# A Modified Method of Reduced Variables for Stress Relaxation

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## INTRODUCTION

In a previous paper[1] it has been shown that the stress relaxation curve of a viscoelastic material can be quantitatively interpreted using a generalized Maxwell model with multiple box distribution of relaxation times. By treating the individual stress relaxation curves at various temperatures separately, the preliminary calculations indicated that there are likely two types of mechanisms involved and that temperature has the same effect on the mechanisms of the same type. These observations not only partly verified the basic assumption of the time-temperature principle or the method of reduced variables but also suggested a modification of these methods.

The preliminary calculations were carried out on the published curves[2] of reduced size. The low precision in the data extracted, combined with the narrow time range covered in the experiment, caused some scattering of the resulting parameters. It was, therefore, of interest to make more precise calculations by applying the suggested modification to the original data recently furnished to us through the kindness of Prof. A. V. Tobolsky. In this way, we expected to obtain a set of parameters of higher precision characterizing the polymer and to test whether the modified method can actually eliminate the uncertainty in shifting the curves in the rubbery region, which had been experienced by some authors.[3]

## METHOD OF REDUCED VARIABLES

The basic assumption in the method of reduced variables or time-temperature superposition principle is that the temperature has the same effect on all mechanisms involved in the stress relaxation. The mathematical expression for the time-temperature superposition principle[4] is

$$E_{T_0}(t) = \frac{T_0}{T} E_T(Kt) \qquad (1)$$

where $E_T$ is the modulus at time $t$ and temperature $T$, $K$ the shift factor, and $T_0$ the reference temperature. The method of reduced variables[5] introduces a correction factor for density change between the experimental and reference temperatures, which is small. Therefore, one can consider that the method of reduced variables is essentially described by eq. (1). This equation implies that when the experimentally determined $E_T$ at any temperature is modified by a factor $T_0/T$ and plotted against log $t$, the resulting curve can be shifted along the log $t$ axis by an amount of log $K$ to coincide with the curve obtained at temperature $T_0$. In this manner a modulus versus log time curve, a so-called "master curve," covering many decades of logarithms of time can be obtained by superposing the curves obtained at various temperatures with relatively short time ranges. Although master curves for various polymers have been constructed and useful information has been extracted from them, the basic assumption is only justified *post facto*. In addition, some authors have experienced some difficulty of shifting the stress relaxation curves in the rubbery region for the construction of master curves.

## MULTIPLE BOX DISTRIBUTION

An attempt was made[1] to treat the stress relaxation data of some polymers extracted from the published curves by the following equation derived for a Maxwell model with multiple box distribution of relaxation times:

$$E_T = S_T/\gamma = \sum_j C_j[E_i(-t/\tau_{lj}) - E_i(-t/\tau_{mj})] \quad (2)$$

where $S_T$ is stress at temperature $T$, $\gamma$ the elongation, $C_j$ the modulus constant, $E_i$ the exponential integral, and $\tau_{lj}$ and $\tau_{mj}$ are the smallest and the largest relaxation times in the $j$th distribution. Based on this equation, in order that the reduced

variables method can be applied, two conditions must be met. First, temperature should have the same effect on all $\tau_{lj}$ and $\tau_{mj}$. In other words, the ratio of $\tau_{mj}$ to $\tau_{lj}$ must be constant at all temperatures, and a relation of the form

$$\log \tau_{mjT} - \log \tau_{mjT_0} = \log K \qquad (3)$$

must exist, and $K$ must be independent of $j$. Secondly, all $C_j$ must obey the proportion $C_{jT}/C_{jT_0} = T/T_0$. In the preliminary study, the values of parameters $C_j$, $\tau_{mj}$, and $\tau_{mj}/\tau_{lj}$ were calculated by fitting eq. (2) to the individual experimental curves. The results showed clearly that these requirements are only partially met.

