0.4, however, a strong dependence on f_r predominates. Thus, depolarized scattering may offer a useful method for characterizing stereochemical composition of PS chains in the atactic and syndiotactic ranges. It is to be observed, however, that our calculations have been confined to polymers in which the distribution of *meso* and racemic dyads is random, or Bernoullian. Calculations could of course be carried out for chains of any given stereochemical sequence, statistical or regular.

It is regrettable that suitable experimental results with which to put the foregoing calculations to test are unavailable, except in the instance of the dimeric analog of PP, namely, 2,4-dimethylpentane, discussed above.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Contract No. F 44620-69-C-0058.

Appendix

The Effect of Random Variations in the Torsional Angle χ. According to the treatment presented for strain birefringence (see especially eq I-33),[4] the polarizability of the CHR–C group subject to a torsional angle χ about the C—R bond is given by

$$\hat{\boldsymbol{\alpha}}'(\chi) = \hat{\boldsymbol{\alpha}}'(\chi = 0) + \Delta\alpha_{\mathrm{R}}(\sin^2 \chi)\boldsymbol{\beta}_{\mathrm{a}} + \Delta\alpha_{\mathrm{R}}(\sin \chi \cos \chi)\boldsymbol{\beta}_{\mathrm{b}} \quad (9)$$

where

$$\boldsymbol{\beta}_{\mathrm{a}} = \boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}})[\mathrm{diag}(0, -1, 1)]\boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}})^{\mathrm{T}} \quad (10)$$

$$\boldsymbol{\beta}_{\mathrm{b}} = \boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}}) \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \boldsymbol{\Omega}_0(\xi', -\psi_{\mathrm{R}})^{\mathrm{T}} \quad (11)$$

with $\Delta\alpha_{\mathrm{R}} = \alpha_{\mathrm{CR};y} - \alpha_{\mathrm{CR};z}$ and $\boldsymbol{\Omega}(\xi', -\psi_{\mathrm{R}})$ given by eq I-26.[4]

If χ is subject to variations, then the average tensor $\hat{\boldsymbol{\alpha}}'$ is obtained from eq 9 by replacement of the trigonometric functions therein by their averages. In the case of the PS chain, the potential affecting χ is symmetric about $\chi = 0$,[4] and we have therefore that

$$\hat{\boldsymbol{\alpha}}' = \hat{\boldsymbol{\alpha}}'(\chi = 0) + \Delta\alpha_{\mathrm{R}}\langle\sin^2 \chi\rangle\boldsymbol{\beta}_{\mathrm{a}} \quad (12)$$

For the treatment of the depolarization (see eq 7) we require also the quantity $\hat{\alpha}_t{}^2$ defined by eq 8. From eq 9 we obtain, for the case of a symmetric potential such that $\langle\sin \chi \cos \chi\rangle = \langle\sin^3 \chi \cos \chi\rangle = 0$

$$\begin{aligned} \hat{\alpha}'^2 &= \alpha'^2(\chi = 0) + \Delta\alpha_{\mathrm{R}}{}^2\langle\sin^4 \chi\rangle\boldsymbol{\beta}_{\mathrm{a}}{}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{a}}{}^{\mathrm{C}} + \\ &\quad \Delta\alpha_{\mathrm{R}}{}^2\langle\sin^2 \chi \cos^2 \chi\rangle\boldsymbol{\beta}_{\mathrm{b}}{}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{b}}{}^{\mathrm{C}} + 2\cdot\Delta\alpha_{\mathrm{R}}\langle\sin^2 \chi\rangle \times \\ &\qquad \boldsymbol{\beta}_{\mathrm{a}}{}^{\mathrm{R}}\hat{\boldsymbol{\alpha}}'^{\mathrm{C}}(\chi = 0) \\ &= \hat{\alpha}'^2(\chi = 0) + 2\cdot\Delta\alpha_{\mathrm{R}}\langle\sin^2 \chi\rangle\boldsymbol{\beta}_{\mathrm{a}}{}^{\mathrm{R}}\hat{\boldsymbol{\alpha}}'^{\mathrm{C}} \times \\ &\qquad (\chi = 0) + 2\cdot\Delta\alpha_{\mathrm{R}}{}^2\langle\sin^2 \chi\rangle \end{aligned}$$

since $\boldsymbol{\beta}_{\mathrm{a}}{}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{a}}{}^{\mathrm{C}} = \boldsymbol{\beta}_{\mathrm{b}}{}^{\mathrm{R}}\boldsymbol{\beta}_{\mathrm{b}}{}^{\mathrm{C}} = 2$. Writing $\hat{\boldsymbol{\alpha}}'$ of eq 12 in its row and column forms and introducing them into the equation above, we obtain

$$\hat{\alpha}'^2 = \hat{\boldsymbol{\alpha}}'^{\mathrm{R}}\cdot\hat{\boldsymbol{\alpha}}'^{\mathrm{C}} + 2\Delta\alpha_{\mathrm{R}}{}^2(\langle\sin^2 \chi\rangle - \langle\sin^2 \chi\rangle^2) \quad (13)$$

The traceless tensor $\hat{\boldsymbol{\alpha}}'$ for a PS chain is given by eq I-37.[4]

The values of $\langle\gamma^2\rangle$ presented in Table I were calculated according to eq 6 and 7 using $\hat{\boldsymbol{\alpha}}'$ and $\hat{\alpha}'^2$ given by eq 12 and 13.

