

## Dielectric $\beta$ -Relaxation in Poly(2-vinylpyridine)

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**ABSTRACT:** The dielectric  $\beta$ -relaxation process of poly(2-vinylpyridine) was found to be scarcely affected by the stereoregularity, in contrast to the  $\alpha$  process. For the  $\beta$  process of isotactic and atactic samples, the following facts were observed: (1) the dielectric behavior for an isotactic sample is similar to that for an atactic one; (2) from the conformational analysis for an isotactic sample, two equilibrium states exist in the rotation of the pendant pyridine ring and, between the two states, both potential and dipole moment differences estimated from the calculation agree with those obtained experimentally; and (3) when the main chain is distorted at the activated position of the rotation of the pendant group, the height of the potential barrier is calculated to be equal to the activation energy determined experimentally. Hence, it was inferred that the  $\beta$ -relaxation process for isotactic and atactic poly(2-vinylpyridine)s can be attributed to the restricted rotation of pendant pyridine rings accompanying a distortion of the main chains.

**KEY WORDS** Poly(2-vinylpyridine) / Dielectric Relaxation / Side Chain Relaxation / Conformational Analysis / Two-State Transition /

It is well known that for the linear vinyl polymers the  $\alpha$ -relaxation process observed at temperatures above the glass-transition temperature ( $T_g$ ) is attributed to the micro-Brownian motion of main chains, and the relaxation processes observed at temperatures below  $T_g$  (e.g.,  $\beta$ -relaxation process) correspond to local motions of the polymer.<sup>1,2</sup> For example, the  $\beta$  process of poly(vinyl chloride) has been attributed to the local motion of main chains,<sup>3</sup> and that of poly(*m*-chlorostyrene), to the hindered rotation of a pendant group.<sup>5</sup>

For poly(2-vinylpyridine), the dielectric behavior has not been studied very much up to now. Although Baccareda, *et al.*,<sup>4</sup> suggested, from a mechanical study of the polymer, that the  $\beta$  process be ascribed to the wagging motion of pendant pyridine rings, the mechanism of the process has not been fully clarified yet. For the mechanism of the  $\beta$ -relaxation process of the polymer, two interpretations can be considered: (1) as a local motion of the main chains with pendant pyridine rings, (2) as an internal rotation of the pendant pyridine rings. One approach to clarify the mechanism is the estima-

tion of the potential energy of the molecular environment related to the motion of the side group; here the stereo-regular polymer is an available sample for the purpose.

In this work, the dielectric spectra of poly(2-vinylpyridine) were measured and the effects of stereoregularity on the dielectric relaxation process were investigated; to elucidate the mechanism of the  $\beta$ -relaxation process, the potential energy as a function of rotation angle of the pendant group was calculated for an isotactic sample by means of conformational analysis. From the experimental and calculated results, the mechanism of the  $\beta$ -relaxation process for poly(2-vinylpyridine) is made clear.

### EXPERIMENTAL

Crude samples of atactic poly(2-vinylpyridine) (ata-P2VP) (polymerized by suspension polymerization) and isotactic poly(2-vinylpyridine) (iso-P2VP) (polymerized by anionic polymerization) were kindly supplied by Prof. S. Arichi. These samples were purified by reprecipitation, with benzene as solvent and petroleum ether as

nonsolvent, and dried for two weeks *in vacuo* at 70°C. The purified samples were molded into discs of about 0.5 mm in thickness by a laboratory press at 130 to 150°C. Silver electrodes were deposited *in vacuo* on both surfaces of the sample disc.

The density of the samples was determined, at 35°C, by the floatation in mixtures of carbon tetrachloride and *n*-hexane. The glass-transition temperature and the molecular weight were determined by dilatometry and the viscosity measurements,<sup>7</sup> respectively. In order to determine the crystallinity, the X-ray diffraction spectra were measured by the X-ray (Cu—K $\alpha$ ) diffractometer (Rigaku Denki Co., type 2122). The high resolution NMR spectra were obtained for the sample with a Varian T-60 spectrometer operating at 60 MHz on CDCl<sub>3</sub> solutions at room temperature.