The quantity $K$ was found to be a semilog linear function of the reciprocal of temperature,

$$\log K = \log \tau_{mjT} - \log \tau_{mjT_0} = B_j(10^3/T$$
$$- 10^3/T_0) \quad (4)$$

where $B_j$ is a parameter. A constant value of $\tau_{mj}/\tau_{lj}$ was found to give the best fit. A similar relation was found to exist between $C_j$ and $T$,

$$\log C_{jT} - \log C_{jT_0} = A_j(10^3/T - 10^3/T_0) \quad (5)$$

where $A_j$ is a parameter. Although this equation shows that $C_j$ is not directly proportional to absolute temperature as required by the method of reduced variables, nevertheless, eqs. (4) and (5) fit the basic assumption that temperature has the same effect on all mechanisms involved, if $A_j$ and $B_j$ in these equations are independent of $j$. In fact, the parameters $A_j$ and $B_j$ were not found invariant at all values of $j$, but separate the box distributions into two groups by remaining constant within each group at all temperatures, except where transition of phase occurs. (One group of box distributions is probably associated with intrachain mechanisms, while the other group is related to interchain mechanisms. Although the identification of these groups of box distributions of relaxation times with these molecular mechanisms is by no means definite, for convenience of discussion, these groups are hereafter referred to as molecular mechanisms.) In other words, the temperature effect is not the same on all mechanisms, but is the same on mechanisms of the same group. Therefore, eqs. (4) and (5) describe a modification to the method of reduced variables which requires, before the construction of master curve, the resolution of stress or modulus into two parts, namely, the contributions of interchain mechanisms and those of intrachain mechanisms. Owing to the

difference in the magnitudes of $C_j$ and $\tau_{mj}$ for these two types of mechanisms, this is, fortunately, not a difficult task.

## MODIFIED METHOD

It has been also observed from the results obtained on NBS polyisobutylene that the relaxation times of the intrachain mechanisms at higher temperatures is relatively short as compared to the experiment time. All intrachain mechanisms are relaxed before the first measurement is taken and the relaxation curves at higher temperatures are chiefly the sum of the contributions of interchain mechanisms. In addition, the value of $A_j$ in eq. (5) is zero, or at least so close to zero that it is not discernible with the present set of experimental data. Under these conditions, the curves at these temperatures can be shifted along the log $t$ axis to construct a master curve which represents the behavior of interchain mechanisms. A set of characterizing parameters of this group of mechanisms can be calculated by fitting eq. (2) to this master curve.

This procedure is illustrated by use of the stress relaxation data on NBS polyisobutylene. When the curves obtained at $-44.3$, $-20.2$, 0, 25, and 50°C. are treated in the manner discussed in the preceding paragraph, the result is the curve shown in Figure 1 with $-44.3$°C. as the arbitrarily chosen reference temperature. Also shown in Figure 1 are the stress relaxation curves of box distribution No. IV, V, and VI, which are resolved from the master curve by means of multiple box distribution
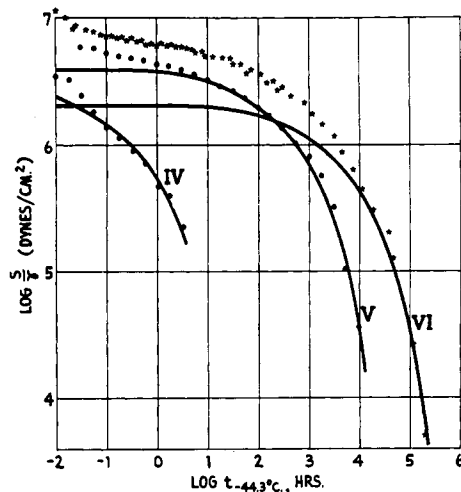


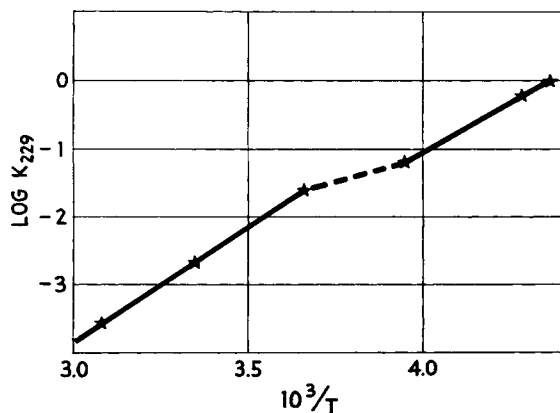Fig. 1. Master curve of interchain mechanisms of NBS polyisobutylene.