A Dielectric Study of Molecular Relaxation in Polyoxymethylene at High Temperatures

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ABSTRACT: Dielectric loss in polyoxymethylene has been measured at temperatures both below and above the crystalline melting point in order to ascertain the effect of crystalline order on molecular relaxation. Discontinuous changes in the relaxation take place upon melting. At least two relaxation regions are present in the melt. A relaxation region (α) occurs at ~4 GHz and further dispersion above 8 GHz is inferred from the dielectric constant at 8 GHz. The α region is characterized by a low activation energy, single relaxation time, and independence of molecular weight. From a study in the solid of the loss at low frequencies and the dc conductivity it was decided that an α dipolar dispersion region could not be extracted. A statistical mechanical calculation of the static dielectric constant of the melt based on the rotational isomeric state model is in good agreement with the experimental.

The study of relaxations in polymers by such techniques as measurement of the torsion modulus and loss *vs.* temperature has proven to be extremely valuable in understanding and summarizing simply their mechanical properties.[2] Although there exists a considerable body of information on relaxations from a variety of mechanical techniques and from dielectric and nuclear magnetic resonance measurements, the exact nature of the molecular motions underlying these relaxation regions remains relatively obscure. This is particularly true of the crystalline polymers where the role of the considerable recent developments in solid morphology is not clear. In fact, it is not clear how many relaxation regions linear chains without

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(1) To whom inquiries should be addressed.

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

side groups would show in idealized situations such as in the liquid state or in solution. Thus, there is no adequate basis for contrasting the effects of solid structure on relaxation.

The purpose of the present work was to consider a highly crystalline polymer of a simple chain structure in which the effects of solid structure could be examined by carrying the relaxation study into the melt. For the experimental technique we have chosen the dielectric method for its ease of frequency variation and its adaptability to high frequency (into the GHz region). The latter feature is essential since the high temperatures implied in melts result in shifts of relaxation peaks to quite high frequency. Polyoxymethylene (melting point 180°) was chosen for study since it has been investigated previously both mechanically and dielectrically.[3] It shows well defined α and γ relaxation regions mechanically. A small β relaxation region has been attributed to water.[3] Dielectrically, the possible presence of an α peak is obscured by ionic conduction, but Arisawa, *et al.*,[4] believe that it can be discerned. The most interesting feature of its relaxation behavior is that the mechanical α region correlates with density and thermal treatment in the way that in a naive description would attribute it to "crystalline regions." One of our purposes was to determine more definitively the effect of melting on this transition.

Read and Williams[5] carried their dielectric study of the γ peak to high enough temperatures to show that the apparent activation energy of the process decreases markedly with increasing temperature. One of our goals was to see if the effect of melting in the γ peak could be observed.

Experimental Section

It was necessary to make measurements in two frequency regions, from 20 Hz to several MHz and from 300 MHz to 8 GHz. A General Radio Model 1615A capacitance bridge and 1232A null detector were used for the measurements from the lower frequency to 100 KHz. A general Radio Model 716CS1 bridge was used from approximately 300 KHz to 5 MHz with heterodyne detection. At the lower frequency end (<10 KHz) the polyoxymethylenes used had a considerable loss due to dc conductivity and it was necessary to load the sample cell in parallel with additional capacitance to keep the dissipation factor in a measureable range. At the higher frequencies, from 300 MHz to 8 GHz, a General Radio Model 900LB coaxial slotted line and Hewlett-Packard 415E SWR meter were used. Hewlett-Packard 3200B, 612A and 8690B oscillators were used as signal sources. The dielectric constant, ϵ', and loss, ϵ'', were calculated from the measured wavelength in the line λ, the node position relative to the sample interface, X_0, the sample length, d, and the inverse standing wave ratio, s, using the short circuit termination equation[6]

$$\tan \gamma_2 d = -C^* \gamma_2 d$$

where

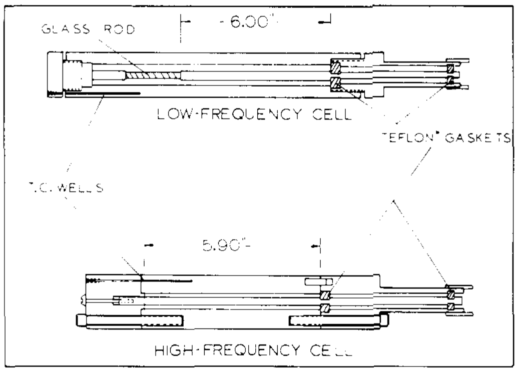

Figure 1. Cells used for dielectric measurements. The low frequency cell was used for bridge measurements (20 Hz to 5 MHz). The high frequency cell was used for the slotted-line measurements (400 MHz to 8 GHz). Low frequency cell, outer conductor diameter = 0.729 in.; high frequency cell, outer conductor diameter = 0.5625 in. Both are 50 ohms (ratio of outer to inner conductor = 2.303).

$$C^* = \frac{j\gamma_1}{2\pi d}\left[\frac{s - j \tan \dfrac{2\pi X_0}{\lambda_1}}{1 - js \tan \dfrac{2\pi X_0}{\lambda_1}}\right] \tag{1}$$

and the relation between the propagation constant, $\gamma_2 d$, and dielectric constant and loss

$$\epsilon' - j\epsilon'' = -\left[\frac{\lambda_1 \gamma_2 d}{2\pi d}\right]^2 \tag{2}$$

Equation 1 was solved for the complex propagation constant, $\gamma_2 d$, by Newton iteration using a digital computer and ϵ' and ϵ'' were calculated using eq 2.