For the measurement of the dielectric constant ( $\epsilon'$ ) and the loss ( $\epsilon''$ ), an inductive-ratio-arm bridge (Ando Elect. Co. Ltd., type TR-10) was employed in the frequency range from 10<sup>6</sup> to 30 Hz, and a resistive-ratio-arm bridge (Ando Elect. Co. Ltd., type TR-4) was used in the range from 10 to 10<sup>-1</sup> Hz. In the range of 10<sup>-2</sup> to 10<sup>-4</sup> Hz, the values of  $\epsilon''$  were determined from the absorption currents.<sup>9</sup> The temperature of the sample cell was held constant within  $\pm 0.1^\circ\text{C}$  for several hours in a dry box submerged in an oil thermostat.

## RESULTS

Some characteristics of the samples are tabulated in Table I. The crystallinity of iso-P2VP was estimated from the X-ray diffraction spectra shown in Figure 1. The number of dipoles in a unit volume of the amorphous region which may contribute to the  $\beta$ -relaxation, ( $N$ ), is evaluated from the values of density and

Table I. Some characteristics of ata-P2VP and iso-P2VP

Sample	$d(\text{g}/\text{cm}^3)$	$T_g(^{\circ}\text{C})$	mol wt	Crystallinity, %	$N$
ata-P2VP	1.142	99	$1.11 \times 10^5$	—	$6.5 \times 10^{21}$
iso-P2VP	1.155	76	$1.19 \times 10^6$	12	$5.8 \times 10^{21}$

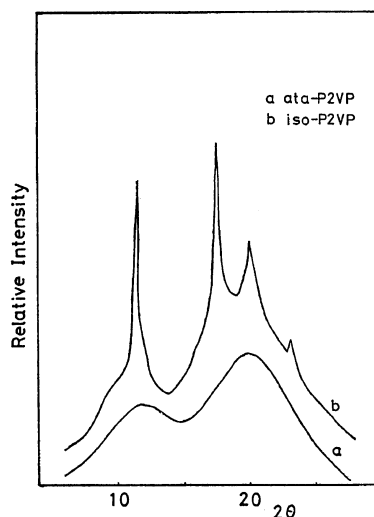


Figure 1. X-ray diffraction spectra of ata-P2VP and iso-P2VP.

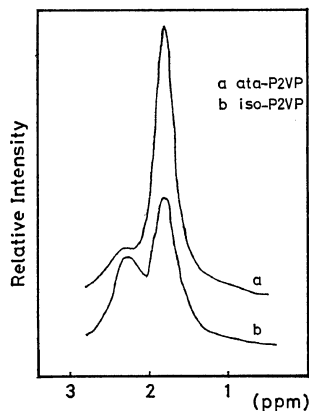


Figure 2. NMR spectra of ata-P2VP and iso-P2VP.

crystallinity. The glass-transition temperature ( $T_g$ ) for iso-P2VP is found to be lower than that for ata-P2VP. Figure 2 shows the high-resolution NMR spectra of the samples. In accordance with Geuskens, *et al.*,<sup>8</sup> we ascertained, from Figure 2, that the sample of iso-P2VP is isotactic-rich.

In Figure 3, the typical plots of the frequency dependence of  $\epsilon''$  at a temperature above  $T_g$  are shown for two samples. The values of  $\epsilon''$  shown in the figure are those corrected by subtracting the loss due to ionic conduction. The loss peaks correspond to the dielectric  $\alpha$

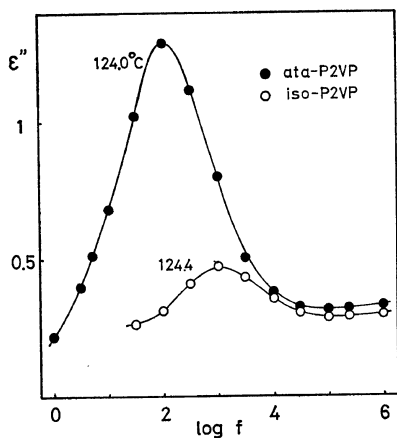


Figure 3. Typical plots of frequency dependences of  $\epsilon''$  at a temperature above  $T_g$  for ata-P2VP and iso-P2VP.