Fig. 2. Shift factor of interchain mechanisms of NBS polyisobutylene.

treatment.[1] The values for log $K_{229}$ are plotted against the reciprocal of absolute temperature in Figure 2. The curve consists of three segments of straight line. As it was indicated on the original data sheet, the data for 0, 25, and 50°C. were obtained from a separate experiment.[6] The change in slope observed, shown by dashes in Figure 2, could be caused by the difference in experimental conditions.

At low temperatures, the value of $C_j$ for interchain mechanisms are comparatively low and the contributions of these mechanisms to the stress or modulus are negligible. Therefore, no resolution procedure is needed and the curves can be treated directly. Relaxation data at temperatures below −65.4°C. were treated in this manner. Unfortunately, the master curve for the intrachain mechanisms, constructed by shifting the low temperature curves both horizontally and vertically, does not usually cover a wide enough range of time for analysis. Additional data may be obtained from the curve determined at intermediate temperatures.

At the intermediate temperatures, approximately in the rubbery region, neither of the two groups of mechanisms dominates in the experimental time range. The contributions to modulus of intrachain and interchain mechanisms must be separated. This can be readily done when the master curve for the interchain mechanisms is already available. By extrapolating the log $K$ versus $1/T$ curve, the value of $K$ at temperature $T$ can be found. The contribution of interchain mechanisms can be read from the master curve after being shifted along the log $t$ axis for an amount equal to log $K$. This contribution is subtracted from the experiment relaxation curve. The resulting curves, the contribution

of intrachain mechanisms, were shifted both horizontally and vertically to complete the long time portion of the master curve for intrachain mechanisms. Experimental data at −49.6, −51.4, −56.2, and −58.8°C. were used for this purpose.

## RESULTS AND DISCUSSION

The master curves thus obtained on NBS polyisobutylene were analyzed by the multiple box distribution method. The parameters calculated are tabulated in Table I. The values for temperatures below −74.1°C. are not included because the original data give only curves showing slight curvature and shifting cannot be done with certainty. The reference temperature is chosen at −65.4°C. for the reason that the glass transition probably starts at this temperature. These parameters are shown combined with the idealized shifting factors in Figures 3 and 4 as log $\tau_{mj}$ versus $1/T$ and log $C_j$ versus $1/T$ curves, respectively. These curves show clearly there is a change in the slope in the neighborhood of the glass transition temperature as determined by other physical methods. The modulus constant-temperature curves show a slight curvature at −74.1°C. As a matter of fact, it is within experimental error if the relation is represented by a broken line.

The time factor $K$ given by the time-temperature superposition (TTS) principle is compared to the corresponding value obtained by this modified method in Figure 5, all being referred to 25°C. It can be readily seen that the curvilinity is removed by the use of multiple box distribution (MBD). In Figure 6 the comparison of the corrections to modulus required by these two methods is shown, which shows the major differences between these methods. The correction prescribed by the reduced variables method is rather small in

TABLE I
Characteristics of NBS Polyisobutylene
($T_0 = -65.4°C.$)

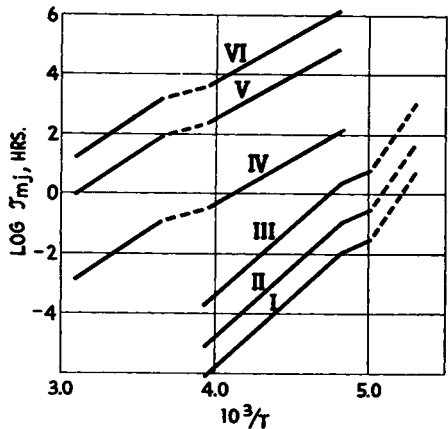| $j$ | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| Log $2.303C_{jT_0}$ | 8.88 | 8.18 | 7.38 | 5.98 | 6.11 | 5.84 |
| Log $\tau_{mjT_0}$ | −2.00 | −0.97 | 0.38 | 2.07 | 4.92 | 6.17 |
| | −20.2°C. to −65.4°C. | | | | | |
| $A_j$ | 2.21 | 2.21 | 2.21 | 0 | 0 | 0 |
| $B_j$ | 4.74 | 4.74 | 4.74 | 2.39 | 2.39 | 2.39 |
| | −65.4°C. to −74.1°C. | | | | | |
| $A_j$ | 8.62 | 8.62 | 8.62 | — | — | — |
| $B_j$ | 2.98 | 2.98 | 2.98 | — | — | — |