Similar sample cells were used for both high and low frequency measurements (slotted line and bridges) and were 50 ohm coaxial configurations (see Figure 1). They were machined from brass and were wrapped with a heating tape and insulation. A thermocouple was imbedded in the wall and connected to a potentiometric controller. The cell could be heated to 200° from room temperature in 10 min. Rapid heat up was important in limiting degradation in polyoxymethylene. The notch in the coaxial radii which was designed for low reflection, was provided to allow a "Teflon" washer to be used to confine the sample. This latter feature was essential in the melt studies to prevent bubbling and outgassing due to slight decomposition and to provide a known sample interface. For the slotted line measurements the center rod was connected directly to the bottom plate (short circuit termination). For the bridge measurements a glass rod insert separated the center rod from the bottom plate. The tops of the cells were fitted with General Radio 900 series connectors. For the high frequency measurements, the cell was connected directly to the slotted line. For the 1615A bridge measurements flexible coaxial cable was used to connect with the bridge but the guard point was established at the top of the cell connector. With the megacycle bridge the flexible cable capacitance entered the measured capacitance. The empty capacitance of the sample-occupied portion of the cell was established by calibration with benzene, toluene, and carbon tetrachloride and was 10.18 pF.

Conductivities were measured by determining the potential drop across a standard resistor in series with the cell and a dc voltage source.

Thermal expansion of the sample was important due to the relatively high temperatures used, and, in the case of the melts, the change in volume on melting. For the solids the

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(3) For a discussion and review of references, see ref 3, Chapter 14.

(4) K. Arisawa, K. Tsuge, and Y. Wada, *J. Appl. Phys.* (Japan), **4**, 138 (1965).

(5) B. E. Read and G. Williams, *Polymer*, **2**, 239 (1961).

(6) A. von Hippel, Ed., "Dielectric Materials and Applications," Technology Press (MIT) and John Wiley & Sons, Inc., New York, N. Y., 1954.

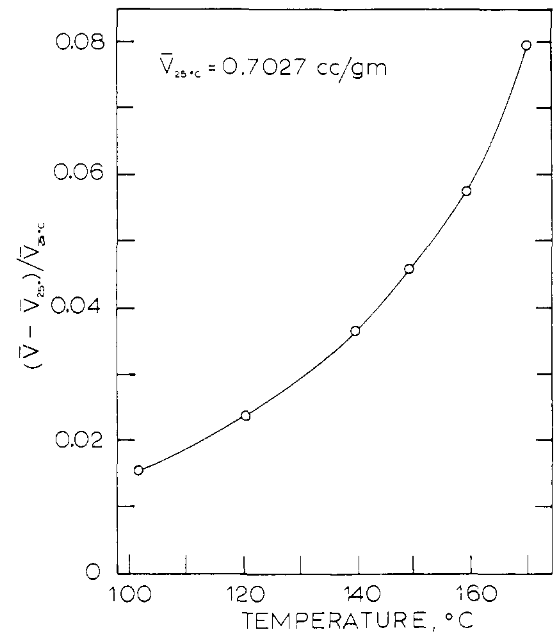

Figure 2. Fractional increase of volume of Delrin 500 with temperature. Specific volume of melt at 190° is 0.835 cc/g.

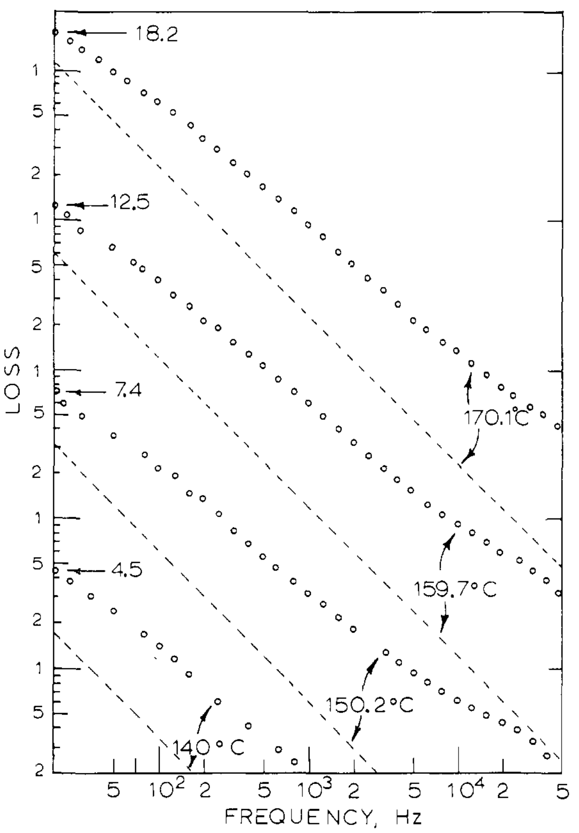

Figure 3. Dielectric loss factor of Delrin 500 at various temperatures plotted logarithmically *vs.* frequency (open circles). Abscissas are shifted for each temperature for clarity. See the indicated values for location of scale. Dashed lines are the contribution to the loss from the measured dc resistance of the sample (see eq 3).

engths but not diameters were undersized to provide for expansion. In the bridge measurements, the solid sample had a free surface but extended past the metal center rod and on to the glass rod. Thus, the results were not sensitive to length and measurements at several temperatures could be made on one sample. In the slotted line, measurements on solids were made with the sample interfaced with the short circuit plane but with a free surface on the other end. The sample length and distance to the node determination required a knowledge of the thermal expansion and the original volume. The melts for both bridge and slotted line measurements had to be confined to prevent bubble formation. The amount of material required to exactly fill the cell to the "Teflon" washer at a given temperature was used. Each temperature required separate filling. The necessary thermal expansion data were measured with a cylinder and piston arrangement and are shown in Figure 2.