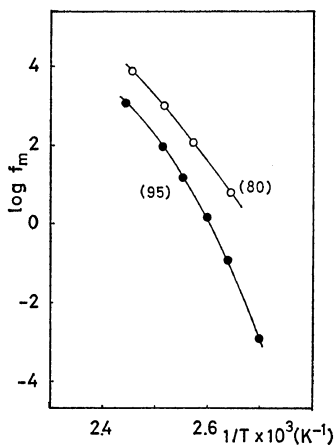


Figure 4. Temperature dependences of the relaxation frequency of the  $\alpha$  process for ata-P2VP (●) and iso-P2VP (○). The value in parentheses the apparent activation energy (kcal/mol) at the temperature where  $f_m$  becomes 10 Hz.

relaxation caused by the micro-Brownian motion of the main chains. The  $\alpha$ -loss peak for iso-P2VP is found to be smaller and broader than that for ata-P2VP. The temperature dependences of the relaxation frequency and the values of apparent activation energy at the temperature where the relaxation frequency becomes 10 Hz, for the  $\alpha$  process, are shown in Figure 4.

The frequency dependences of  $\epsilon'$  and  $\epsilon''$  at temperatures below  $T_g$  are shown in Figures 5

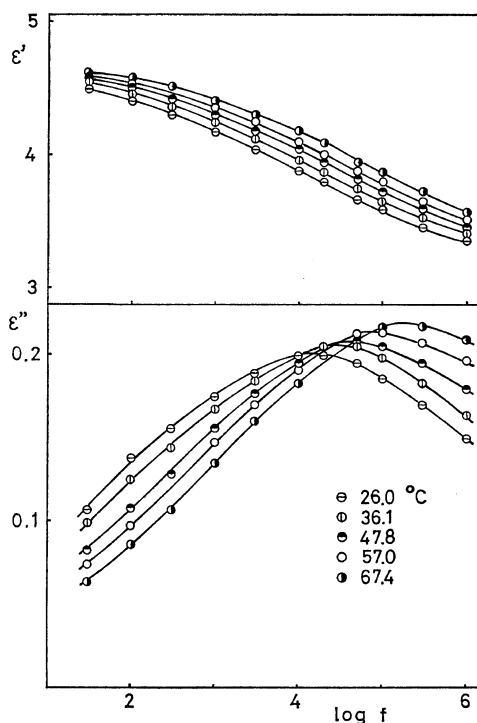


Figure 5. Frequency dependences of  $\epsilon'$  and  $\epsilon''$  at temperatures below  $T_g$  for ata-P2VP.

and 6. The loss peaks observed in the figures are ascribed to the  $\beta$ -relaxation process. Although the  $\beta$ -loss peak for iso-P2VP is found to be somewhat broader than that for ata-P2VP, the relaxation frequency of the process is scarcely affected by the stereoregularity. The temperature dependences of the relaxation frequency for the  $\beta$  process are shown in Figure 7. From the line slope in the figure, the apparent activation energy for the processes of both samples is estimated to be 11 kcal/mol.

The values of relaxation strength ( $\Delta\epsilon$ ) for the  $\beta$  process determined from the Cole's circular arc plot<sup>10</sup> are plotted against temperature in Figure 8a. The dielectric relaxation strength is given by the following equation<sup>18</sup>:

$$\Delta\epsilon = \epsilon_0 - \epsilon_\infty = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \left( \frac{\epsilon_\infty + 2}{2} \right)^2 \frac{4\pi N\mu_0^2}{3kT} \quad (1)$$

where  $\mu_0$  is the effective dipole moment of the motional unit,  $\epsilon_0$  and  $\epsilon_\infty$  are the limiting values of the dielectric constant at low and high frequency,  $N$  is the number of effective dipoles

