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LOW FREQUENCY THERMOMECHANICAL SPECTROMETRY OF POLYMERIC MATERIALS: COMPUTERIZED TORSIONAL BRAID EXPERIMENTS

I. Overview
II. Data Processing
III. Tactic Polymethylmethacrylates

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ABSTRACT

The torsional braid experiment has been interfaced with a centralized Hierarchical Computing System for data acquisition and data processing. Such a system, when matched by the appropriate upgrading of the monitoring techniques, provides high resolution thermomechanical spectra of rigidity and damping, and their derivatives with respect to temperature.

LOW FREQUENCY THERMOMECHANICAL SPECTROMETRY OF POLYMERIC MATERIALS: COMPUTERIZED TORSIONAL BRAID EXPERIMENTS - I. OVERVIEW.

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INTRODUCTION. Torsional Braid Analysis (TBA), a variant of the torsional pendulum technique, is a low frequency ($\sim$ 1 Hz) dynamic mechanical method for determining the thermomechanical spectra of polymers (1). A TBA experiment may run over the course of several days and generate more than 1000 damped sine waves. Manual data reduction techniques to obtain the frequency and damping constant for each analog wave, using a stopwatch and graduated scale or even a strip-chart recorder, are slow and limited in accuracy.

It is because of difficulties in the data acquisition and data reduction procedures that the torsional pendulum has not developed to the level of being regarded as a thermomechanical spectrometer. The usefulness of the technique has been limited mainly to the monitoring of transition temperatures and time-temperature hysteresis phenomena. It is apparent that further extension of the scope of research employing the torsional pendulum will require a breakthrough in methodology.

A technological breakthrough will permit a deeper and more extensive study of problems, such as: a) Characterization of the thermomechanical spectra in terms of analytical expressions. Such analytical formulae will introduce new parameters to better characterize the spectra, and make it possible to resolve the temperature dependent data in terms of contributions from primary and secondary transitions. These developments could lead to a better understanding of the underlying physics and chemistry of the observed transformations; b) Comparison of the thermomechanical spectra of systematic series of related polymeric materials. This will allow verification of the structural origin of the observed phenomena; c) Time-temperature hysteresis phenomena. In such experiments the time-temperature cycle may be used as a well controlled variable in order to sort out the time constants which characterize the kinetics of the physical and/or chemical transformations; d) Non-linear mechanical effects. Inspection of typical dynamic mechanical response curves reveals that the derived parameters are amplitude dependent. Study of the amplitude dependence would provide additional parameters to characterize the thermomechanical behavior of polymeric materials; and e)Frequency dependence of the response function. It is possible to alter the frequency range of measurements by at least an order of magnitude by changing the specimen geometry and the inertial mass. This will be required to represent the thermomechanical spectra in frequency-independent form.

A factor common to the above experiments is the need for the acquisition of a large volume of data in a meaningful way. That is, the resolving power of the sensor system as well as that of the control functions must be such that the observed small differences between different experimental sequences be significantly larger than the experimental errors. Further, in order to be able to pursue such experiments, the reduced data must be consulted prior to the termination of the current experiment so that a timely decision with regard to the next step may be made.

The present paper discusses the results of the on-line interface of the TBA experiment to an Hierarchical Computer System for data acquisition, data reduction and control of experimental variables (2). Some experimental results are demonstrated and the data reduction procedures are outlined. Several modes of presentation of the final computer-reduced data are discussed in an attempt to elucidate possible interrelations between the thermal variation of the rigidity and loss parameters.

OVERVIEW OF THE DATA PROCESSING SYSTEM. An important guideline for the implementation of a computer network for laboratory application is that the success of a research project in a particular field should not depend on the proficiency of the researcher in computer technology. The experimentalist can benefit from the advantage of the batch computer with a minimal acquaintance with a high-level programming language such as Fortran. The computer

can be used in a rather sophisticated multi-level data reduction operation without knowledge of the inner workings of the particular computer or of sophisticated coding in machine or even assembler language. The "non-expert" use of the batch computer is quite common in theoretical work and in the present paper such an application with a laboratory TBA experiment is discussed.