Polyoxymethylene is relatively unstable to oxidative decomposition but when rapid heat up and a nitrogen-purged (bridge measurements) or sealed nitrogen-filled (slotted line) cell is used adequate time for accurate reproducible measurements up to 230° is available. When decomposition does occur it produces a rapid irreversible rise in dielectric constant and on cool down is accompanied by visual yellowing or browning and bubble formation. In a normal run the sample is unchanged after cool down except for voids produced by shrinkage. The upper temperature limit of the slotted line measurements (206°) was the mechanical stability with the melt interfaced against it of the "Teflon" washer, which must also be designed for low electrical reflection. A dielectric constant at 230° was obtained with the slotted line at 400 MHz using a heavier gasket but useful loss data could not be obtained due to reflection.

Du Pont "Delrin 500" and Celanese "Celcon U 10-01" (melt index 1.0) were used for samples. Based on melt index the "Celcon" molecular weight should be roughly twice that of the "Delrin."

Results and Discussion

Arisawa, *et al.*,[4] found that there is a considerable conductivity loss which obscures the low frequency portion of the loss spectrum of "Delrin." However, they believed that it conformed to a simple dc mechanism and that plots of log ϵ'' *vs.* log frequency give straight lines of unit slope at low frequency ($<\sim$100 Hz). Changes in slope of these plots at slightly higher frequency were interpreted as a relaxation peak (the α peak) that was resolved by subtraction of the dc loss. We have confirmed this behavior in the temperature region of their study (up to 147°) in both "Delrin" and "Celcon" although the dc loss is considerably higher in molten "Celcon." However, we are reluctant to ascribe much singificance to this treatment of the data. In particular we have found that the loss curve calculated from the measured dc conductivity through the relationship

$$\epsilon'' = \frac{1}{\omega R C_0} \tag{3}$$

where R is the sample dc resistance and C_0 the empty cell capacitance, does not represent a reasonable asymptote for the measured loss curves to be interpreted in terms of a superimposed dipole relaxation. Figure 3 shows measured loss data compared with the loss calculated from the measured dc conductivity. Figure 4 shows dielectric constant data under the same conditions. It is seen that the calculated loss lies well below the measured loss and a dipole peak would not result from subtraction of the dashed curves. Although electrode polarization effects could possibly

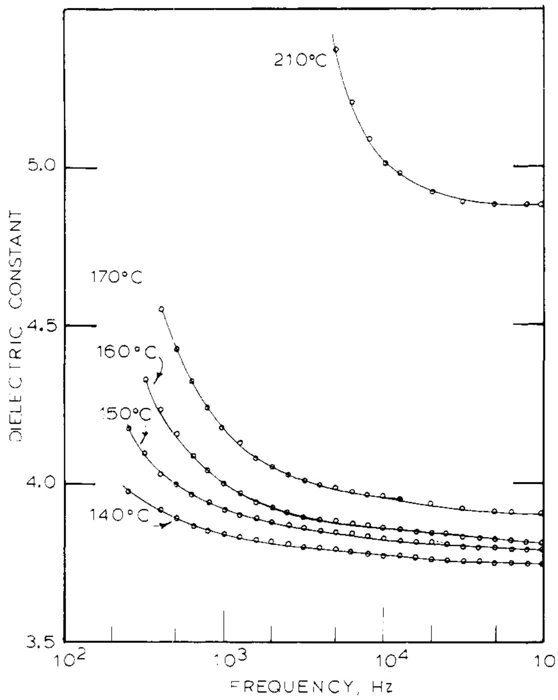

Figure 4. Dielectric constant of Delrin 500 at various temperatures at low frequency.

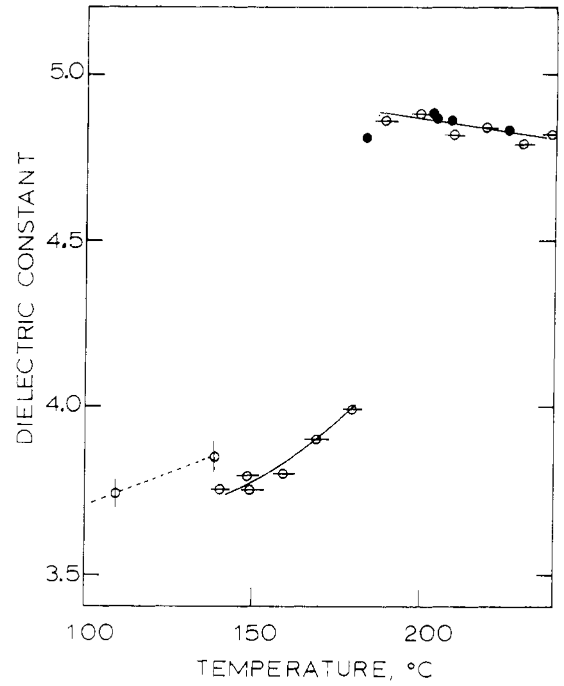

Figure 5. Dielectric constant of Delrin 500 at 100 KHz (⊖) and $\sim$0.5 GHz (●) *vs.* temperature. 100 KHz points are to be regarded as the static dielectric constant. Data of Read and Williams (ref 6) for static dielectric constant (ϕ) are included for comparison.

obviate the legitimacy of using the measured dc resistance we take the view that it is not possible to extract an α dipole relaxation peak from the data. It would appear that ionic conductance (presumably due to additives and impurities) need not conform to a simple parallel resistor and capacitor model.

