A Dielectric Study of the Effects of Melting on Molecular Relaxation in Poly(ethylene oxide) and Polyoxymethylene

Christopher H. Porter and Richard H. Boyd*

Department of Chemical Engineering and Division of Material Science and Engineering, University of Utah, Salt Lake City, Utah 84412.
Received April 22, 1971

ABSTRACT: The effect of melting on dielectric relaxation in poly(ethylene oxide) (PEO) and polyoxymethylene (POM) has been studied. The β relaxation region in PEO and the γ relaxation region in POM, which have been believed to be "amorphous" loss peaks, go continuously into the melt with respect to the location of the loss region ($f_{\max}$) and the width of the dispersion region. The strengths of the relaxations ($\epsilon_R - \epsilon_u$) are discontinuous on melting and roughly in proportion to the amount of amorphous material present. The above results are consistent with a model for the crystalline solid where the relaxations take place in discrete amorphous regions similar to the melt. A study of the dielectric properties at low frequency of PEO was not able to discern an α region. It is pointed out that in "lossy" materials at high frequency a previously unrecognized type of solution to the slotted-line equation can appear. In a previous study of dielectric loss in POM, the melt results at high frequencies (>4 GHz) are in error owing to neglect of this "extra" solution and have been redetermined in the present work.

In a previous study[1] we pointed out the possibility that by contrasting the relaxation behavior of a crystalline polymer with that of its melt one might gain valuable insight into the effects of crystalline order on relaxations. In order to accomplish this experimentally, measurements at high frequencies are necessary owing to the high temperatures implied by the melt. We thus undertook the study of the relaxations of a simple linear crystalline polar polymer, polyoxymethylene (POM), at high temperatures, both in the solid and in the melt, by the dielectric method, where frequencies into the gigahertz region are available. The purpose of the present study was to use this technique to determine the effect of melting on poly(ethylene oxide). In the course of the present work it was found that, for reasons discussed in the Experimental Section and in Results and Discussion, our previous results[1] for molten POM at high frequencies (>4 GHz) were in error. The present work, therefore, also presents a redetermination of the melt data for polyoxymethylene (POM).

A brief review of the relaxation behavior of PEO and POM in the solid is in order here. The relaxations in PEO are molecular weight dependent, presumably through the resultant degree of crystallinity. High molecular weight (2.8×10^6) PEO shows mechanically[2] α, β, and γ transitions. In intermediate and low molecular weight samples the α and β processes merge. Dielectrically, the β and γ transitions are active.[2,3] It has also been proposed that the α transition is observable dielectrically,[4] although this is dubious owing to a high loss contribution from some conductance or interfacial polarization mechanism at low frequency. From the variations of crystallinity in samples of varying molecular weight, Connor, *et al.*,[2] assigned the resolved (in high molecular weight samples) α region to a crystal-disordering mechanism and the β region as an amorphous peak. The merged peaks (in intermediate and low molecular weight samples) were considered to be a combination of crystalline and amorphous processes. The dielectric β peak was assigned as an amorphous peak in all samples. Ishida, *et al.*,[3] studied single-crystal mats of PEO dielectrically and also assigned the β region as an amorphous peak and found that the γ region was still present in single crystals. From the temperature dependence of the γ peak,[5] it is probable that it merges with the β peak at high temperatures. POM shows α, β, and γ peaks mechanically, and β and γ dielectrically.[5] The α peak is apparently a crystal-disordering transition, the β peak is weak and possibly due to segmental chain reorientation in amorphous material, and the γ peak is apparently an amorphous transition, probably involving shorter segments than the β peak.

Experimental Section

Measurements were taken over two frequency ranges, one ranging from 20 to 10^5 Hz and the other from 3×10^8 to 8×10^9 Hz. The equipment used for the low-frequency range included a General Radio Model 1615A capacitance bridge, a G.R. 1232A null detector, and a G.R. 1310 oscillator. The experimental technique used is similar to that described elsewhere,[1] with the exception that the low-frequency sample cell was jacketed and heated using circulated ethylene glycol. This allowed temperatures to be known accurately to 0.1° and controlled to 0.05°.