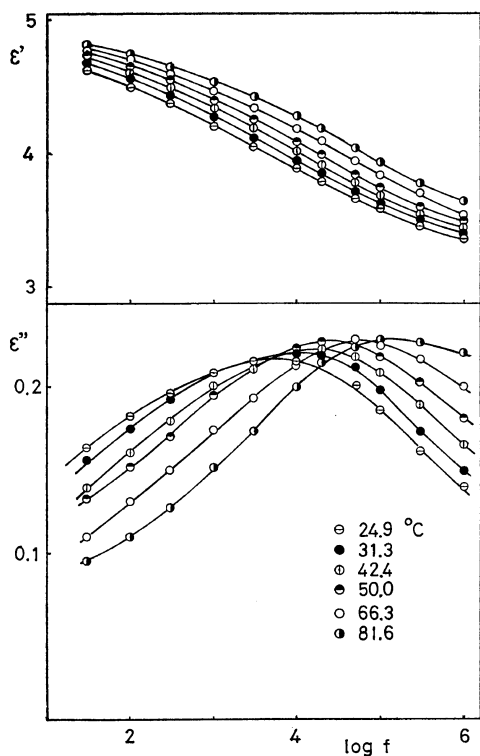


Figure 6. Frequency dependences of  $\epsilon'$  and  $\epsilon''$  at temperatures below  $T_g$  for iso-P2VP.

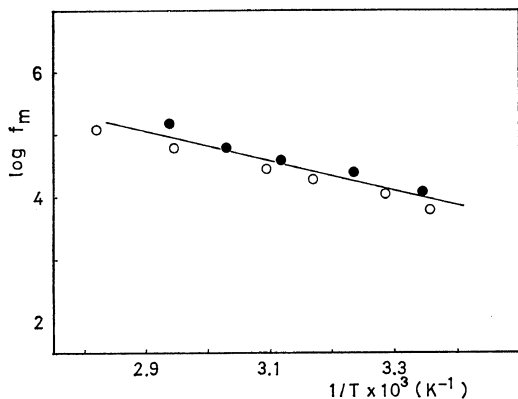


Figure 7. Temperature dependences of the relaxation frequency of the  $\beta$  process for ata-P2VP (●) and iso-P2VP (○).

in a unit volume, and  $k$  is the Boltzmann constant. The values of  $\mu_e$  estimated from  $\Delta\epsilon$  are shown in Figure 8b.

From the values of relaxation frequency,

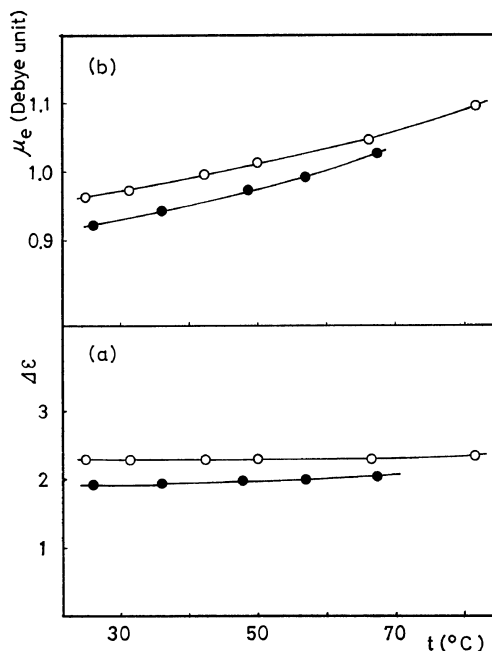


Figure 8. (a) Temperature dependences of  $\Delta\epsilon$  for ata-P2VP (●) and iso-P2VP (○); (b) temperature dependences of  $\mu_e$  for ata-P2VP (●) and iso-P2VP (○).

activation energy,  $\Delta\epsilon$ , and  $\mu_e$ , the dielectric  $\beta$ -relaxation process of poly(2-vinylpyridine) is found to be scarcely affected by the stereoregularity, in contrast to the  $\alpha$ -relaxation process.

### DISCUSSION

If the  $\beta$ -relaxation process of poly(2-vinylpyridine) is attributable to the local motion of main chains, the relaxation strength can be estimated theoretically. As for the case of an atactic polymer, the strength of the local-mode relaxation is given by Yamafuji's equation:<sup>3</sup>

$$\Delta\epsilon = \frac{4\pi E_r}{3E} \frac{N\mu_0^2}{G'aN^{2/3}} \quad (2)$$

where  $N$  is the number of repeating units in a unit volume;  $a$ , the effective Stokes' radius for a repeating unit;  $\mu_0$ , the mean dipole moment of a repeating unit;  $G'$ , the real part of the shear modulus;  $E$ , the electric field; and  $E_r$ , the local field. In the case of ata-P2VP, by substituting