Fig. 3. Maximum relaxation time–temperature curve.
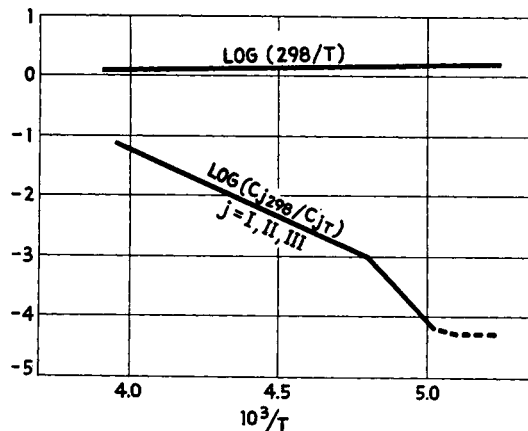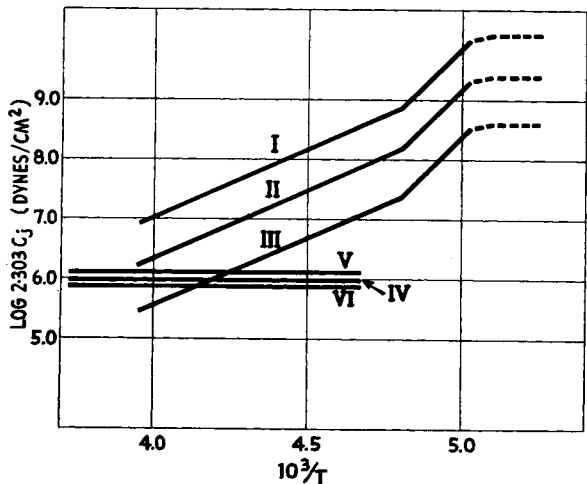


Fig. 6. Comparison of corrections to modulus.



Fig. 4. Modulus constant–temperature curve.
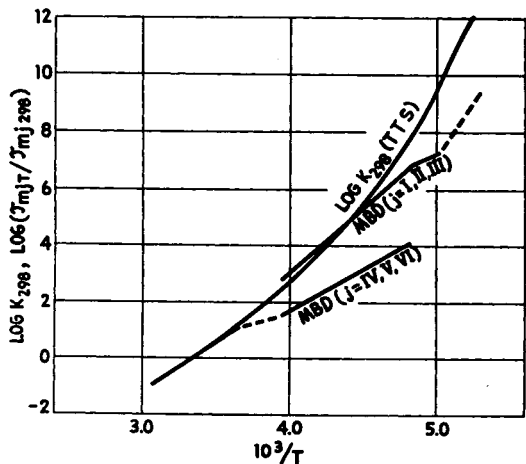
magnitude and increasing with decreasing temperature, while the same quantity specified by the multiple box distribution is the opposite, which could be large and is decreasing with decreasing temperature. This radical difference is pictured more clearly in Figure 7, in which the master curves at 25°C. are shown. The master curve for interchain mechanisms (MBD II) is the same as the long time part of that by the time-temperature superposition principle, as expected. The master curve for intrachain mechanisms (MBD I), however, is much lower—four decades of logarithm lower, actually—than the short time half of the conventional master curve, even though they have the same general appearance.

For the same reason, the relaxation curves at various temperatures predicted by these methods are different outside the experimental time range.



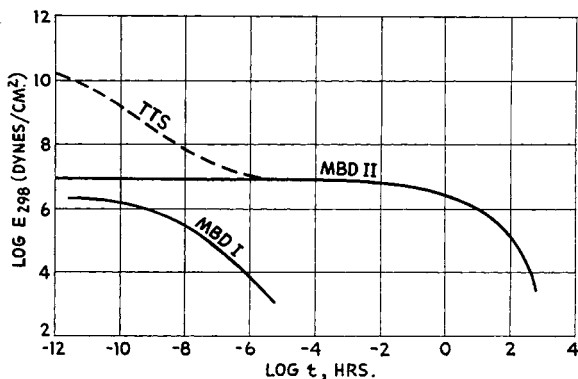Fig. 5. Comparison of shift factors: TTS principle and MBD method.