The high-frequency techniques were similar to those described earlier.[1] However, a number of refinements were made which permit more accurate determination of the dielectric constant and loss on polymeric melts using the slotted line in the microwave region. In addition, it was found that solutions to the slotted-line equation can exist in addition to the multiple solutions possible due to the possibility of having any number of half-wavelengths in the sample. The latter are well known in the Roberts–von Hippel method.[6] There can exist, however, another solution or solutions in addition to those suggested by the periodic nature of the slotted-line equation. These are encountered when dealing with materials with relatively high dissipation factors (in excess of ~0.1) and above ~1 GHz. These "high-loss" solutions were found to be the physically appropriate ones in a number of cases. The existence

---

[1] C. H. Porter, J. H. L. Lawler, and R. H. Boyd, *Macromolecules*, **3**, 308 (1970).

[2] T. M. Connor, B. E. Read, and E. Williams, *J. Appl. Chem.*, **14**, 74 (1964).

[3] Y. Ishida, M. Matsuo, and M. Takayanagi, *J. Polym. Sci., Part B*, **3**, 321 (1965).

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

[5] N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, N. Y., 1967.

[6] A. von Hippel, Ed., "Dielectric Materials and Applications," Technology Press, MIT, and Wiley, New York, N. Y., 1954.

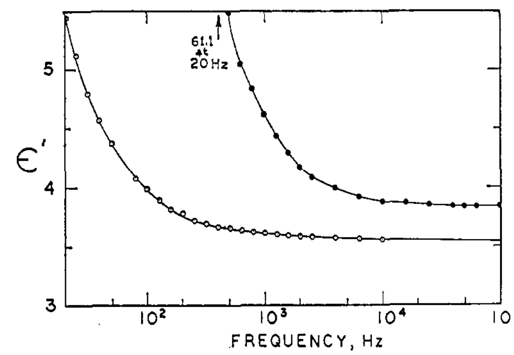

Figure 1. Dielectric constant of PEO (Carbowax 20M) as a function of frequency at 23.4° (○) and at 53.0° (●).

of the high-dissipation-factor solution does not appear to have been previously recognized in the literature on the slotted line. A more extended consideration of this point and a detailed description of the overall measurement system will appear in a separate work.[7]

The effect of temperature on unrelaxed (high frequency) dielectric constants was represented by the Clausius–Mosotti formula[8]

$$\frac{\epsilon_u'(T) - 1}{\epsilon_u'(T) + 2} = \frac{A}{1 + \dfrac{\bar{V}_T - \bar{V}_{25°}}{\bar{V}_{25°}}} \qquad (1)$$

where $A = (\epsilon_{25°}' - 1)/(\epsilon_{25°}' + 2)$ and $\bar{V}_T$ is the specific volume.

Two materials were studied in this work, polyoxymethylene (POM) and poly(ethylene oxide) (PEO). The samples used in the POM studies were machined from Du Pont "Delrin 500" and Celanese "Celcon U 10-01." Based on melt index, the molecular weight of the Celcon was twice that of the Delrin. The PEO used was Union Carbide "Carbowax 20M" poly(ethylene glycol). This material was made into rod form by melting the flake in cylindrical molds under vacuum (0.5 mm) and at 90° until all voids disappeared. The material was then either slowly cooled at a rate of 5°/hr or rapidly cooled by placing the polymer-containing molds in ice water. Attempts at cooling the material more rapidly than the ice water method resulted in the rods cracking in the molds, rendering them useless for high-frequency work. The density of the rapidly cooled PEO was found to be 0.826 g/cm³ at 25°. Using values for crystalline and amorphous PEO reported by Simon and Rutherford,[9] this density predicts an 80% degree of crystallinity.

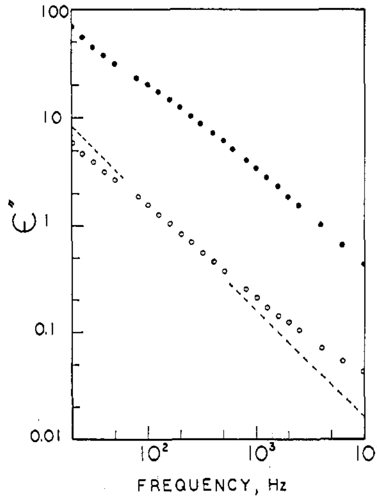

Figure 2. Dielectric loss of PEO (Carbowax 20M) as a function of frequency at 23.4 (○) and 53.0° (●). Dashed line is the contribution to the loss of 53.0° (upper curve) calculated from the measured dc resistance.