Turning now to the nature of the dipolar relaxation loss in the melt we first point out that there is no such loss up to high frequencies, *i.e.*, the high MHz region. First of all, the dielectric constant (Figure 4) is invariant to frequency in the bridge measurements from 10 KHz to 5 MHz, indicating no relaxation loss in this region. Further, as seen in Figure 5 the dielectric constant measured at 100 KHz agrees well with that measured in the slotted line at 400–500 MHz. The excellent agreement indicates both the absence of loss in the intermediate frequencies and the consistency of the experiments. We regard it as very unlikely that there would be dielectrically active dipolar loss in the melt at the temperatures involved at frequencies below 10 KHz. The upturn in ϵ' and the loss below 10 KHz are very similar to the behavior of the solid except that the melt is even more conductive. Thus, we may turn our attention to the loss measured in the slotted line in the GHz region. The melts show (Figures 6 and 7) a dispersion region centered at $\sim$4 GHz that is independent of temperature over the limited temperature range we were able to measure it. It is also essentially the same in "Delrin" and "Celcon." Since the molecular weights differ by approximately a factor of 2 it is apparently not sensitive to molecular weight. Cole–Cole plots[7] (Figure 8) show that it is characterized by a single relaxation time. It is apparent that there is another stronger relaxation region or regions beyond the frequency range measured. This is evidenced by the fact that the dielectric constant at the upper frequency side of the above region ($\sim$4.1, Figure 8) is still considerably higher than the high frequency limit, ϵ_∞, expected for dipole relaxation. A good estimate of the latter can be made from ϵ_∞ measured at high frequency at room temperature on the solid and assuming it to be directly proportional

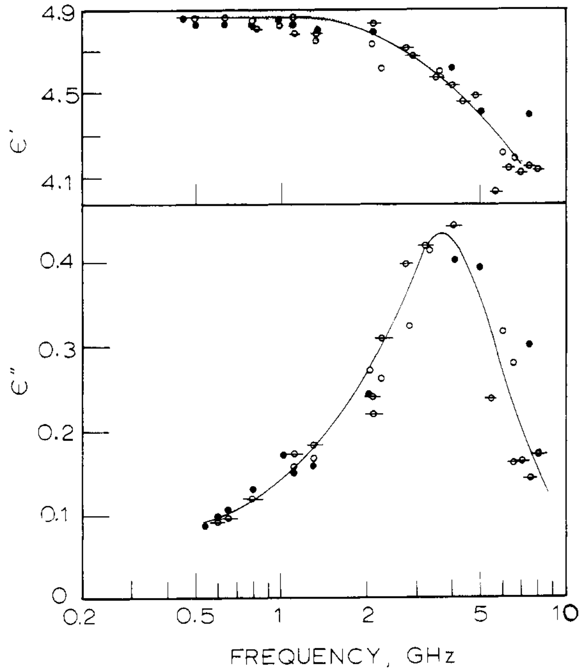

Figure 6. Dielectric constant and loss factor of polyoxymethylene in the melt *vs.* frequency. Celcon U 10-01, 192.0°, ●; Delrin 500, 191.2°, ⊖; Delrin 500, 193.0°, ○.

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(7) R. H. Cole and K. S. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

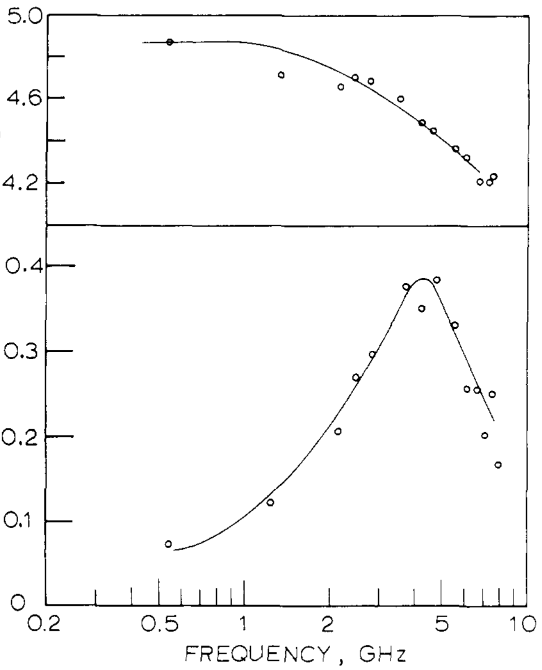

Figure 7. Dielectric constant and loss factor of Celcon U 10-01 in the melt at 206.8°.