Fig. 7. Comparison of master curves: (TTS) time–temperature superposition principle: (MBD I) for intrachain mechanisms, (MBD II) for interchain mechanisms by multiple box distribution method.
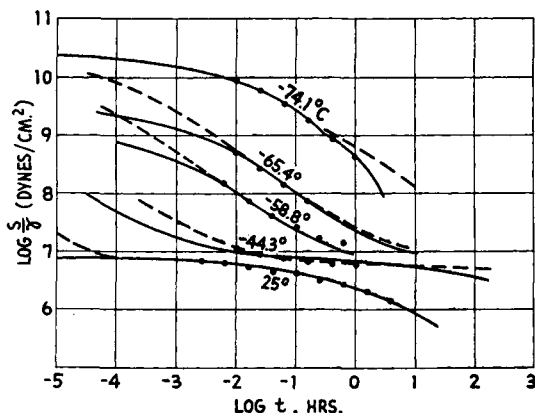
Fig. 8. Predicted relaxation curves: (●) experimental, (–) time-temperature superposition principle, (—) multiple box distribution method.

Several of these predicted curves are reproduced in Figure 8 as illustrations. The curves predicted by the multiple box distribution method are shown as solid lines, while the broken lines show those derived from the conventional master curve. It is obvious that both methods account for the experimentally measured points equally well. However, there are disagreements in the predicted moduli outside the time range covered in the experiment. Generally speaking, the time-temperature principle gives higher values. Long time stress relaxation involves complications, such as chemical relaxation, the analysis of which deserves caution. Stress relaxation data collected under high speed stretching conditions are required for better elucidation of the short time behavior of viscoelastic material. Experiments are in progress in this laboratory to collect data for this purpose.

### SUMMARY

The present work has, in summary, achieved the following:

*1.* The earlier observations have been confirmed, namely: (a) viscoelastic material can be represented by a generalized Maxwell model with multiple box distribution of relaxation times; (b) the effect of temperature on mechanical behavior of amorphous polymers is a simple semilogarithmic linear relation; and (c) it is possible to determine the glass transition temperature range by stress relaxation.

*2.* The applicability of the modified method of constructing master curves to circumvent the handicap of a narrow experimental time range has been proved.

*3.* A set of characterizing parameters for polyisobutylene has been derived from stress relaxation data. These characteristics may serve as the basis for future comparison of mechanical behavior of polymers with various molecular structures.

### References

1. Chang, F. S. C., *International Symposium on Macromolecular Chemistry*, Montreal, Canada, 1961.
2. Catsiff, E., and A. V. Tobolsky, *J. Colloid Sci.*, **10**, 375 (1955).
3. Fujino, K., K. Senshu, and H. Kawai, *J. Colloid Sci.*, **16**, 262 (1961).
4. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960, p. 145.
5. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 209.
6. Andrews, R. D., and A. V. Tobolsky, unpublished results.

### Synopsis

It has recently been shown that stress relaxation data may be conveniently interpreted using multiple box distribution of relaxation times. The multiple box distribution treatment suggested the possibility of modifying the method of reduced variables or time-temperature superposition principle to avoid the difficulty of shifting curves in the rubbery region. This modification has now been applied to the experimental stress relaxation data for polyisobutylene. The results obtained verify the earlier observations that the logarithms of relaxation times and modulus constant are related to the reciprocal of temperature linearly, that the slope of these semilog linear relations changes when there is a phase transition, and that two types of mechanisms are operating in the relaxation of mechanical stress. The theorized stress-time curves predicted by both methods fit the experimental data equally well, but the modulus at very short time predicted by the reduced variables method generally is higher than that by the multiple box distribution method. Relaxation data collected under high speed stretching condition are needed for better elucidation of the short time behavior of viscoelastic material.