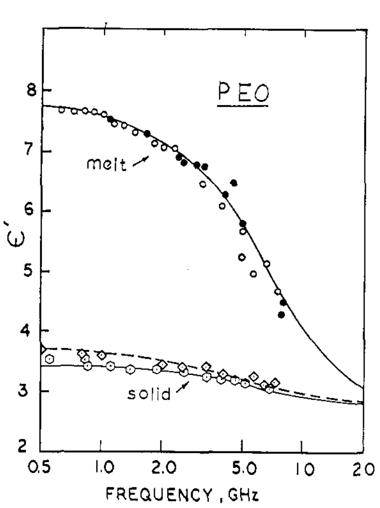

Figure 3. Dielectric constant of PEO (Carbowax 20M): molten at 65.7° (○, ●); rapidly quenched crystalline (~80%) solid (◇); slowly cooled crystalline (80%+) solid (○).

Representative samples of PEO were measured for dc conductivity using a Keithly Electrometer in a three-terminal cell. These samples were then zone refined for about 2 days and the dc conductivity was measured again. No significant change was noted in the measured values, which indicated that there were no easily removable ionic impurities in the sample. The samples used to obtain dielectric data were not zone refined prior to use. However, the low-frequency conductivity losses of our samples were more than an order of magnitude lower than those found by Arisawa, *et al.*[4]

Results and Discussion

Poly(ethylene oxide) (PEO). (1) Low-Frequency Loss Behavior. Arisawa, *et al.*,[4] found that at low frequencies a plot of log ε'' *vs.* log *f* approached a straight line with slope −1. They believed that this behavior was due to a simple conduction mechanism and that the line with slope −1 represented a loss due to the dc resistance

$$\epsilon'' = 1/(\omega R_{dc} C_0) \qquad (2)$$

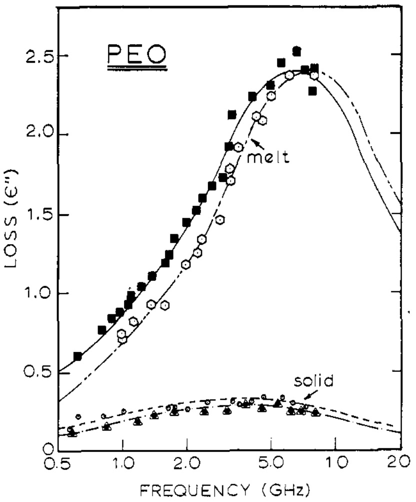

Figure 4. Dielectric loss of PEO (Carbowax 20M): molten at 65.7° (■); molten at 75.2° (○); rapidly quenched crystalline (80%) solid (○); slowly cooled crystalline (80%+) solid (△).

---

[7] C. H. Porter and R. H. Boyd, in "Dielectric Properties of Polymers," F. E. Karasz, Ed., Plenum Press, New York, N. Y., in press.

[8] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955.

[9] F. T. Simon and J. M. Rutherford, Jr., *J. Appl. Phys.*, **35**, 82 (1964).

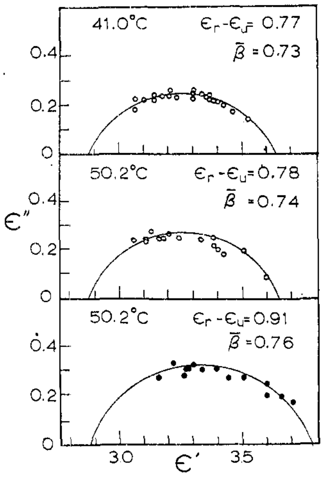

Figure 5. Cole–Cole plots of data obtained on two solid samples of Carbowax 20M with differing thermal pretreatments; slowly cooled (○) and rapidly quenched (●).

This dc loss was then subtracted from the total loss, resulting in a resolved loss which resembled a loss peak. This peak had a relaxation strength, found by integrating the loss with respect to frequency, of 3.5 and maximum at 200 Hz at 15°. From the location of this peak, they concluded that this corresponded to the α mechanism found in mechanical studies on solid PEO and hence labeled it the α dielectric dispersion.

