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<th>Dielectric Properties of Polyethylene Glycols: Dielectric Relaxation in Solid State (Special Issue on Polymer Chemistry, I)</th>
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<td>Koizumi, Naokazu; Hanai, Tetsuya</td>
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Kyoto University
Dielectric Properties of Polyethylene Glycols

Dielectric Relaxation in Solid State

Naokazu Koizumi and Tetsuya Hanai*
(Koizumi Laboratory)

Received March 10, 1964

The dielectric properties of polyethylene glycols have been investigated for the liquid and solid states over a frequency range from 20 cps to 3 Mc at temperatures from —70°C to +60°C. Relatively high dielectric constants of the liquids were ascribed to the end hydroxyl groups and the flexible oxyethylene chain of the molecule. In the solid state, two types of dielectric relaxation were observed separately: The one was the Debye type or the relaxation of orientation polarization, and the other the wedge type relaxation which supposedly resulted from the space change polarization. The general features of the latter are discussed also in connection with low-frequency relaxation found for other materials.

INTRODUCTION

The dielectric properties of low molecular-weight polyethylene glycols have been reported in previous papers1-3. In the case of this particular type of polymer the molecular chain of polyoxyethylene is fairly flexible due to the rotation around the CO bond in the chain skeleton and thus the mean relaxation time is small, being of the order of the magnitude of 10^-10 sec in the liquid state at room temperature and does not depend much on the molecular weight or the degree of polymerization. These features have been confirmed with higher molecular-weight polymer by Davies, Williams, and Loveluck4 who worked on the liquids and solutions in benzene of a series of polyethylene glycols with molecular weights of 200 to 29,000.

In the present work an attempt was made to elucidate the dielectric properties of polyethylene glycols (MW=600-6000) in the solid state, since few work was made on the solids and since a small dielectric dispersion was observed for the solids of lower polymers11. Also preliminary measurements on solid 'Carbowax' which was made in this laboratory exhibited a considerable dispersion at very low frequencies. It is another point in this work to examine the nature of the low-frequency dispersion.

EXPERIMENTAL

Materials

Polyethylene glycols used were 'Carbowax' polyethylene glycols with molecular weights ranging from 600 to 6000 which were supplied from Union
Naokazu Koizumi and Tetsuya Hanai

Carbide International Company. Although the original samples were fairly well fractionated, each one was purified by continuous extraction with dry diethyl ether in order to remove ionic impurities. The molecular weight was determined from the end hydroxyl groups. The observed molecular weights were consistent with those designated by the manufacturer except for Carbowax 4000. Some physical constants of materials are listed in Table 1. The average molecular weight was slightly reduced by the extraction procedure. As shown in Table 1, the original materials contained a small amount of moisture. Although the moisture content was reduced by extraction in most cases, no further desiccation was made in this work. Each polymer melted fairly sharply, showing a well-defined melting point. Diethyl Carbitol, i.e. diethylene glycol diethyl ether from Union Carbide was fractionated twice under reduced pressure. Heptaethylene glycol was the same sample as used before.

Table 1. Molecular weights and melting points of Carbowax.

<table>
<thead>
<tr>
<th>Carbowax</th>
<th>Molecular weight designated</th>
<th>Molecular weight observed</th>
<th>Moisture content %</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>570—630</td>
<td>633</td>
<td>0.80</td>
<td>26.5</td>
</tr>
<tr>
<td>600 EEa</td>
<td>950—1050</td>
<td>937</td>
<td>1.08</td>
<td>39.5</td>
</tr>
<tr>
<td>1000</td>
<td>950—1050</td>
<td>918</td>
<td>0.88</td>
<td>39.0</td>
</tr>
<tr>
<td>1000 Eb</td>
<td>1300—1600</td>
<td>1260</td>
<td>1.26</td>
<td>47.0</td>
</tr>
<tr>
<td>1540</td>
<td>1300—1600</td>
<td>1410</td>
<td>1.92</td>
<td>46.0</td>
</tr>
<tr>
<td>1540 EEa</td>
<td>3000—3700</td>
<td>2920</td>
<td>1.38</td>
<td>56.0</td>
</tr>
<tr>
<td>6000</td>
<td>6000—7500</td>
<td>7800</td>
<td>0.58</td>
<td>64.0</td>
</tr>
</tbody>
</table>

a Value determined by the Karl Fischer method. b Extracted with diethyl ether. c Extracted twice. d After extraction, exposed to saturated water vapor to increase moisture content.