The Hierarchical Computer System is designed to interface the laboratory experiment to the tremendous power of the large scale batch computer (IBM 360/91) for the purpose of the "on-line" processing of large volume of data with no involvement of the researcher in this stage of the data handling (2). In order to accomplish this on-line interface, two additional computers are interconnected in the hierarchical fashion between the experiment and the batch computer (Figure 1). The actual data acquisition is performed by a small real-time computer (IBM System 7) which serves as a digital front-end for the system. The front-end computer is equipped with a 20 Kcps analog-to-digital converter and an analog multiplexer providing for the simultaneous monitoring of many analog signals from one or several experiments. The incoming signals are digitized and tested by the front-end computer for the purpose of scan rate optimization as well as for other criteria which are imposed by the requirements of the final data reduction procedures by the central batch computer. Following this preliminary optimization and trimming of the data, it is coded for the purpose of data management and shipped to the central facility. In order to interface between the vastly different timing requirements of the real-time and batch computers, a third intermediate computer is used for data buffering and timing matching. In the initial design of the network, this role has been played by an IBM 1800 computer which has been recently replaced by an IBM 370/155 (Fig. 1) operating as the buffer computer for the real-time applications (in addition to providing time sharing services).

The advantage of the Hierarchical Computer System, as compared with the application of a dedicated minicomputer, is twofold: 1) it allows for maximum flexibility in the further development of the procedures for data acquisition and experimental control by the digital front-end, and 2) it sets the power of the central batch computer as the ultimate limitation on the magnitude and sophistication of the data reduction procedures. By separation of the two distinctly different functions, a high degree of optimization in the utilization of the resources of the hierarchical system is achieved.

The obvious disadvantage of the use of a batch computer in the environment of laboratory experiments is the rather slow turn-around time. Typically, it takes from one to several hours before the reduced data are available for consultation and for a decision to be made with regard to the following step of the experiment. For faster decisions having to do with the control of the sequence of the experiment, processing procedures must be developed for use by the digital front-end. The front-end would be used in such an instance as a mini-computer. It is clear, however, that there is a definite conflict between the two modes of operation. The trade-off requires that the amount of data processing going on in the digital front-end be kept at a minimum in order to maintain its power and flexibility for data acquisition and control. In the present application, a minimal amount of data processing by the front-end is concerned with setting the scan-rate, phase angle and amplitude boundary conditions. These have been in effect dictated by the optimization requirements of the processing routines in the central batch computer. The interplay between the processing power of the front-end in real-time and that of the central computer in the batch mode is a most important feature of the hierarchical system and can have a substantial conceptual impact on the design of the experiment.

OVERVIEW OF THE DATA REDUCTION PROCEDURES. The response function of the torsional pendulum to mechanical excitation is described to a good approximation by

$$\theta(t) = \theta_o e^{-\alpha t} \cos\omega(t-t_o) \qquad (1)$$

which is a solution to the equation of motion

$$\ddot{\theta} + 2\alpha\dot{\theta} + (\omega^2 + \alpha^2)\theta = 0 \qquad (2)$$

where θ is the amplitude, α is the damping constant and ω is the frequency in radians/sec. Eqn. 2 may be recast in complex format

$$\ddot{\theta} + (G' + iG'')\theta = 0 \qquad (3)$$

where G' and G'' are the in-phase and out-of-phase shear moduli, respectively. These expressions do not include effects of experimental non-linearity of transducers and circuits, noise, drift, as well as possible amplitude-dependent terms. Equation 1 is commonly used in the analysis of torsional pendulum data, manually or by dedicated analog and digital systems. This is done by monitoring the maxima to determine the frequency and the amplitude ratios to determine the damping constant. In the environment of the batch computer it is possible to apply universal methods of nonlinear least mean squares fitting. These are susceptible to generalizations designed to incorporate in the fitting procedures contributions due to noise, drift and non-linearities. If the sampling rate is very much faster than the frequency of oscillation it is possible to substitute