Our data, illustrated in Figures 1 and 2, are similar in form to those of Arisawa, *et al.*;[4] however, our loss factors are considerably lower than those reported by them. They report a loss factor of 2.3 at 1000 Hz at 15°, which is an order of magnitude higher than the loss we found at 25° at the same frequency. Although our data are similar in form, we do not believe that the low-frequency loss behavior can be interpreted in terms of a simple conductivity mechanism represented by a parallel resistor of constant value. The model in addition to eq 2 predicts a dielectric constant that is independent of frequency. In contrast, we found an enormous increase in dielectric constant at low frequency (61 at 20 Hz, 50°; see Figure 1). This increase is much too large to be ascribed to a dipole-orientation dispersion. Furthermore, we find that directly measured values of R_{dc} (by a technique previously described[1]) used in eq 2 do not represent the measured loss. Figure 2 shows this comparison. In view of the failure of the low-frequency loss to conform to a simple conduction model, we feel that it is not legitimate to try to extract an unresolved dipole orientation loss peak from it. Furthermore, although our losses are more than an order of magnitude lower than those reported in ref 4, we find no resolved loss peak at low frequency.

In light of the preceding discussion, we take the position that if a low-frequency α dielectric dispersion does exist, then it cannot be resolved from low-frequency loss data. A similar conclusion was made by us previously concerning polyoxymethylene.[1]

(2) Effect of Degree of Crystallinity (Thermal Treatment) in the Solid. High frequency data were obtained on PEO at 31, 41, 50, 66, and 75°. The final melting point of the material studied was 62 ± 1°. Figures 3 and 4 show the data obtained on two samples at 50° (1) a sample which had been rapidly cooled from the melt and (2) a sample which had been slowly cooled from the melt at a rate of 5°/hr. The degree of crystallinity determined from the density crystallinity correlation of ref 9 of the rapidly quenched sample was 80%. Connor, *et al.*,[2] report an X-ray value of 76% for slowly cooled Carbowax 20M. The crystalline content of the slowly cooled material used in this work was unknown, but presumably slightly higher than 80%. Figure 5 contains Cole–Cole[10] plots of the solid data presented in Figures 3 and 4 as well as data taken on a slowly cooled sample at 41°.

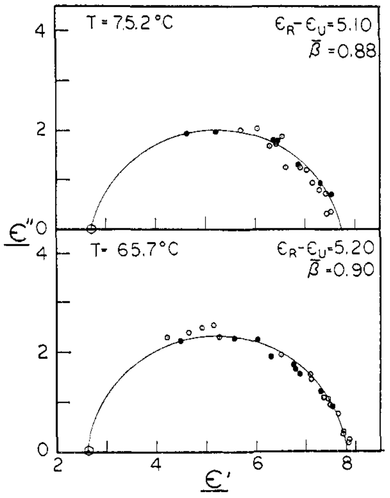

Figure 6. Cole–Cole plots of molten Carbowax 20M at 75.2 and 65.7°.

Comparison of the two 50.2° samples shows that the rapidly cooled sample had a slightly larger relaxation strength than the slowly cooled sample. The distribution of relaxation times, as indicated by $\bar{\beta}$, was apparently unaffected by the differing thermal pretreatment. The high-frequency dielectric constant, ϵ_u, of the indicated dispersion was found to be 2.87 for both the 50.2° runs.

(3) Dielectric Constant and Loss Factor in Molten PEO. Figure 3 compares the dielectric constants as a function of frequency of the solid 50.2° material and molten PEO at 65.7°. Figure 4 shows loss factor data for two temperatures in the melt as compared to the 50.2° solid material. Figure 6 shows Cole–Cole[10] plots of molten PEO. The value of ϵ_u in these plots was calculated from the 50.2° value, 2.87, corrected by eq 1 for a 9% increase in specific volume upon melting. This results in a value of 2.70 for the molten material. The location of ϵ_{max}'' on the frequency axis, f_{max}, of the molten material was calculated from the Cole–Cole[10] parameters and found to be 6.3 GHz for the 65.7° data and 8.0 GHz for the 75.2° data.

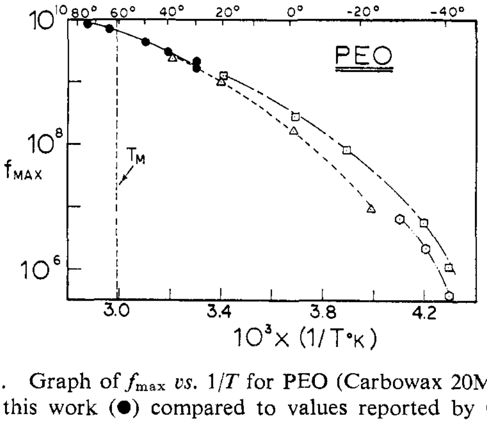

Figure 7. Graph of f_{max} *vs.* $1/T$ for PEO (Carbowax 20M) measured in this work (●) compared to values reported by Connor, *et al.* (ref 2), for Polyox 2464 (△), Polyox FC 118 (□), and Polyox FC 2075 (○).