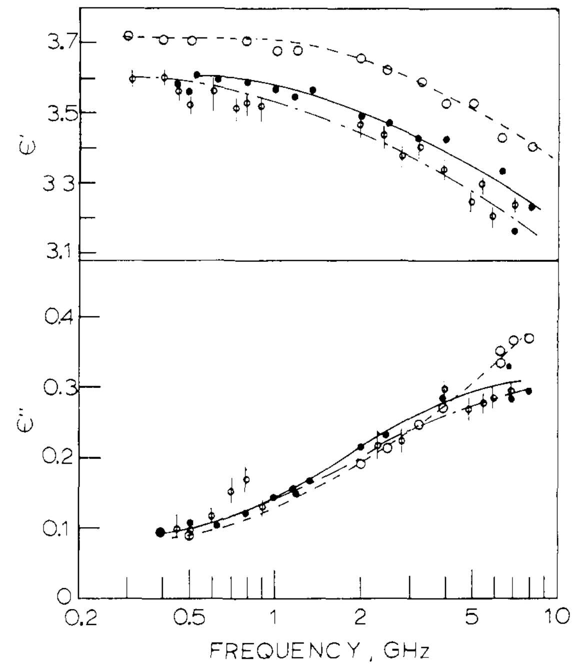

Figure 9. Dielectric constant and loss of Delrin 500 in the solid at three temperatures (ɸ, 142.5°; ●, 151.5°; O, 165.8°) *vs.* frequency.

to density. At 23° we have measured ϵ_∞ to be 2.70 (compared to a value of 2.87 reported by Read and Williams[5]). From the melt density measured here of 1.200 g/cm^3 at 190°, compared to 1.423 at room temperature, we infer ϵ_∞ at 190° to be equal to 2.27. Thus, further relaxation of strength $\Delta\epsilon = \sim 1.8$ may be expected above 8 GHz.

We may now compare the relaxation in the melt with that in the solid. Figure 9 shows our loss data for the solid at three high temperatures below the melting region (165–180°). Our data are in reasonable agreement with those of Read and Williams.[5] Cole–Cole plots of these data are shown in Figure 10. High frequency ϵ_∞ values in the plots were derived from the room temperature value above and the assumption of proportionality to the density (Figure 2). Values of ν_{max} were derived from the Cole–Cole plots assuming them to be semicircular over the entire absorption region. It is apparent that there is a definite discontinuity in the loss behavior on melting. What appears to be a single loss region in the solid[5] and whose center moves above 8 GHz at higher temperatures becomes two regions in the melt. Figure 11 summarizes the effect of temperature on the position of maximum absorption. One of the latter two regions is at lower frequency than the single region in the solid. It is also apparent in Figure 5 that there is a discontinuity in the low frequency (static) dielectric constant on

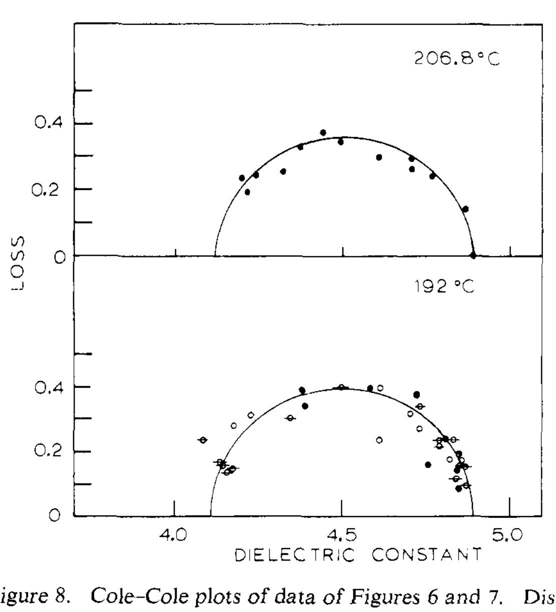

Figure 8. Cole–Cole plots of data of Figures 6 and 7. Distribution parameter, β = 1.00 for both plots.

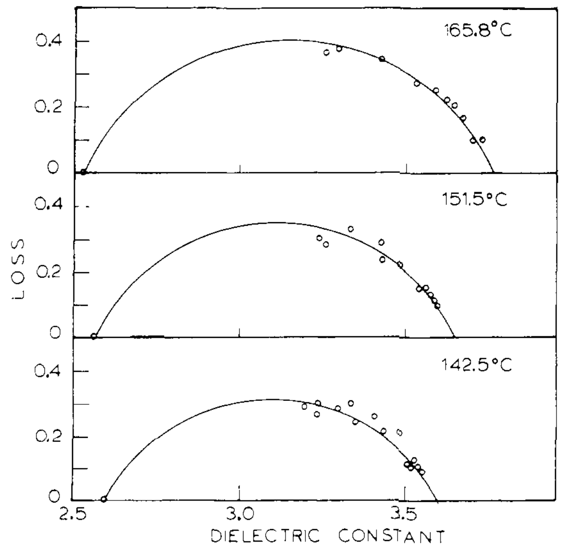

Figure 10. Cole–Cole plots of data of Figure 9. Distribution parameter, β and ν_{max} = 0.71, 10.4 GHz, 142.5°; 0.75, 12.7 GHz, 151.5°; 0.73, 11.5 GHz, 165.8°.