the appropriate values ( $N \sim 6.5 \times 10^{21}/\text{cm}^3$ ,  $\mu_0 \sim 1.9 \text{ D}$ ,<sup>20</sup>  $a \sim 8 \times 10^{-8} \text{ cm}$ ,  $G' \sim 1 \times 10^{10} \text{ dyn/cm}^2$ , and  $E_r/E \sim 3$ ) into the right-hand side of eq 2, the strength of the  $\beta$ -relaxation process is estimated to be 0.1. The value of  $\Delta\epsilon$  thus obtained is much smaller than the observed value ( $\Delta\epsilon = 1.9$  at  $30^\circ\text{C}$ ). In the case of the isotactic form, the strength of the local-mode relaxation is given by the following Hayakawa's equation:<sup>6</sup>

$$\Delta\epsilon = \frac{2\pi E_r}{3E} \frac{N\mu_0^2}{f(1 - \cos\varphi)} \quad (3)$$

where  $f$  is the torsional force constant and  $\varphi$  is the angle specifying the direction of the dipole with respect to the chain axis. For iso-P2VP, using the appropriate values ( $N \sim 5.8 \times 10^{21}/\text{cm}^3$ ,  $\mu_0 \sim 1.9 \text{ D}$ ,  $\varphi \sim 120^\circ$  as 3/1 helix,  $f \sim 5 \times 10^{-13} \text{ erg}$ , which is half of the value for polyethylene,<sup>21</sup> and  $E_r/E \sim 3$ ), the strength of the  $\beta$  process is estimated to be 0.7. This is smaller than the observed value ( $\Delta\epsilon = 2.3$  at  $30^\circ\text{C}$ ).

From the comparison of the estimated value of  $\Delta\epsilon$  for the local mode relaxation with the experimental value, the  $\beta$ -relaxation process of poly(2-vinylpyridine) may be better attributed to the internal rotation of the pendant pyridine ring. To confirm this, the following conformational analysis was carried out for the isotactic sample.

In the analysis, we assumed that the main chain of isotactic poly(2-vinylpyridine) in the amorphous phase maintains locally the 3/1 helix (internal rotation angles of main chain,  $\chi_1 = -120^\circ$  and  $\chi_2 = 0^\circ$ ). For the assumption we referred to the following facts: Natta, *et al.*,<sup>11</sup> have characterized, by X-ray analysis, the identical period of crystalline isotactic poly(2-vinylpyridine) to be about  $6.7 \text{ \AA}$ , which is similar to that of crystalline isotactic polystyrene;<sup>13</sup> Gorin<sup>23</sup> also reported, from the conformational analysis, that the probable structure of the backbone of isotactic poly(2-vinylpyridine) is similar to that of isotactic polystyrene; and Weil, *et al.*,<sup>12</sup> reported from the high-resolution NMR measurements that the main chain of isotactic poly(2-vinylpyridine) in the solution may have the 3/1 helix, similar to the backbone structure of isotactic polystyrene.

The potential energy as a function of rotation angle of pendant pyridine ring was calculated

by summing up the torsional energy of the rotating C—C bond, the van der Waals interaction, and the electrostatic interaction between nonbonded atoms. To calculate the torsional energy, the following sinusoidal function was used:

$$V = \frac{V_0}{2}(1 + \cos 6\theta) \quad (4)$$

where  $\theta$  is the rotation angle and  $V_0$  the barrier height. The value of  $V_0$  is assumed to be 0.5 kcal/mol, as it is for the rotation of the methyl group of toluene.<sup>14</sup> In the calculation of the van der Waals interaction, the following Lenard—Jones potential function was used:

$$V = A_{ij}R_{ij}^{-12} - B_{ij}R_{ij}^{-6} \quad (5)$$

where  $R_{ij}$  is the distance between the  $i$ -th and  $j$ -th atoms, and the parameters of  $A_{ij}$  and  $B_{ij}$  are quoted from the work of Scheraga, *et al.*<sup>15</sup> The electrostatic interaction between two partial charges was calculated by use of a potential function of Coulomb's rule type:

$$V = \frac{332q_iq_j}{\epsilon R_{ij}} \quad (6)$$

where  $q_i$  and  $q_j$  are partial charges of the  $i$ -th atom and  $j$ -th atom respectively, and  $\epsilon$  is the apparent dielectric constant. For the value of  $\epsilon$ , we adopted 4 (the mean value of the observed dielectric constant). Using the bond length and the bond moment of C—N bond estimated from the dipole moment of pyridine,<sup>16</sup> the partial charges of the nitrogen atom and the adjoining carbon atom in a pyridine ring were calculated to be  $-0.56$  and  $0.28$  (electron charge units), respectively.