---

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

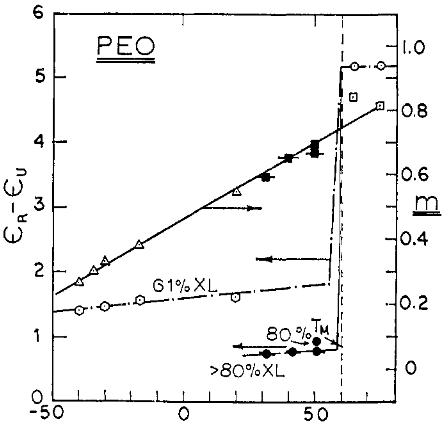

Figure 8. Relaxation strengths and Fuoss-Kirkwood parameter, m, as a function of temperature for PEO (Carbowax 20M) measured in this work for (80%+) crystalline solid (-●-, -■-), rapidly quenched (~80%) crystalline solid (●, ■), molten material (○, □), and for 61% crystalline Polyox FC 118 measured by Connor, *et al.* (ref 2) (○, △).

(4) Effect of Melting on $f_{\max}$ (β Region). Values of $f_{\max}$ *vs.* $1/T$ for the dispersion found in this work are compared to those found by Connor, *et al.*,[2] in Figure 7. From this figure it can be seen that the functional relationship between $f_{\max}$ and $1/T$ is continuous through the melting point. Further, there is good agreement in values between our data and those of Connor, *et al.*,[2] although their data were for a much higher molecular weight polymer than the one studied in this work. The present dispersion region has been previously designated as the β mechanism.[5]

(5) Effect of Melting on Relaxation Strength and Relaxation Width. The effect of melting the polymer is best illustrated in Figure 8. This figure shows the relaxation strengths and the Fuoss-Kirkwood parameters[11]

$$m = 2\epsilon_{\max}''/(\epsilon_R - \epsilon_u) \qquad (3)$$

of the data obtained in this study and the data taken on Polyox FC-118 by Connor, *et al.*[2] The FC-118 sample was reported to have a molecular weight of 2.8×10^6 and have a 61% degree of crystallinity. The Fuoss-Kirkwood m parameter was chosen rather than the Cole-Cole[10] $\bar{\beta}$ since m could be easily calculated from the $\epsilon_{\max}''$ and $\epsilon_R - \epsilon_u$ values from plots in ref 2.

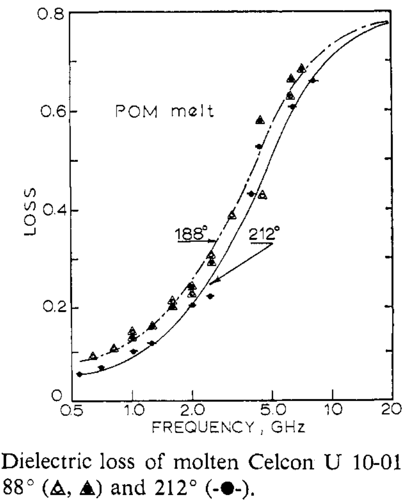

Figure 9. Dielectric loss of molten Celcon U 10-01 at two temperatures, 188° (△, ▲) and 212° (-●-).

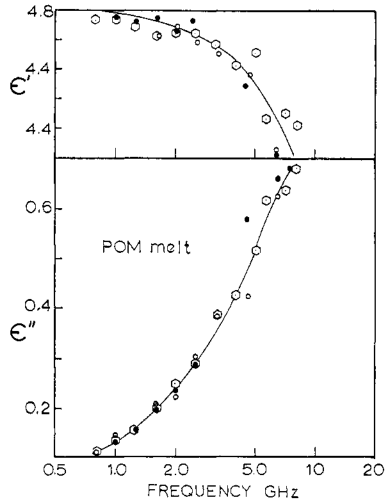

Figure 10. Dielectric constant and loss factor of molten Celcon U 10-01 at 188° (○, ●) and molten Delrin 500 at 192° (○). The molecular weight of the Celcon is twice that of the Delrin.