$$\dot{\theta}_j = (\theta_{j+1} - \theta_{j-1})/2\Delta t \qquad (4)$$

and

$$\ddot{\theta}_j = (\dot{\theta}_{j+1} - \dot{\theta}_{j-1})/2\Delta t$$

$$= (\theta_{j+2} + \theta_{j-2} - 2\theta_j)/4(\Delta t)^2 \qquad (5)$$

into Eqn. 2, resulting in (n-4) linear equations in terms of the n observations of the amplitude θ_j (j = 1....n). These may be solved by standard methods of *linear* least mean squares fit for the parameters α and $(\omega^2 + \alpha^2)$. The obvious advantages of the linear procedure is that it does not require initial estimates, and that it eliminates the need for iterations. An enormous computational simplification is obtained by the elimination of the use of exponentials and trigonometric expressions (Eqn. 1) in the fitting procedure.

In both cases (Eqns. 1 and 2) the interplay between the use of the computational powers of the digital front-end and the central batch computer plays a crucial role in the application of the above procedures in a fully automated mass-production effort of data analysis. The digital front-end is responsible for the scan-rate optimization over the range of change of the frequency and loss during a complete experiment. In using Eqn. 2 a faster scan-rate is employed to ensure the validity of the substitution of the derivatives. The second method (Eqn. 2) provides a straight forward and a more economical (in computing costs) approach to the data reduction problem than the first one (Eqn. 1).

In order to minimize effects of non-linearity in the behavior of the pendulum and the optical transducer, the front-end ensures that the data is being recorded within the correct boundary conditions with respect to the vibrational amplitude. The front-end also verifies the correct phase relationship of the data taken (equivalent to setting the t_o value in Eqn. 1). This requirement, which has been found necessary empirically, might have to do with the approximate nature of the correction for the baseline drift as done by a more generalized version of Eqn. 2 [see part II (3) of this paper].

In the early development of the computerized experimental setup, the linear least mean squares fitting procedure produced unacceptable scatter in the thermal variation of the loss parameter. Attempts were made to eliminate this scatter both by analog filtering (signal conditioning by hardware) and by digital filtering, the latter being pursued in the batch computer. This problem was first solved by the digital method using an iterative process to optimize the sample size with regard to the signal to noise ratio. The optimal signal to noise ratio was obtained when the least mean squares analysis was performed over an integral number of oscillations. The number of data points used in the analysis was determined by the frequency obtained in the previous iteration. Typically, the iteration procedure converged after three

cycles producing results as shown in Fig. 2. Later, as a result of improvements in the data monitoring hardware, the quality of the primary signals had been upgraded to the point of eliminating the need for digital filtering. This interplay between the analog and digital filtering in the optimization of the signal-to-noise ratio is another demonstration of the power and flexibility of the Hierarchical Computer System for laboratory application.

At the completion of the first level of data analysis (which had been described above), the reduced data is available in the batch computer in the form of the temperature dependence of two variables: the damping constant, α, and the relative in-phase shear modulus, $G' = \omega^2 + \alpha^2$. This particular presentation derives from the use of Eqn. 2 in the data reduction procedure. Alternative modes of data presentation may be derived from the use of Eqns. 1 and 3 (Table I). The logarithmic decrement is defined as the natural logarithm of the ratio of two successive maxima of the damped cosine function (Eqn. 1). The relative rigidity of the composite specimen is a simplification of the relative in-phase shear modulus, G' (elastic shear modulus), the two parameters being equivalent for low damping values. Absolute values are not specified for the above parameters because the configuration of the polymer-impregnated glass braid precludes precise measurements of dimensions. It is the relative thermal variation of the two parameters which is being monitored by the TBA technique.