melting. It is interesting to note that the strength of the newly appearing lower frequency loss region in the melt ($\Delta\epsilon = \sim 0.8$, Figure 8) is no greater than, and, in fact, somewhat less than, the discontinuity in $\epsilon_s - \epsilon_\infty$ upon melting. Thus, one interpretation might be that the γ region in the solid moves abruptly to higher frequency upon melting and a new (α) mechanism appears at somewhat lower frequency. It is perhaps appropriate to regard molten polyoxymethylene as similar to an amorphous polymer and to compare its loss with that in such polymers at high temperatures. Most linear amorphous polymers without flexible side groups do show two loss regions. These regions tend to become sharper, closer together, and have lower activation energy as the temperature is increased. These features would be similar to the loss in molten polyoxymethylene. The α region is usually stronger than the β region which is the reverse of the behavior found here. Regardless of the interpretation, it is apparent from the effect of melting that the molecular motion does depend sensitively on the solid structure. The α peak in the melt presumably has little relation molecularly to the α peak observed in the solid mechanically[5] (90°, ~0.1 Hz). The latter would appear to extrapolate to the melt temperature at about 10^2 Hz. The γ peak in the solid also undergoes a discontinuous shift to higher frequency upon melting (entirely beyond 8 GHz). It also increases in strength (from $\Delta\epsilon = \sim 1.2$ at 165°, Figure 10, to ~1.8, at 190°, see above) with melting. Thus, the short-range rearrangements believed to be responsible for regions of this type[8] are sensitive to the local environment. To our knowledge, the present work represents the first useful study of the relaxation of a crystalline polymer in the melt. We are confident that this type of experiment can be extended to other crystalline polymers and that information useful in formulating a model for the relaxation in solids will result.

Finally, we wish to show on theoretical grounds that the 100-KHz dielectric constant is consistent with being interpreted as the static dielectric constant in the molten polymer by making a statistical mechanical calculation of the static dielectric constant. The details are given in the Appendix and below is a table comparing the calculated and 100 KHz dielectric constants in the melt region. It can be seen that the agreement is very satisfactory, perhaps in view of the approximate nature of the calculation, fortuitously so. The calculated values are of the right magnitude and temperature dependence. It is perhaps worthy of comment that the calculated factor, f, in eq 5 is far from the value for free rotation (see Table I). The value of f is 0.5 in the latter case so that the $g^+(g^-)$ interference and preferential population of *gauche* over *trans* states would appear to be real effects in polyoxymethylene melts. The success of the present calculation would also imply that the γ transition is better interpreted in terms of rotational rearrangements than the local torsional mode model.[8] We defer a discussion of the effects of changes in the parameters used until a study of the dipole moments of model polyoxymethylene dimethyl ethers now in progress is completed.

TABLE I
COMPARISON OF CALCULATED AND EXPERIMENTAL STATIC DIELECTRIC CONSTANTS OF MOLTEN POLYOXYMETHYLENE

t	f^b (calcd)	ϵ_s (calcd)	ϵ_s (exptl)
175[a]	0.1762	4.79	4.90
200	0.1934	4.70	4.86
225	0.2101	4.60	4.82
250	0.2262	4.49	4.78

[a] Final melting temperature = 180° for polyoxymethylene.
[b] See eq 5 of text.

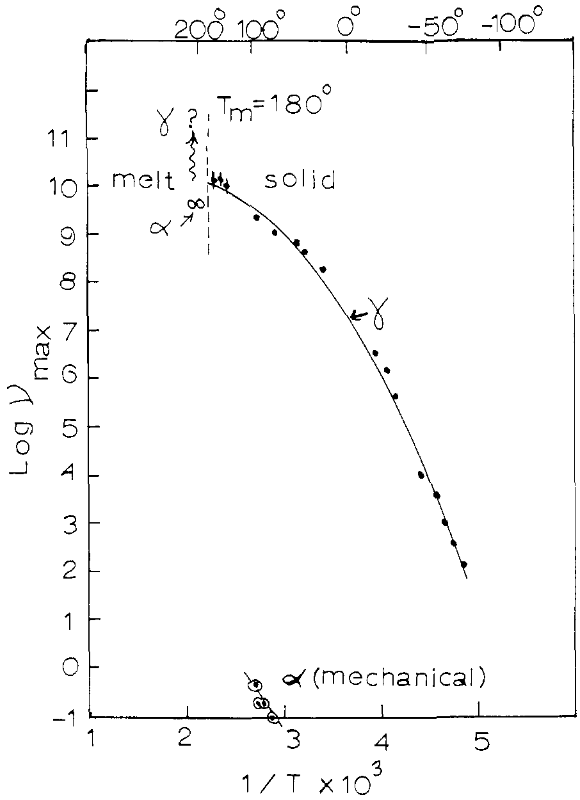

Figure 11. Plot of $\nu_{\max}$ *vs.* 1/T: ●, dielectric data of Read and Williams (ref 6); ⧳, ○, present work; ⊙, mechanical G'' data of Read and Williams (ref 5).

Acknowledgment. The authors are pleased to acknowledge the financial support of the National Science Foundation. C. H. P. was the recipient of a National Defense Educational Act Fellowship and J. H. L. L. was the holder of a National Aeronautics and Space Administration Fellowship during part of this research.

Appendix

The Calculation of the Static Dielectric Constant of Molten Polyoxymethylene. The Kirkwood–Fröhlich equation[9, 10] was assumed to apply to individual polymer molecules as

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(8) Reference 3, Chapter 5.5.

(9) J. G. Kirkwood, *J. Chem. Phys.*, 7, 911 (1939).