Inspection of Figure 8 reveals that m is continuous through the melting point, and those values of m obtained from the work of Connor, *et al.*,[2] agree well with those found in this study. It is apparent from Figure 8 that the relaxation strengths ($\epsilon_R - \epsilon_u$) are not continuous functions of temperature through the melting point. The relaxation strength found in the melt, average 5.15, was 6.5 times that predicted by extrapolation of the data of this work for a slowly cooled solid at 65°, and this strength in the melt is 2.6 times that which would be predicted from extrapolation of the data of Connor, *et al.*[2]

An explanation of the behavior exhibited upon melting is that the dispersion is due to motions in the disordered regions of the polymer, the relaxation strength depending upon the amount of disordered material present. This explanation would then imply that the motions in the disordered regions of the semicrystalline polymer are of the same nature as those motions in the melt. This is supported by the fact that the functional relationships between m and temperature and $f_{\max}$ and $1/T$ are continuous through the melting point.

Evidence that the β dispersion arises from the disordered regions can be taken from a number of sources. Ishida, *et al.*,[3] found that the dielectric β peak (which they labeled α) was present in melt-crystallized PEO but disappeared when

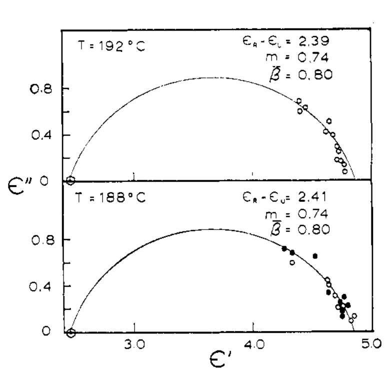

Figure 11. Cole-Cole plots of data in Figure 10.

---

[11] R. M. Fuoss and J. G. Kirkwood, *J. Amer. Chem. Soc.*, 63, 378 (1941).

studying a single-crystal laminate of solution-grown PEO crystals. This would indicate that the observed dispersion in the melt-crystallized material was due to motions in the noncrystalline regions. Connor, *et al.*,[2] studied PEO of varying molecular weights and concluded that the β relaxation was affected by the crystalline content of the polymer, the crystalline content being a function of the molecular weight. It is interesting to note that their data on Polyox FC-118, shown in Figure 8, extrapolate to $\epsilon_R - \epsilon_u = 2.0$ at 65°. If this is divided by the fractional amount of disordered material, 0.39 (Connor, *et al.*,[2] reported a 61% degree of crystallinity), the quotient predicts a relaxation strength of 5.15/(100% disordered material). We found a relaxation strength of 5.20 for molten PEO at that temperature. The rapidly quenched material studied in our work had a relaxation strength of 0.93, which, when divided by the fractional amount of disordered material, 0.20, predicts a relaxation strength of 4.65/(100% disordered material). This agrees fairly well with the 5.20 strength found in the melt, especially in light of the fact that 1% error in the degree of crystallinity causes a 5% error in the predicted relaxation strength.

Polyoxymethylene (POM). On reassessing our previous data[1] on POM, we believe that the reported melt data at frequencies higher than ~4 GHz are in error owing to our not recognizing the existence of the "extra" high-dissipation-factor solution discussed in the Experimental Section. We present here a redetermination of the melt data. Figure 9 shows the loss factor of Celcon at two temperatures and Figure 10 compares dielectric constant and loss factors of molten Celcon and Delrin. In contrast to our previous conclusion, there is no maximum in the loss factor in the frequency range studied and much higher losses and changes in the dielectric constant are observed.

Cole–Cole[10] plots of the 188° Celcon and the 192° Delrin data drawn assuming a *single* dispersion region in the melt are shown in Figure 11. These plots predict relaxation strengths of about 2.40 and β of 0.80 at both temperatures. The high-frequency dielectric constant, ϵ_u, of the molten material was calculated from eq 1. The constant A was determined from the ϵ_u value of the solid at 25°, 2.77. Specific volume data were obtained from our previous work.[1] The value of $f_{\max}$ of the dispersion was calculated using the Cole–Cole[10] parameters and found to be between 20 and 24 GHz at 188° and 28 and 35 at 212°. These values, as a function of $1/T$, are shown in Figure 12 along with values obtained from the solid data, data obtained in our earlier work,[1] and data obtained from Read and Williams.[12] It can be seen from this figure that the functional relationship between $f_{\max}$ and $1/T$ is continuous through the melt. The relaxation strengths and the Fuoss–Kirkwood parameters obtained in this work are compared in Figure 13 to values for the solid obtained in our earlier work[1] and values obtained by Read and Williams.[12] This figure shows that the values from different sources agree well and that the Fuoss–Kirkwood parameter, m, is continuous through the melting point. The relaxation strengths obtained from different sources also agree well. As previously concluded, this strength is discontinuous upon melting. The solid material used in this work and that used in our previous work[1] had a density of about 1.420 g/cm³. This density, using published values of 1.265 g/cm³ for amorphous and 1.502 g/cm³ for crystalline POM,[13] corresponds to a 69% degree of crystallinity. Using this value, the content of disordered material increased from 31% in the solid to 100% in the melt, a 3.2-fold increase, while the relaxation strength increased about 2.4-fold upon melting.