In addition to the above forms of data presentation, derivatives of the reduced data with respect to temperature are calculated and plotted. These are obtained by a least mean squares fit of a third order polynomial, over nine consecutive temperature points, centered at the point of evaluation. The respective derivatives are given by the calculated coefficients of the appropriate terms in the fitted polynomial. The first derivative of G' with respect to temperature is shown in Fig. 2 together with the G' curve. Figures 3-5 present the loss data in three of the four ways summarized in Table I. A plot of tanδ data is not presented because it is very similar to that for the logarithmic decrement.

DISCUSSION. The experimental data shown in Figs. 3-5 represent one experiment where a sample of syndiotactic polymethylmethacrylate (4) has been monitored on cooling from 473°K to 93°K at a rate of 2 degrees per minute. There are noticeable differences between the various loss curves (Figs. 3-5) as well as the first derivative of the elastic shear modulus with respect to temperature (Fig. 2). The out-of-phase shear modulus, G" (inelastic shear modulus) is best suited for the purpose of resolving the α and β peaks. This is because the two maxima are better resolved and there is less ambiguity in the assignment of the "base-line" of the curve for more quantitative analysis.

A more significant difference between the various presentations is that they indicate slightly different transition temperatures (Table I) as determined by the respective maxima in the curves. Since all are derived from the same experimental data, the notion of a discrepancy between the assigned transition temperatures as obtained from the rigidity and loss curves, is unacceptable. A description of the data in terms of the inelastic (G") and the derivative of the elastic (d(G')/dT) shear moduli, provides internally consistent values of the transition temperatures. Figure 6 provides an expanded view of the Tg region for various modes of data presentation.

Inspection of the mathematical descriptions of the different presentations of the loss data (Table I), points to the origin of the observed differences in the derived transition temperatures. Since the frequency of the torsional pendulum enters differently in the expressions, the fact that it varies dramatically across the temperature region in which the phase transformation occurs, results in the apparent shifts in the observed maxima in the data. The description of the data in terms of the complex shear moduli (Eqn. 3) provides a unique determination of the transition temperature Tg and T_β, indicating that this presentation is preferable in the context of future attempts at theoretical discussions of the physics of the phase transitions.

It is noteworthy that while the G" and dG'/dT curves are quite similar in their gross features and are internally consistent insofar as the

transition temperatures are concerned, they are substantially different in the details and contain therefore complementary rather than redundant information.

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TABLE I. DIFFERENT MODES OF DATA PRESENTATION - SYNDIOTACTIC PMMA.

	T_g, °K	T_β, °K
A. Rigidity* (G')		
$\omega^2 + \alpha^2$	399	
Relative rigidity = ω^2	399	
$\omega^2 - \alpha^2$	399	
B. Loss Parameter		
$G'' = 2\alpha\omega$	399	294
Damping coefficient = α	400	298
Log decrement = $\Delta = 2\pi\alpha/\omega$	403	298
$\tan\delta = 2\alpha\omega/(\omega^2 + \alpha^2)$	403	298

*T_g values obtained from dG'/dT; the theoretical basis for the different rigidity parameters is discussed in, Nielsen, L. E., *Mechanical Properties of Polymers*, Chapter 7, Reinhold Publishing Corp., New York, 1965.