RESULTS AND DISCUSSION

Liquid Carbowax

Static or equilibrium dielectric constants and conductivities are listed in
### Table 2. Static dielectric constants of liquid Carbowax.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>600</th>
<th>600 EE</th>
<th>1000</th>
<th>1000 E</th>
<th>1000 EE</th>
<th>1000 EEH</th>
<th>1540</th>
<th>1540 EE</th>
<th>4000</th>
<th>6000</th>
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</thead>
<tbody>
<tr>
<td>70°</td>
<td>10.38</td>
<td>10.76</td>
<td>11.17</td>
<td>11.60</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>60°</td>
<td>10.47</td>
<td>10.84</td>
<td>11.22</td>
<td>11.62</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50°</td>
<td>10.74</td>
<td>11.15</td>
<td>11.55</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40°</td>
<td>9.48</td>
<td>9.76</td>
<td>10.09</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30°</td>
<td>9.46</td>
<td>9.76</td>
<td>10.09</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbowax</td>
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<td></td>
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<td></td>
<td>-</td>
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<tr>
<td>1000</td>
<td>10.62</td>
<td>10.95</td>
<td>11.33</td>
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<tr>
<td>1540</td>
<td>9.86</td>
<td>10.19</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4000</td>
<td>9.53</td>
<td>9.81*</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6000</td>
<td>8.20</td>
<td>8.30(65°)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Supercooled state.

### Table 3. Conductivities of liquid Carbowax.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>600</th>
<th>600 EE</th>
<th>1000</th>
<th>1000 E</th>
<th>1000 EE</th>
<th>1000 EEH</th>
<th>1540</th>
<th>1540 EE</th>
<th>4000</th>
<th>6000</th>
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</thead>
<tbody>
<tr>
<td>70°</td>
<td>75.6</td>
<td>57.0</td>
<td>40.4</td>
<td>26.7</td>
<td>-</td>
<td></td>
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<tr>
<td>60°</td>
<td>11.57</td>
<td>8.64</td>
<td>6.08</td>
<td>4.02</td>
<td>-</td>
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</tr>
<tr>
<td>50°</td>
<td>102.3</td>
<td>77.0</td>
<td>54.3</td>
<td>-</td>
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<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40°</td>
<td>20.3</td>
<td>15.60*</td>
<td>11.15</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbowax</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>1000</td>
<td>5.65</td>
<td>4.26</td>
<td>3.04</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>1540</td>
<td>9.88</td>
<td>6.85</td>
<td>4.89</td>
<td>-</td>
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<tr>
<td>4000</td>
<td>16.13</td>
<td>11.85</td>
<td></td>
<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>6000</td>
<td>5.08</td>
<td>3.68</td>
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<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4000</td>
<td>54.4</td>
<td>39.1*</td>
<td></td>
<td>-</td>
<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>6000</td>
<td>5.70</td>
<td>5.05(65°)</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

*Supercooled state.

Tables 2 and 3, respectively. Since relatively high dielectric constants may be ascribed to the end hydroxyl groups and the flexible oxyethylene chain of the molecule, it is reasonable that the higher molecular-weight Carbowax has the lower dielectric constant. The contribution of the dipole moment of the oxyethylene chain to the dielectric constant is evident from the high dielectric constant of diethyl Carbitol that has no end hydroxyl groups. The values of dielectric constant of these polyethylene glycols are very consistent with those studied by Davies et al. and also in the previous work on lower polymers. The extracted sample showed a slightly smaller dielectric constant, while the molecular weight was reduced. In this case the dielectric constant was decreased not by a change in the molecular weight but by a decrease in the moisture content. It is clear that a small amount
of water affects the dielectric constant (Table 2). Since the relaxation time of liquid polyethylene is of the order of magnitude of $10^{-10}$ sec. at room temperature, no dielectric dispersion was found in the present experimental range of frequency. The apparent increase in dielectric constant due to the electrode polarization took place below about 1 kc. This would be caused by ionic impurities present in Carbowax. The magnitude of the electrode polarization for Carbowax 1000's decreased in proportion to reduction in the conductivity of the sample (Fig. 1). As seen from Table 3, the conductivity