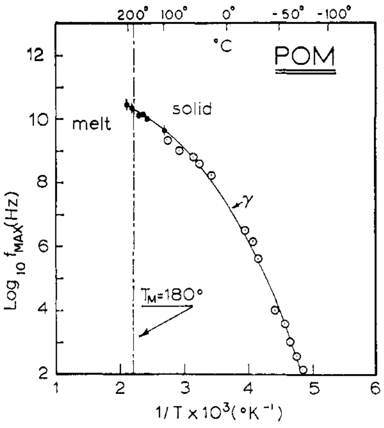

Figure 12. Plot of $f_{\max}$ of POM *vs.* $1/T$: (○) dielectric data of Read and Williams (ref 11), (●) present work, (●) our earlier work (ref 1).

Summary and Conclusions

The PEO β and the POM γ are the principal dielectric relaxations in the solid and appear to be the only loss regions in the melt. In the solid state, both of these loss regions have been previously shown to correlate with measures of crystallinity in the way to be designated as "amorphous" loss peaks. It is therefore very interesting to note that the characteristics of the loss regions that are indicative of the character of the molecular motions involved, namely $f_{\max}$ and the dispersion width parameter, are continuous through the melting regions. This in turn implies that the nature of these amorphous molecular motions is essentially identical with that of the molecular motions in the melt. On the other hand, the strength of the relaxation, which is a measure of the amount of material undergoing similar relaxation processes, is discontinuous on melting and is at least roughly proportional to the amount of amorphous material in an amorphous-crystalline two-phase interpretation of the density–crystallinity correlation. The above observations strongly favor a classical discrete two-phase picture of amorphous and crystalline regions, at least as far as the nature of these relaxations is concerned. In fact, it is very difficult to see how the very large increases in free volume associated with melting could not influence the nature of the relaxation unless

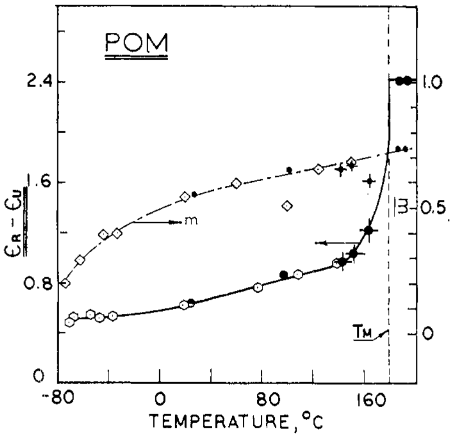

Figure 13. Relaxation strength $\epsilon_R - \epsilon_U$ and Fuoss–Kirkwood width parameter, m, of POM as a function of temperature: (○, ◇) data of Read and Williams (ref 12), (●) present work, (✚) our earlier work (ref 1).

---

(12) B. E. Read and G. Williams, *Polymer*, **2**, 239 (1961).
(13) C. F. Hammer, *J. Appl. Polym. Sci.*, **1**, 169 (1959).

the relaxation in the solid already takes place in discrete regions organized similarly to the melt and whose dimensions are large compared to the molecular correlation dimensions involved in the molecular motions responsible for the relaxation. It should be noted, however, that this result could possibly be appropriate to higher temperatures where the correlation distances involved in the molecular motions may be relatively short. At lower temperatures, it has been observed in some polymers[5] that thermal treatment and, in the case of PEO, crystallinity variations with molecular weight influence the location of the loss regions on the frequency axis as well as its strength. If we identify the discrete amorphous regions as interlammelar material our results show that at higher temperatures the chain lengths involved in the molecular motions are shorter than typical interlamellar chain lengths.