For the molecular parameters of iso-P2VP, the following bond lengths and bond angles in the main chain were adopted: C—C =  $1.54 \text{ \AA}$ , C—H =  $1.09 \text{ \AA}$ ,  $\angle\text{CCC} = 116^\circ$ ,  $\angle\text{HCC} = 110^\circ$ . The bond lengths and bond angles in the pyridine ring were adopted according to the data obtained by Bak, *et al.*:<sup>17</sup> C—N =  $1.31 \text{ \AA}$ , C—C =  $1.39 \text{ \AA}$ , C—H =  $1.08 \text{ \AA}$ ,  $\angle\text{CNC} = 116^\circ$ ,  $\angle\text{NCC} = 124^\circ$ ,  $\angle\text{CCC} = 118^\circ$ .

In the calculation of potential energy, we took into account all the nonbonded atoms in the region within five monomer units from the given monomeric unit, and assumed that the

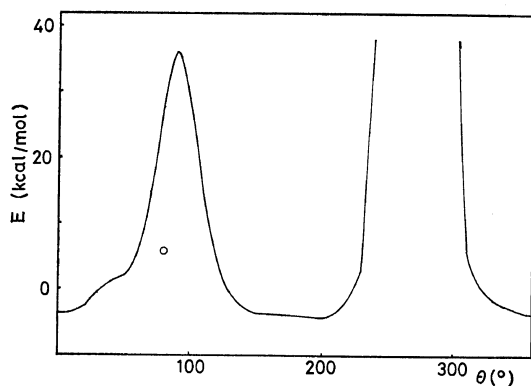


Figure 9. The calculated potential energy as a function of rotation angle ( $\theta$ ). The circle (O) denotes a energy maximum when the internal rotation angle of the main chain ( $\chi_2$ ) is varied by  $+12^\circ$ .

contribution of intermolecular interaction is negligible. The calculation was carried out on the electronic computer TOSBAC 3400 in Hiroshima University's Computation Center.

The calculated potential energy is shown as a function of  $\theta$  in Figure 9, where the value of  $\theta$  was put to be 0 when N—C—C—H is the *trans* conformation and the sign of  $\theta$  is positive for counter-clockwise rotation. The figure shows two maxima and minima in the rotation of the pendant pyridine ring; the potential difference between the two minima ( $\Delta E$ ) is 0.6 kcal/mol, the height of the lower potential barrier between the two minima is 40 kcal/mol, and the angle difference between the two minima ( $\Delta\theta$ ) is  $200^\circ$ . Thus, there are two equilibrium states considered in the  $\beta$ -relaxation process.

According to the two-state transition theory,<sup>19,22</sup> the value of  $\mu_e^2$  is given by the following equation:

$$\mu_e^2 = (\Delta\mu)^2 \frac{\exp(-\Delta G/RT)}{\{1 + \exp(-\Delta G/RT)\}^2} \quad (7)$$

where  $\Delta\mu$  is the change in dipole moment when a motional unit moves from one equilibrium state to another and  $\Delta G$  is the standard free energy difference between the two states. In determining the  $\Delta\mu$  from the observed  $\mu_e$  value, the value of  $\Delta G$  in the narrow temperature range is taken as constant. Using the reference temperatures  $T_1$  and  $T_2$ ,  $\Delta\mu$  is eliminated from

eq 7 as follows:

$$\frac{\mu_e^2(T_2)}{\mu_e^2(T_1)} = \frac{\exp(-\Delta G/RT_2)\{1 + \exp(-\Delta G/RT_1)\}^2}{\exp(-\Delta G/RT_1)\{1 + \exp(-\Delta G/RT_2)\}^2} \quad (8)$$

In the case of  $T_1=303^\circ\text{K}$  and  $T_2=308^\circ\text{K}$ ,  $\mu_e^2(T_2)/\mu_e^2(T_1)$  was calculated for the given  $\Delta G$  value; the relation between  $\mu_e^2(T_2)/\mu_e^2(T_1)$  and  $\Delta G$  is shown in Figure 10. Comparing the experimental value of  $\mu_e^2(308)/\mu_e^2(303)$  with the plot in Figure 10,  $\Delta G$  was determined as listed in Table II. The value of  $\Delta\mu$  was estimated by introducing the estimated value of  $\Delta G$  into eq 7, as shown in Table II.