### Résumé

On a montré récemment que les données concernant la relaxation de la tension peuvent être interprétées d'une façon commode en utilisant les notions de distribution multiples des temps de rélaxation. Le traitement de la distribution multiple suggère la possibilité d'apporter une modification à la méthode des variables réduites ou en principe de superposition temps-température afin d'éviter la difficulté due au glissement des courbes dans la région caoutchouteuse. A présent, cette modification a été appliquée aux résultats de la rélaxation expérimentale de la tension dans le cas de l'isobutylène. Les résultats obtenus confirment les obser-

vations de première heure à savoir que les logarithmes des temps de rélaxation et du module sont liés linéairement à l'inverse de la température, que la pente de ces relations linéaires semi-logarithmiques varie lorsqu'il y a transition de phase et que deux types de mécanismes entrent en jeu dans la rélaxation de la tension mécanique. Les courbes théoriques de tension en fonction du temps prévues par l'une et l'autre méthode s'accordent également bien avec l'expérience, mais le module à des temps très brefs prévu par la méthode des variables réduites est généralement supérieur au module calculé par la méthode de distribution multiple. Les résultats concernant la rélaxation sous des conditions de tension à vitesse élevée sont nécessaires pour une meilleure compréhension du comportement des substances viscoélastiques pour des temps très brefs.

## Zusammenfassung

Kürzlich wurde gezeigt, dass die Spannungsrelaxationsdaten mit einer multiplen Rechtecksverteilung der Relaxationszeit befriedigend dargestellt werden können. Die Behandlung mit der multiplen Rechtecksverteilung legt die Möglichkeite nahe, die Methode der reduzierten Variablen oder das Prinzip der Zeit-Temperaturüberlagerung zu modifizieren, um die Schwierigkeit einer Kurvenverschiebung im Kautschukbereich zu vermeiden. Diese Modifizierung wurde nun auf die experimentellen Spannungsrelaxationsdaten von Polyisobutylen angewendet. Die erhaltenen Resultate bestätigen die frühere Beobachtung, dass der Logarithmus der Relaxationszeit und des Moduls eine lineare Abhängigkeit vom Reziprokwert der Temperatur zeigen, dass sich die Neigung dieser halblogarithmischen linearen Abhängigkeit bei einer Phasenumwandlung ändert und dass zwei verschiedene Mechanismen bei der Relaxation von mechanischer Spannung wirksam sind. Die mit beiden Methoden erhaltenen theoretischen Spannungs-Zeitkurven entsprechen den experimentellen Ergebnissen in gleicher Weise; der mit der Methode der reduzierten Variablen bei sehr kurzen Zeiten erhaltene Modul ist jedoch im allgemeinen höher als der mit der Methode der multiplen Rechtecksverteilung berechnete. Relaxationsdaten, die bei hoher Streckungsgeschwindigkeit gewonnen wurden, sind zur besseren Aufklärung des Kurzzeitverhaltens von viskoelastischem Material erforderlich.

## Discussion

**Question:** Would you comment on the effect of increasing rate of loading on the measurable distribution of relaxation times?

**Answer:** It has been shown by McGarry et al. [McGarry, F. J., et al., *Rubber Age*, **88**, 973, (1961)] that the stress relaxation curve obtained at one stretching speed is different to that obtained at another speed. When a higher speed is used, the mechanisms of relatively short relaxation times are not relaxed at the beginning of relaxation measurement. When the relaxation experiment is done at slow speed, some mechanisms whose relaxation times are shorter than the time of stretching may be already relaxed before the stretching is stopped. Therefore, one cannot get the stress relaxation curves at two stretching speeds to coincide with each other.

**Question:** Do you think the assumption that $C$ is independent of temperature is a reasonable one?

**Answer:** This is an assumption based on the results obtained from our preliminary calculations (Chang, F. S. C., International Symposium on Macromolecular Chemistry, Montreal, Canada, 1961; *J. Polymer Sci.*, in press). In the preliminary study the individual curves were separately treated. It was found that $C$ is constant or almost invariant for interchain mechanisms.

**Question:** Do you think the concept of multiple-box distribution has any advantage over the concept of a continuous relaxation spectrum, or is it just easier to handle mathematically?

**Answer:** A little of both. At the present time we are not able to identify the individual box distributions with specific molecular mechanisms. On the other hand, a continuous relaxation spectrum from zero to infinite relaxation times is hard to interpret in a molecular sense. The multiple-box distributions resolve the modulus into several parts. It may be possible to identify these boxes with molecular mechanisms when more data are collected and a comparison of the characteristics of different molecules is made. In other words, this is just a first step.

**Question:** Did there appear to be two different mechanisms with every configuration? That is, did you get two separate types of relaxation with each form?

**Answer:** Yes. Two types of mechanisms were also observed in other polymers.