TBA AND PYROLYSIS LABORATORY

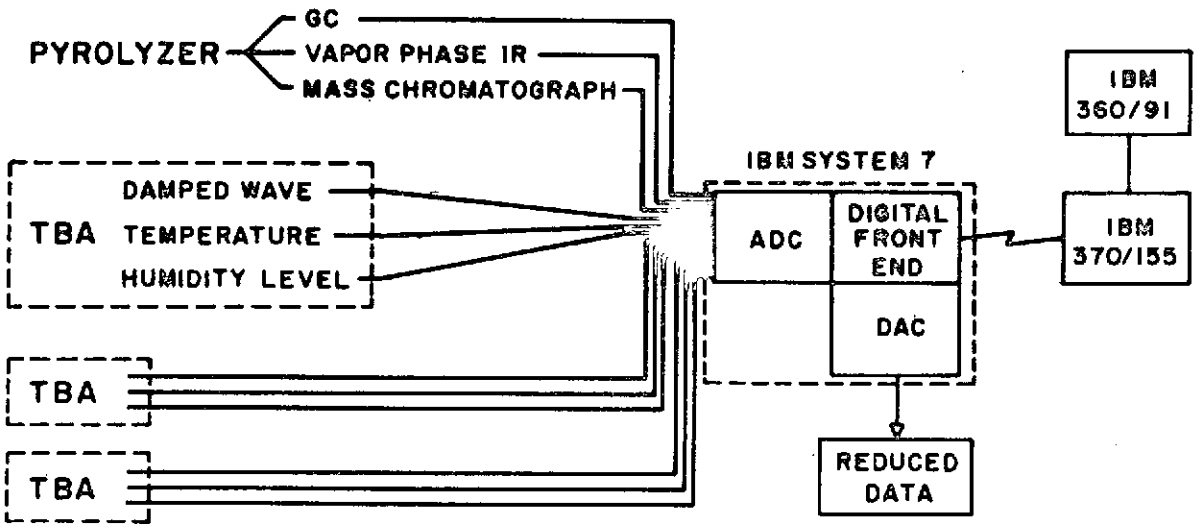
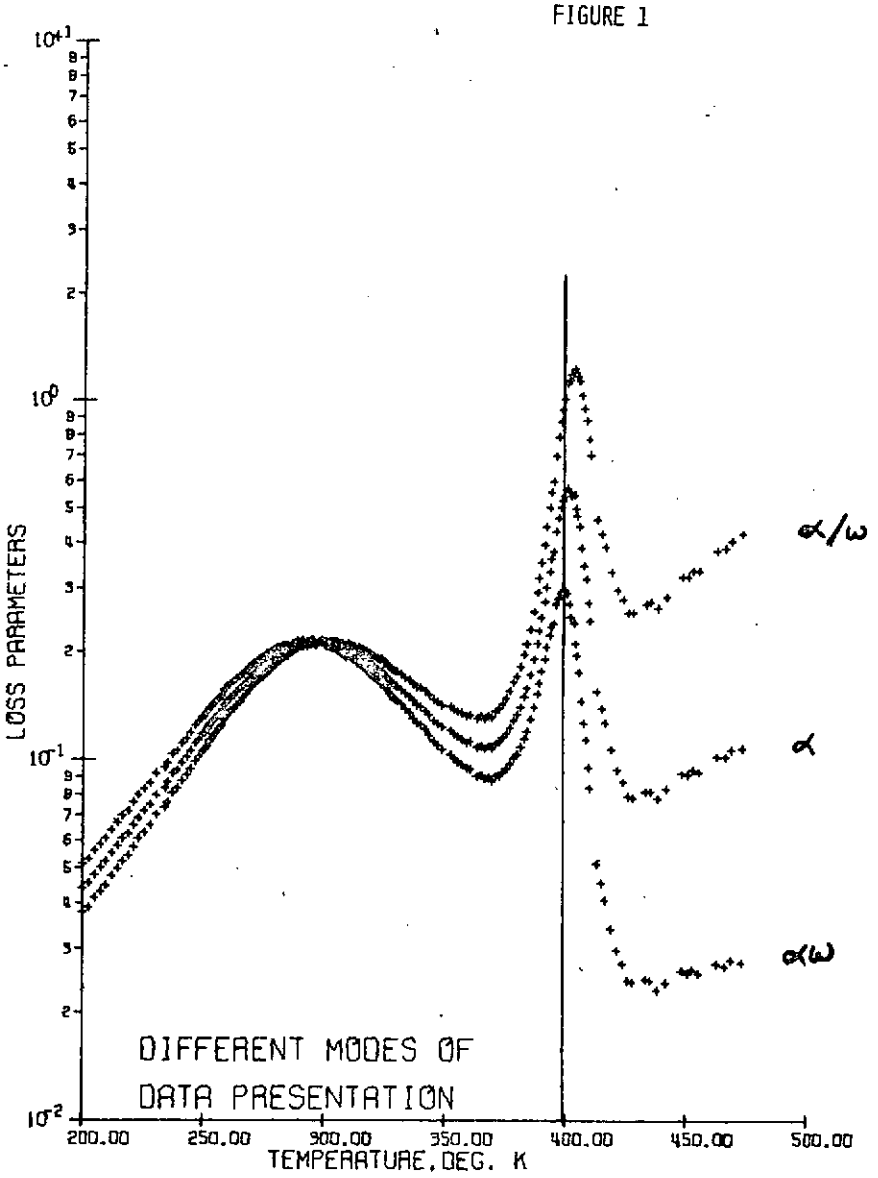
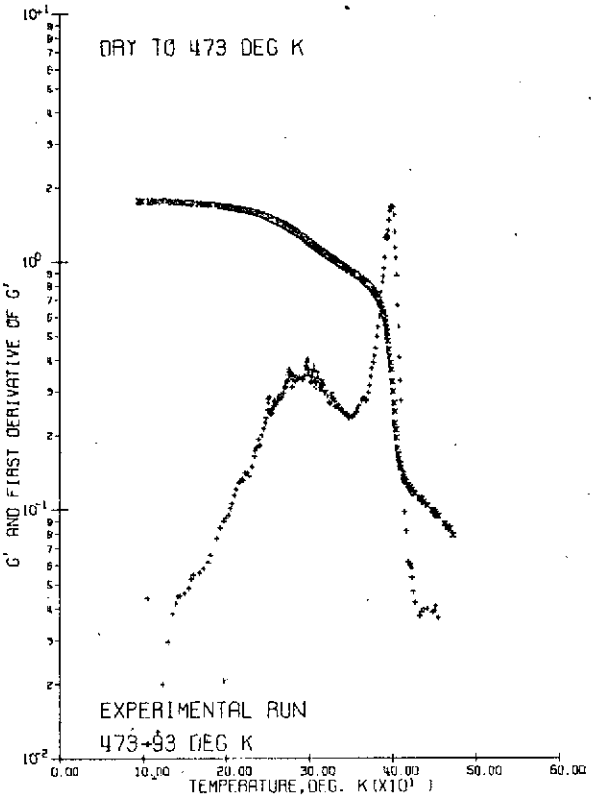