The value of  $\Delta\mu$  for iso-P2VP can be calculated from the dipole moment of the pyridine ring (1.9 D) and from the two angles specifying the direction of the dipole with respect to the rotation axis. One of the two angles is  $\Delta\theta(200^\circ)$ , which was determined from the conformational analysis, while the other is the angle between the direction of the pyridine dipole and the rotation axis, assumed to be  $60^\circ$  from the position of the nitrogen atom in the pyridine ring. The calculated value of  $\Delta\mu(3.2 \text{ D})$  agrees with the experimental value (2.9 D).

It is found that when  $T(303^\circ\text{K})$  and the estimated value of  $\Delta G$  are introduced into the denominator in eq 7, it becomes approximately unity. Hence, assuming that the denominator in eq 7 is unity and that the volume does not change in the transition, the following equation is derived:

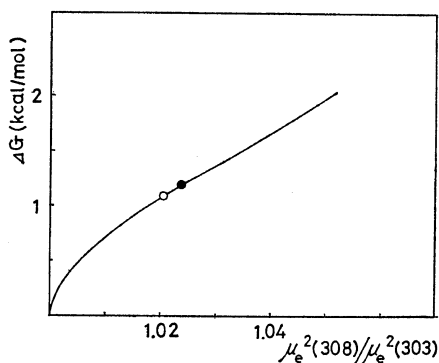
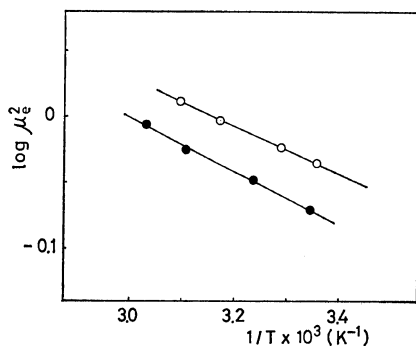


Figure 10. Plots of  $\mu_e^2(308)/\mu_e^2(303)$  against  $\Delta G$ . The circles denote the experimental value; (●) for ata-P2VP, (○) for iso-P2VP.

**Table II.** Parameters related to the  $\beta$  process for iso-P2VP and ata-P2VP<sup>a</sup>

Sample	$\Delta G_{(\text{obs})}$ , kcal/mol	$\Delta\mu_{(\text{obs})}$ , D	$\Delta\mu_{(\text{cal})}$ , D	$\Delta E_{(\text{obs})}$ , kcal/mol	$\Delta E_{(\text{cal})}$ , kcal/mol
iso-P2VP	1.1	2.9	3.2	0.8	0.6
ata-P2VP	1.2	3.1	—	0.9	—

<sup>a</sup> (obs), denotes the value obtained from the experimental values of  $\mu_e$ ; (cal), the value calculated from the conformational analysis; D means Debye units.

**Figure 11.** Plots of  $\log \mu_e^2$  against  $1/T$ .

$$\ln \mu_e^2 = A - \frac{\Delta E}{RT} \quad (9)$$

where  $\Delta E$  is the internal energy difference between the two states, and  $A$  is a constant involving the terms relative to the entropy change and  $\Delta\mu$ . From the slope of the plot for  $\log \mu_e^2$  vs.  $1/T$  in Figure 11, the value of  $\Delta E$  is estimated; this is tabulated in Table II. The value of  $\Delta E$  thus obtained (0.8 kcal/mol) for iso-P2VP is found to be agree with that estimated from the conformational analysis. The small discrepancy between the experimental and calculated values of  $\Delta E$  may be attributed to the intermolecular interaction among the polymer chains.

The calculated value of the potential barrier (40 kcal/mol) is much larger than the value of the activation energy for the  $\beta$  process of iso-P2VP (11 kcal/mol). This seems to imply that the activated state in the rotation of the pendant group accompanies a distortion of the main chains. To elucidate further, the potential height for the internal rotation angle of the

main chain ( $\chi_2$ ) varied by  $+12^\circ$  was calculated to be 10 kcal/mol. This agrees with the value of activation energy for the  $\beta$  process.

