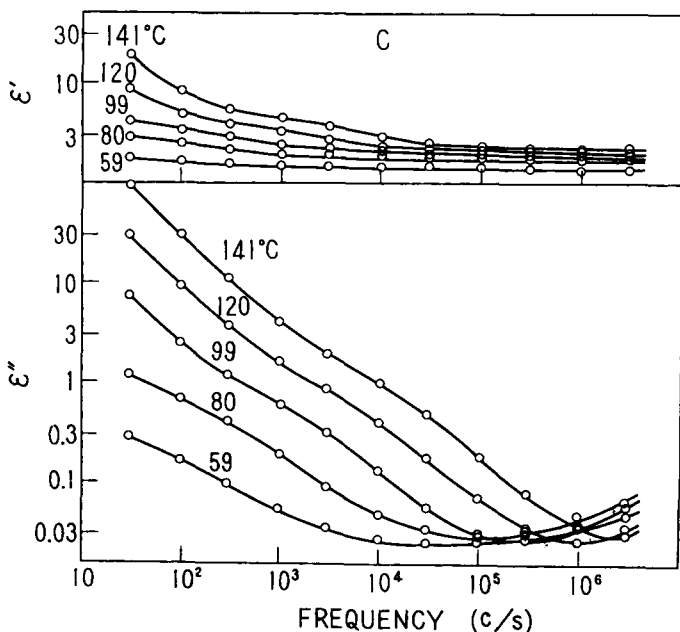


Fig. 11. Dielectric constant and loss of crystal aggregate of atactic PVA at high temperatures (packing density = 21% in volume).

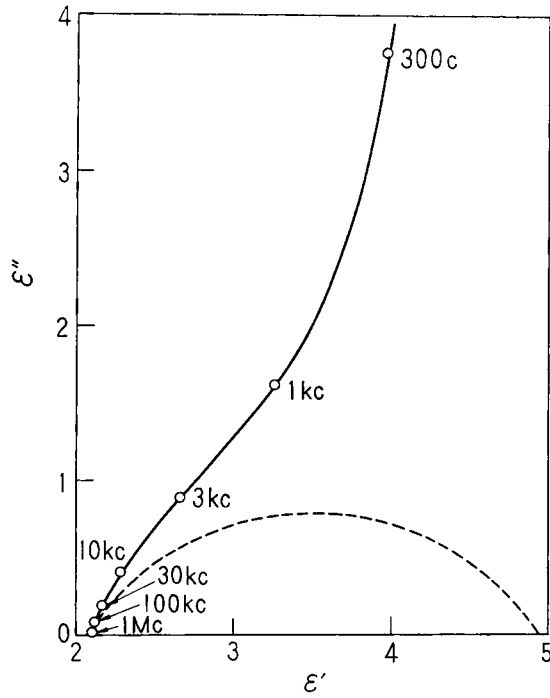


Fig. 12. Cole-Cole plot for crystal aggregate of atactic PVA at 120°C.: (—) total loss; (---) relaxational loss.

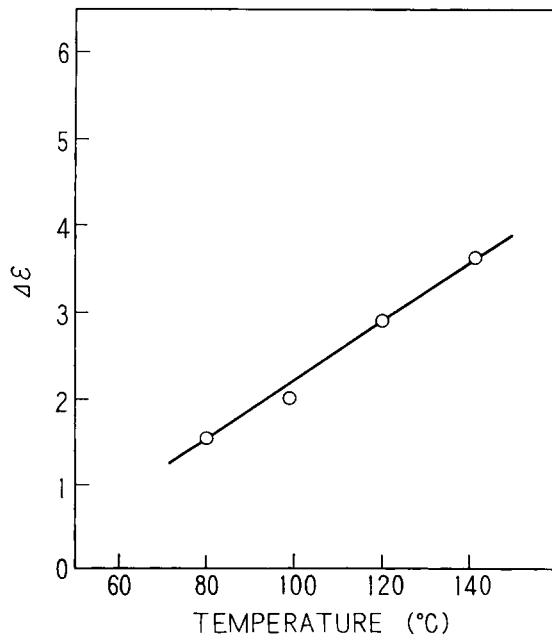


Fig. 13. Relaxation strength of crystalline relaxation of crystal aggregate of atactic PVA.

loss is equal to σ/ω (where σ is dc conductivity and ω is angular frequency), the arc was so drawn that the difference in ϵ'' between the observed loss (solid line in Fig. 12) and the arc may be inversely proportional to frequency. The relaxation strength and the loss maximum frequency were estimated at each temperature by this procedure.

Figure 13 shows $\Delta\epsilon$ as a function of temperature. True values of $\Delta\epsilon$ are ten times as large as these values, as described in the preceding section of this paper.