was reduced greatly by the extraction procedure. When the equivalent impedance of the electrode polarization is taken as $Z_0(j\omega)^{-n}$, the dielectric increment $\varepsilon_{app} - \varepsilon_0$ due to the electrode polarization is given by

$$\varepsilon_{app} - \varepsilon_0 = \frac{g^2 Z_0}{C_0} \left( \frac{\sin n\pi/2}{2} \right) \omega^{-n},$$

(1)

and the apparent conductance is

$$g_{app} = g + g^2 Z_0 \left( \frac{\cos n\pi/2}{2} \right) \omega^{-n},$$

(2)

\[118\]
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where $\epsilon_0$ is the static dielectric constant, $g$ is the conductance of liquid, $C_0$ the capacitance of the empty cell, $Z_0$ the magnitude of the impedance of the electrode polarization, $n$ an empirical constant ($1 \geq n > 0$) and $\omega$ the angular frequency.

The value of $n$ for these polyethylene glycols was about 0.9. The experimental results on the apparent increase of dielectric constant and no appreciable change in the conductivity with respect to frequency are consistent with those expected from Eqs. (1) and (2), since the second term on the right-hand side of Eq. (2) is negligibly small for $n \approx 1$. The extracted Carbowax was still contaminated with a trace of ionic impurity, because the conductivity shown in Table 3 is higher than those of pure low-membered polymers. Further reduction of ionic impurity could be possible by repeated extraction. With diethyl Carbitol no electrode polarization effect was observed in accordance with a low conductivity.

Solid Carbowax

Dielectric constants and losses of these polyethylene glycols in the crystalline solid state were considerably dependent on frequency and temperature. Plots of dielectric constants and losses versus temperature are shown with Carbowax 1000 in Figs. 2 and 3 respectively. Other polyethylene glycols also showed similar results. The temperature and frequency dependence of this kind are found for several solid dielectrics. There are two types of dielectric dispersion and absorption in Figs. 2 and 3: The one appears at higher temperatures and the other at lower temperatures. The
Dielectric Dispersion of the Wedge Type

The frequency dependence of dielectric constant and conductivity at higher temperatures are shown with Carbowax 1000’s in Fig. 4, where the dielectric constant decreases with increasing frequency, reaching a limiting value, while the conductivity increases with frequency, levelling off above a certain frequency. Thus, it is evident that logε′′ − ε′, and logσ are linear with logf over a range of frequency.

Now one can put

\[ \sigma = A\omega^n, \]

where A and n are empirical constants. Then the dielectric loss ε′′ is given by

\[ \epsilon'' = B\omega^{n-m} = B\omega^{-m}, \quad m = 1 - n, \]

where B and m are also numerical constants. Using Fourier transformations, one can obtain the decay function a(t) from the expression for ε′′, where

\[ a(t) = \frac{2}{\pi} \int_0^\infty \epsilon''(\omega) \sin \omega t d\omega \]

\[ = \frac{2B}{\pi} \int_0^\infty \omega^{-m} \sin \omega t d\omega \]

\[ = \frac{2B}{\pi} \Gamma(1-m) \cdot \cos \frac{\pi m}{2} \cdot \Gamma^{-m-1}, \quad 1 > m > 0, \]

where \( \Gamma(1-m) \) is the Gamma function. Now the real part ε′ can be derived
Dielectric Properties of Polyethylene Glycols

Fig. 4. Frequency dependence of dielectric constant and conductivity in the wedge type relaxation of solid Carbowax 1000's at 30°C.

from the decay function obtained,

\[ \varepsilon' - \varepsilon_\infty = \int_0^\infty a(t) \cos \omega t \cdot dt \]

\[ = \frac{2}{\pi} B \Gamma(1-m) \cos \frac{\pi m}{2} \int_0^\infty t^{m-1} \cos \omega t dt \]

\[ = B \cot \frac{\pi m}{2} \omega^{-m}. \quad (6) \]