Nomenclature

ϵ'	dielectric constant
ϵ''	dielectric loss
ω	angular frequency
ϵ_R	low-frequency dielectric constant
ϵ_u	high-frequency dielectric constant
m	Fuoss–Kirkwood parameter defined by eq 3
$\bar{\beta}$	Cole–Cole parameter
T	temperature

Acknowledgments. The authors are indebted to the National Science Foundation for financial support of this work. They are also grateful to Professor Carl Durney of the University of Utah for discussions concerning plotting the solutions to complex functions.

Irradiation of Linear Polyethylene. Partitioning between Sol and Gel[1]

A. M. Rijke and L. Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, The Florida State University, Tallahassee, Florida 32306.

Received April 13, 1971

ABSTRACT: Molecular weight fractions of linear polyethylene were irradiated at 133°, in the completely molten and highly crystalline states, for the purposes of assessing the importance of chain-scission processes and establishing the critical conditions for gelation. The partitioning between sol and gel in either state was found to adhere to the theory for the intermolecular cross-linking of monodisperse species for dosages just beyond the gel point. Deviations from theory occurred as the dosage was increased further, but at high dosages the fraction of gel formed was found to be in the range 0.98–1.00. It was concluded that main-chain scission, at these temperatures, is not a significant process. High molecular weight samples, in the completely molten state, obeyed the Flory–Stockmayer condition for critical gelation. However, as the molecular weight was reduced below about 1×10^5, the critical dosage required for gelation systematically became less than that required by theory. These results are attributed to the influence of the vinyl end groups. This postulate is confirmed by the behavior of the hydrogenated samples. The lower molecular weight, highly crystalline samples display still greater deviations from theory. The results for the higher molecular weight crystalline samples are equivocal because of the difficulty of preparing very sharp fractions and maintaining a constant level of crystallinity.

The two major chemical events that can occur when polymers in general and linear polyethylene in particular are subject to the action of high-energy ionizing radiation are gel formation and main-chain scission. Although the radiation chemistry of polyethylene has been extensively studied,[2,3] the relative importance of chain-scission processes has not as yet been established nor has a quantitative analysis of the critical gelation conditions been given. For example, Alexander and Toms[4] and Shumacher[5] have concluded that main-chain scission is negligible. On the other hand, Charlesby and Pinner[6] have reached contrary conclusions. More recently, Kang, Saitô, and Dole[7] have also concluded that chain scission is a major consequence of irradiation. There are several important and fundamental reasons for the difficulties and contrary conclusions that have been reached. Foremost among these is the fact that all the investigations reported heretofore have been conducted with unfractionated polymers. The most commonly studied unfractionated linear polyethylene samples are notorious in possessing very broad molecular weight distributions. On the other hand, all the theories utilized in analyzing the experimental data, including the more sophisticated ones, require a very precise analytical specification of the molecular weight distribution.[6,8–10] This, of course, cannot be provided, and various approximations have to be invoked. Alternatively, if a careful study is made of the limiting gel fraction that is obtained at high irradiation dose, an assessment can be made of the relative importance of chain scission. Unfortunately, since the usual materials studied possess a relatively low ratio of number- to weight-average molecular weight, this necessitates high irradiation dosages and an inherent difficulty in establishing the asymptotic limit. These difficulties can obviously be alleviated by studying molecular weight fractions.

---

(1) This work was supported by the National Aeronautics and Space Administration under Research Grant No. NSG-247-62 to Florida State University.

(2) A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience, New York, N. Y., 1962.

(3) M. Dole in "Crystalline Olefin Polymers Part I," R. A. V. Raff and K. W. Doak, Ed., Interscience, New York, N. Y., 1965, Chapter 16.

(4) P. Alexander and D. Toms, *J. Polym. Sci.*, **22**, 343 (1956).

(5) K. Schumacher, *Kolloid-Z. Z. Polym.*, **157**, 16 (1958).

(6) A. Charlesby and S. H. Pinner, *Proc. Roy. Soc., Ser. A*, **249**, 367 (1959).

(7) H. Y. Kang, O. Saitô, and M. Dole, *J. Amer. Chem. Soc.*, **89**, 1980 (1967).

(8) P. J. Flory, *ibid.*, **63**, 3096 (1941).

(9) M. Inokuti, *J. Chem. Phys.*, **38**, 2999 (1963).

(10) O. Saitô, H. Y. Kang, and M. Dole, *ibid.*, **46**, 3607 (1967).