(10) H. Frölich, "Theory of Dielectrics," 2nd ed, Oxford University Press, Oxford, 1958.

$$\epsilon_s - \epsilon_\infty = \left[\frac{3\epsilon_s}{2\epsilon_s + \epsilon_\infty}\right]\left[\frac{\epsilon_\infty + 2}{3}\right]^2 \frac{4\pi\bar{N}}{3RT}\langle\mu^2\rangle \qquad (4)$$

where ϵ_s and ϵ_∞ are the static and high frequency dielectric constants and $\bar{N}$ is the number of molecules per cubic centimeter. The average square molecular dipole moment, $\langle\mu^2\rangle$, can be decomposed for a high molecular weight polymer into

$$f = \langle\mu^2\rangle/(n\mu_0^2) = 1 + \frac{2}{n}\sum_{j=1}^{n}(n - j)\langle\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_{1+j}\rangle/\mu_0^2 \qquad (5)$$

where μ_0 is the chain bond moment, n is the number of chain dipoles per molecule, and $\boldsymbol{\mu}_i$ is a chain dipole vector. For a model of polyoxymethylene in which the C–O bonds are individually assigned moments, the molecular dipole moment is then made up of alternating bond moments along the chain bonds. The evaluation of the right-hand side of eq 5 is then very similar to the evaluation of the average square radius of a polymer chain. For our alternating dipole case, a formula due to Lifson[11] may be modified by changes in sign to read

$$\mu^2/(n\mu_0^2) = 1 - 2\mathbf{a}_3(\mathbf{T}^* + \mathbf{U}/\lambda)^{-1}\mathbf{a}_3^* \qquad (6)$$

where $\mathbf{T}^*$ is the transpose of the 9 × 9 bond transformation matrix and $\mathbf{U}$ is the 9 × 9 statistical weight matrix both as defined by Lifson.[11] The $\mathbf{a}_3$ and $\mathbf{a}_3^*$ matrices are nine element row and column matrices with zero elements except for the last three positions which contain the eigenvectors of the largest eigenvalue, λ, of the 3 × 3 statistical weight matrix

$$U = \begin{bmatrix} g^+(g^+) & g^+(T) & g^-(g^-) \\ T(g^-) & T(T) & T(g^-) \\ g^-(g^+) & g^-(T) & g^-(g^-) \end{bmatrix} \qquad (7)$$

where $g^-(g^+)$, $T(g^+)$, etc., indicate the Boltzmann factors assigned to pair sequences of bond conformations, $g^+(g^+)$ = *gauche* conformation (followed by *gauche* of the same sense), $T(g^+)$ = *trans* conformation (followed by *gauche*), etc. We have assigned the following values[12] to these elements

$$g^+(g^+) = g^-(g^-) = g^-(T) = g^-(T) = 1$$

$$g^+(g^-) = g^-(g^+) = 0$$

$$T(g^+) = T(T) = T(g^-) = T = \exp(-\epsilon/kT)$$

$$\epsilon = 1740 \text{ cal/mol}^{13}$$

The largest eigenvalue is given by

$$\lambda = ((T + 1) + \sqrt{(T + 1)^2 + 4T})/2 \qquad (8)$$

and its eigenvector by

$$a = (1, \lambda - 1, 1)/\sqrt{2 + (\lambda - 1)^2} \qquad (9)$$

In computing the elements of T we have used ϕ = 77° for the *gauche* state[14] and ϕ = 180° for the *trans*. The bond angle was taken to be the same[14] for O–C–O and C–O–C as 109.5°. Values of ϵ_∞ = 2.27 at 190° with a temperature coefficient of −1% per 10° and melt density of 1.20 g/cm^3 at 190° with a temperature coefficient of −1% per 10° temperature were used. The value of the C–O bond moment in polyoxymethylene was taken from the work of Uchida, *et al.*,[14] as 1.31 D.

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[11] S. Lifson, *J. Chem. Phys.*, **30**, 964 (1959).

[12] H. Starkweather and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).

[13] T. Uchida, Y. Kurita, and M. Kubo, *J. Polym. Sci.*, **19**, 365 (1956).

[14] E. Sauter, *Z. Phys. Chem.*, **21B**, 186 (1933).

Absorption Spectroscopy of Irradiated Poly(vinyl chloride)

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ABSTRACT: Radiolysis of poly(vinyl chloride) (PVC) was studied by ultraviolet and visible spectroscopy following post-irradiation storage at selected temperatures in a cryostatic cell. A sequence of alkyl, allyl, and polyenyl radicals followed by chain transfer to PVC leads to polyene formation. Allyl, dienyl, and trienyl radicals were associated with absorption bands at 2520, 2910, and 3300 Å, respectively. Radical intermediates react readily with oxygen.

A study of the irradiation behavior of poly(vinyl chloride) (PVC) is of importance in elucidating the effects of ionizing radiation, the properties of irradiated PVC, and the relation between radiolytic and thermal stability. Unlike most polymers in which either cross-linking or chain scission predominates following energetic irradiation, the major reaction in PVC is dehydrochlorination.[2] Color formation associated with long sequences of conjugated unsaturation (polyenes) ensues.[3] In order to determine radiation behavior intrinsic to pure PVC, incipient changes must be studied.[4a] Fortunately, sensitive thermogravimetric[4b]

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[2] A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).

[3] G. J. Atchison, *J. Appl. Polym. Sci.*, **7**, 1471 (1963).

[4] (a) R. Salovey, H. E. Bair, and J. P. Luongo, *Polym. Lett.*, 7, 241 (1969); (b) R. Salovey and H. E. Bair, *J. Appl. Polym. Sci.*, in press.