Combining Eqs. (4) and (6), the expression in terms of complex dielectric constant, \( \varepsilon^* = \varepsilon' - j\varepsilon'' \), is given by,

\[ \varepsilon'^* - \varepsilon_\infty = \frac{B}{\sin(\pi m/2)} (j\omega)^{-m}, \quad 1 > m > 0. \quad (7) \]

Also

\[ \frac{\varepsilon''}{\varepsilon'^* - \varepsilon_\infty} = \tan \frac{\pi m}{2}. \quad (8) \]

The decay function is related with the distribution function \( G(\tau) \) of relaxation times by the equation,

\[ a(t) = \int_0^\infty G(\tau) e^{-\nu t} \frac{d\tau}{\tau}. \]

Thus, one can obtain

\[ G(\tau) = \frac{2B}{\pi} \cos \frac{\pi m}{2} \tau^{-m-1}. \quad (9) \]
Therefore log $G(\tau)$ must be linear with log $\tau$.

The experimental results shown in Fig. 4 are quite consistent with those expected from the relations derived above. Eq. (4), however, means that the linear relation of log $\sigma$ with log $f$ extends to higher frequencies and that there is no levelling-off of the conductivity. The fact that the conductivity attains a limiting value at a certain frequency is connected with the distribution of relaxation times that is somewhat different from prediction of Eq. (9): There must be the smallest or cut-off relaxation time in the actual system while the function $G(\tau)$ of Eq. (8) has no such a value. It is interesting features that the magnitude of polarization or dielectric constant due to the wedge type relaxation is proportional to the conductivity of the sample in the liquid state (see Table 3). The higher the conductivity, the polarization was the larger and extended to higher frequencies. With Carbowax 1000 the log $\sigma$--log $f$ curve levels also below 50 cps. This may be due to the contribution of d. c. conductivity in the solid state. As temperature was reduced, the d. c. conductivity became smaller and the linear relation of log $\sigma$ with log $f$ hold even at lower frequencies. Eq. (8) predicts that the frequency dependence of $\epsilon^\infty$ in a complex plane should be a straight line with the slope of tan $\pi m/2$. A typical example is illustrated for Carbowax 1540 at 0°C in Fig. 5. The value of $m$, that is, the slope of log $(\epsilon' - \epsilon^\infty)$ -log $f$ and log $\epsilon''$ -log $f$ plots was in a range of 0.3 to 0.62, depending on individual polymers and temperature.

The decay function of Eq. (5) is essentially the same as that obtained from the absorption current in solid dielectrics by Schweidler8). Fricke found the wedge type relaxation for an aqueous dispersion of solid particles or macro-

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![Complex plane plots of the wedge type relaxation of solid Carbowax 1540 at 0°C.](image)

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Fig. 5. Complex plane plots of the wedge type relaxation of solid Carbowax 1540 at 0°C.
molecules and he ascribed the effects to the polarization of water molecules bound at or near the dispersed phase. The present authors have found the wedge type relaxation for solid powders dispersed in paraffin. In the case of Carbowax, however, the existence of a small amount of ions as well as the water molecules contained is connected with the mechanism of the wedge type polarization.

It is well known that solid long-chain alcohols exhibit very high dielectric constants and conductivities in the α-phase between melting and transition points and that the dielectric constant is considerably dependent on frequency. Hoffman and Smyth interpreted the dispersion of the dielectric constant in terms of the Maxwell-Wagner effect for the mixture of two solid phases, the α- and β-phases, which have different dielectric constants and conductivities. Asai et al. proposed that very high dielectric constant of higher alcohols at low frequency may be attributable to the electrode polarization of the conductive proton in the α-phase. He noticed that the polarization was increased markedly by adding foreign ions. The frequency dependence of the dielectric constant for octadecyl alcohol examined in this laboratory was fitted with the relation for the wedge type relaxation.