It is inferred, therefore, that the  $\beta$  relaxation process for iso-P2VP is ascribable to the restricted rotation of a pendant pyridine ring involving distortion of the main chains.

As for ata-P2VP, since the conformation of the main chain cannot be specified, it is difficult to apply the conformational analysis. The mechanism of the  $\beta$ -relaxation process for ata-P2VP is therefore discussed by comparing the characteristics of the  $\beta$  process with those for iso-P2VP. As for experimental results, such dielectric properties as relaxation frequency and activation energy of the  $\beta$  process for ata-P2VP are found to be similar to those for iso-P2VP. Then for ata-P2VP the values of  $\Delta G_{(\text{obs})}$ ,  $\Delta\mu_{(\text{obs})}$ , and  $\Delta E_{(\text{obs})}$  shown in Table II were estimated from the experimental value of  $\mu_e$ , assuming that two equilibrium states exist in the  $\beta$  process of ata-P2VP, as in the case of iso-P2VP. From the comparison of the characteristics of the  $\beta$  process for both samples, it is suggested that the molecular environment responsible for the  $\beta$  process of ata-P2VP is similar to that of iso-P2VP, and that the  $\beta$  process for ata-P2VP is due to the restricted rotation of the pendant group.

Through the present study, the following conclusions are derived: (1) the dielectric  $\beta$ -relaxation process of poly(2-vinylpyridine) is scarcely affected by the stereo-regularity, in contrast to the  $\alpha$  process; (2) there are two equilibrium states in the rotation of pendant pyridine rings for isotactic poly(2-vinylpyridine); and (3) the  $\beta$  process of isotactic and atactic poly(2-vinylpyridine) is due to the restricted rotation of the pendant group accompanying a distortion of the main chains.

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## REFERENCES

1. N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", John Wiley and Sons, New York, N.Y., 1967.

2. Y. Ishida, *J. Polym. Sci. Part A-2*, **7**, 1635 (1969).
3. K. Yamafuji, *J. Phys. Soc. Japan*, **15**, 2295 (1960).
4. M. Baccareda, E. Butta, V. Frosini, and S. Petris, *Mater. Sci. Eng.*, **3**, 157 (1968).
5. A. J. Curtis, *Soc. Plastics Engrs. Trans.*, **18**, 82 (1962).
6. R. Hayakawa and Y. Wada, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 2119 (1974).
7. S. Arichi, *Bull. Chem. Soc. Japan*, **41**, 244 (1968).
8. G. Geuskens, J. C. Lubikulu, and C. David, *Polymer*, **7**, 63 (1966).
9. B. V. Hamon, *Progr. Inst. Elect. Engr.*, **20**, 252 (1948).
10. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
11. G. Natta, G. Mazanti, P. Longi, G. Dall'Asta, and F. Bernardini, *J. Polym. Sci.*, **51**, 487 (1961).
12. G. Weil and G. Herman, *ibid. Part A-2*, **5**, 1293 (1967).
13. R. L. Miller and L. E. Nielsen, *ibid.*, **55**, 643 (1961).
14. M. V. Volkenstein, "Configurational Statics of Polymeric Chains", Interscience, New York, N.Y., 1963, p. 72.
15. R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **45**, 2091 (1966).
16. G. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, N.Y., 1955.
17. B. Bak, L. Hansen, and J. R. Andersen, *J. Chem. Phys.*, **22**, 2013 (1954).
18. H. Fröhlich, "Theory of Dielectrics", Oxford Univ. Press, Oxford, 1955, p. 183.
19. J. I. Lauritzen, *J. Chem. Phys.*, **28**, 118 (1958).
20. C. W. N. Cumper, A. I. Vogel, and S. Walker, *J. Chem. Soc.*, 3621 (1956).
21. B. Szigeti, *Trans. Faraday Soc.*, **48**, 400 (1952).
22. K. Shimizu, O. Yano, Y. Wada, and K. Kawamura, *J. Polym. Sci. Polym. Phys. Ed.*, **11**, 1641 (1973).
23. S. Gorin, *J. Chem. Phys.*, **67**, 878 (1970).