The crystalline relaxation has been attributed to the large amplitude vibration of crystalline chains. Ishikawa and his co-workers¹⁹ found an

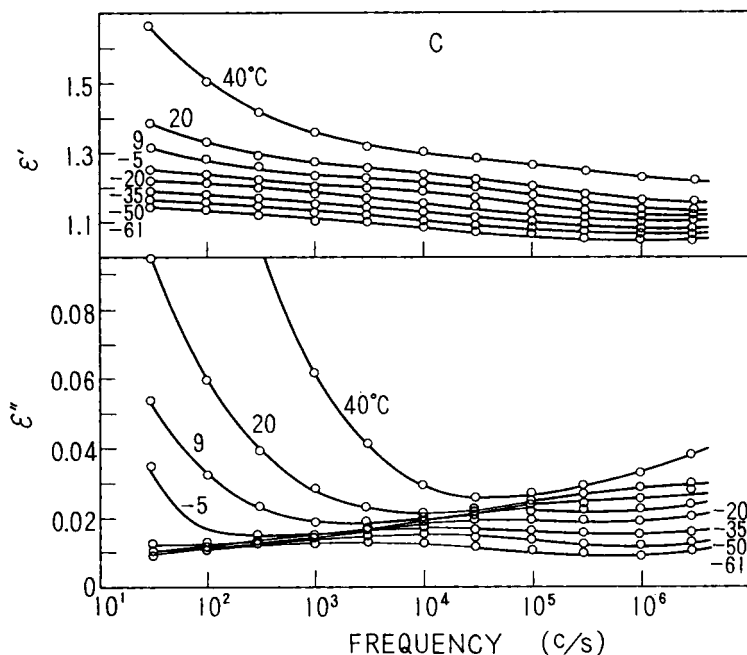


Fig. 14. Dielectric constant and loss of crystal aggregate of atactic PVA at low temperatures.

anisotropic thermal expansion of lattice constants of PVA at temperatures above 130°C ., where the crystalline relaxation occurs. This is a manifestation of the vibration as in the case of polyethylene.^{5,6} As is well known, atactic PVA chain is rich in syndiotactic portions and the crystal of atactic PVA is essentially the same as syndiotactic one in its structure. Consequently, we will discuss the crystalline relaxation of atactic PVA crystals assuming the chain to have a syndiotactic configuration.

As readily seen in Figure 13, $\Delta\epsilon$ increases with increasing temperature for the same reasons as the local mode relaxation. With the use of the numerical values: $N_{\text{dip}} = 1.7 \times 10^{22}/\text{cm}^3$, $N = 100$, $\mu = 1.06 \text{ D}$., $f = 10^{-12} \text{ erg}$,¹⁵ $g_0 = 3 \times 10^{-14} \text{ erg}$,¹⁸ $\epsilon' = 10$, $n = 1.5$, and $T = 400^{\circ}\text{K}$., $\Delta\epsilon$

was calculated as 20 from eq. (3). This is in a satisfactory agreement with the observed value when the latter is calibrated to 100% packing density.

The relaxation strength of local mode relaxation for zero crystallinity is appreciably smaller than that of crystalline relaxation for 100% crystallinity. The amorphous phase is rich in disorder in chain arrangement, which results in a small value of N (N is the number of backbone atoms in a segment coherently vibrating). This brings about small relaxation strength, small activation energy, and low temperature position of local mode relaxation as compared with crystalline relaxation.

Local Mode Relaxation of PVA Crystals

In the case of polyethylene and polyoxymethylene crystals, the local mode relaxation has been observed in mechanical and dielectric measurements and attributed to the surface disorder of polymer crystals.^{11,12} In case of PVA crystals (sample C), the local mode relaxation is found as illustrated in Figure 14. The relaxation strength is plotted against temperature in Figure 15. The strength is considerably smaller than that of bulk samples, even if it is reduced to perfect packing density. The loss maximum frequency is plotted in Figure 9. The frequency is higher than that of bulk samples, just with polyoxymethylene.¹¹

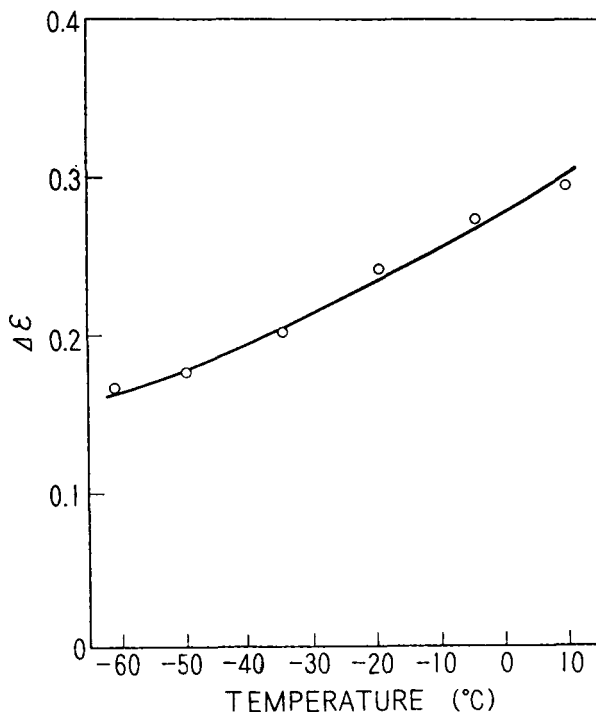


Fig. 15. Relaxation strength of local mode relaxation of crystal aggregate of atactic PVA plotted against temperature.