The exacts mechanism of this type of relaxation have not been established yet. Possibly the relaxation of the space charge in solids would give rise to such frequency dependence.

Relaxation of Orientation Polarization

The wedge type relaxation diminishes with decreasing temperature and the Debye type relaxation of orientation polarization predominates below 40°C. The dielectric loss for Carbowax 1000 EE at low temperatures are plotted against log f in Fig. 6. The δ''-log f are not symmetrical about the frequency for the maximum δ'', i.e. the critical frequency, showing a shoulder on the low-frequency wing. No contribution of the wedge type polarization are found at these indicated temperatures. It is evident in Fig. 6 that there

Fig. 6. Frequency dependence of δ'' for solid Carbowax 1000 EE.
exist two absorption regions: The one appears at 100 kc to 1 Mc and the other between 1 and 10 kc. The absorption in the high-frequency region may be ascribed to the end hydroxyl groups, because the heat of activation obtained from the temperature dependence of the critical frequency was about 10 kcal/mol for these Carbowax. The low-frequency absorption might be due to the motion of polyoxyethylene chain. Unfortunately no confirmation was possible on account of limited results.

Variation of the relaxation time with molecular weight was not made clear, whereas the critical frequency for the loss maximum scattered for polymers with different molecular weights as shown in Fig. 7. The reason for this would be due to the interaction between water molecules present and the end hydroxyl groups or the oxyethylene group.

![Fig. 7. Plots of \( \epsilon'' \) versus frequency for Carbowax at \(-60^\circ \mathrm{C}\).]

The Cole-Cole plots of low temperature data give very flat circular arcs, showing a quite broad distribution of relaxation times. Corresponding to the existence of two dispersion regions the \( \epsilon'' - \epsilon' \) curve may be divided into two circular arcs, as shown in Fig. 8. Another example for Carbowax 1540

![Fig. 8. Cole-Cole plots for solid Carbowax 1540 EE at \(-50^\circ \mathrm{C}\).]
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Fig. 9. Cole-Cole plots for solid Carbowax 1540 at -60°C.

at -60° in Fig. 9 shows a much depressed arc. But this would not be a single arc either, possibly consisted of two dispersion region which can be expected from the $\epsilon'' - \log f$ plot in Fig. 7.

In the case of pure heptaethylene glycol, $\epsilon' - \log f$ and $\epsilon'' - \log f$ plots in Figs. 10 and 11 show typical relaxation of the Debye type which corresponds

Fig. 10. Plots of $\epsilon'$ versus frequency for solid heptaethylene glycol.

Fig. 11. Plots of $\epsilon''$ versus frequency for solid heptaethylene glycol.
to a small dielectric dispersion noticed before. A slight increase in dielectric constant below 30 cps at −40°C might be from the wedge type polarization. No shoulder was found with the ε''−log f curve, but a small peak of ε'' near 30 cps could be corresponding to the low-frequency absorption observed for high polymers. The heat and entropy of activation for relaxation of heptaethylene glycol was about 15 kcal/mole and 36 e. u., respectively. These values are higher than those for higher polymers. It is likely that hindrance in the orientation of the hydroxyl groups is greater for heptaethylene glycol.

The dielectric constant of solid diethyl Carbitol was as small as 2.6 near −60°C. Neither the wedge type relaxation nor the Debye type was observed. This means that the oxyethylene groups has no freedom of orientation in solid diethyl Carbitol.

CONCLUSION

It was found that the wedge type relaxation for solid Carbowax is closely related to the existence of ions and water molecules. Although the exact mechanism have not been established yet, the space charge polarization of ions co-operated with water molecules would be responsible for relaxation of this type. No particular attention was paid usually to the wedge type relaxation which is common to solid dielectric material at high temperatures and low frequencies, since this type of relaxation seems to be trivial for the dielectric study of the molecular structure. However in the particular cases such as long-chain alcohols, analysis of the dielectric dispersion would be important in connection with the proton transfer mechanism in the α-phase.

The Debye type relaxation found for solid Carbowax would be due to the hydrogen-bonded hydroxyl groups, whereas the heat of activation obtained is slightly higher than those for many other cases.

ACKNOWLEDGMENTS

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