References

1. A. Nagai and M. Takayanagi, *Rept. Progr. Polymer Phys. Japan*, **7**, 249 (1964).
2. Y. Ishida, Y. Takeda, and M. Takayanagi, *Kolloid-Z.*, **168**, 121 (1960).
3. S. Nohara, *Kobunshi Kagaku*, **15**, 105 (1958).
4. T. Kajiyama, S. Togami, Y. Ishida, and M. Takayanagi, *J. Polymer Sci. B*, **3**, 103 (1965).
5. K. Tsuge, H. Enjoji, H. Terada, Y. Ohzawa, and Y. Wada, *Japan. J. Appl. Phys.*, **1**, 270 (1962).
6. K. Tsuge, *Japan. J. Appl. Phys.*, **3**, 588 (1964).
7. K. Okano, *Rept. Inst. Phys. Chem. Research (Tokyo)*, **40**, 273 (1964).
8. C. W. Bunn, *Nature*, **161**, 929 (1948).
9. S. Murahashi, H. Yuki, U. Yoneyama, T. Sano, H. Tadokoro, and Y. Chatani, *J. Polymer Sci.*, **62**, S77 (1962).
10. N. Hirai, K. Mononobu, H. Fujiwara, and Y. Nishikawa, paper presented at the 13th Symposium on Polymer Science, Tokyo, Japan, November 1964.
11. K. Arisawa, K. Tsuge, and Y. Wada, *Japan. J. Appl. Phys.*, **4**, 138 (1965).
12. Y. Wada and K. Tsuge, *Japan. J. Appl. Phys.*, **1**, 64 (1962).
13. I. Sakurada and Y. Nukushima, *Kobunshi Kagaku*, **12**, 483 (1955).
14. Y. Hotta, K. Tsuge, and Y. Wada, *Rept. Progr. Polymer Phys. Japan*, **8**, 325 (1965).
15. K. Okano, *Rept. Inst. Phys. Chem. Res. (Tokyo)*, **40**, 295 (1964).
16. R. Hayakawa and Y. Wada, paper presented at the Annual Meeting of the Physical Society of Japan, Okayama, October 1965.
17. A. Peterlin and E. W. Fischer, *Z. Physik*, **159**, 272 (1960).
18. A. Peterlin, E. W. Fischer, and C. Reinhold, *J. Chem. Phys.*, **37**, 1403 (1962).
19. T. Shirakashi, K. Ishikawa, and K. Miyasaka, paper presented at the 12th Symposium on Polymer Science, Nagoya, Japan, November 1963.

Résumé

On a mesuré la constante diélectrique et la perte diélectrique de films d'alcool polyvinyliques de différentes stéréo-régularités et cristallinités à des fréquences allant de 30 cycles/sec. à 3Mcycles/sec. dans un domaine de températures de -50°C à 25°C . La force de relaxation des relaxations locales est plus élevée pour les échantillons atactiques et syndiotactiques que pour l'isotactique si on les compare à cristallinité nulle. Ce comportement peut raisonnablement être expliqué sur la base de liaisons hydrogènes intercaténares dans les premiers et des liaisons hydrogènes intramoléculaires dans les seconds. La constante et la perte diélectrique dans les agrégats cristallins d'alcool polyvinylique atactique ont été mesurées à des températures de -50 à $+140^{\circ}\text{C}$. La force de relaxation de la partie cristalline est en bon accord avec la théorie suivant laquelle la relaxation est attribuée à la vibration torsionnelle des chaînes cristallines. Le faible pic de perte à basse température qui s'accorde le mieux avec le mode de relaxation locale des échantillons en bloc dans le domaine fréquence-température est attribué au désordre des monocristaux en surface.

Zusammenfassung

Dielektrizitätskonstante und Verlust von Polyvinylalkoholfilmen mit verschiedener Stereoregularität und Kristallinität werden bei Frequenzen von 30 Hz bis 3 MHz im Temperaturbereich von -50 bis 25°C gemessen. Die Relaxationsfestigkeit der lokalen Modenrelaxation ist bei Vergleich bei der Kristallinität Null bei ataktischen und syndiotaktischen Proben höher als bei isotaktischen. Dieses Verhalten ist auf Grund der Annahme der Bildung von Wasserstoffbindungen zwischen den Ketten bei ersteren und innerhalb der Ketten bei letzteren verständlich. Dielektrizitätskonstante und Verlust des Kristallaggregats von ataktischem Polyvinylalkohol werden bei Temperaturen von

–50 bis 140°C gemessen. Die Relaxationsfestigkeit der kristallinen Relaxation stimmt gut mit der Theorie überein, in welcher die Relaxation der Torsionsschwingung kristalliner Ketten zugeschrieben wird. Das schwache Verlustmaximum bei niedrigen Temperaturen, welches in der Frequenz-Temperatur-Lage fast mit der lokalen Modenrelaxation übereinstimmt, wird auf die Unordnung an der Oberfläche von Einkristallen zurückgeführt.

Received April 18, 1966

Prod. No. 1389