FIGURE 1



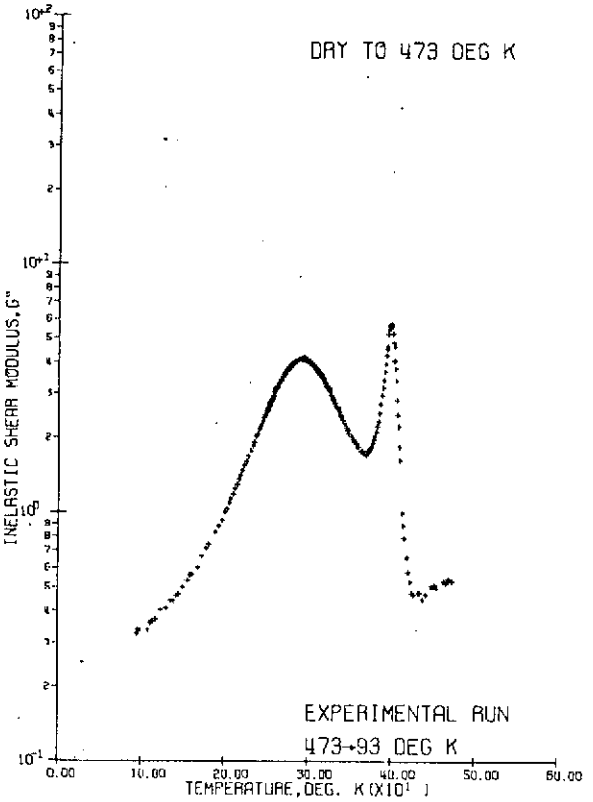
SYNDIOTACTIC PMMA

FIGURE 6



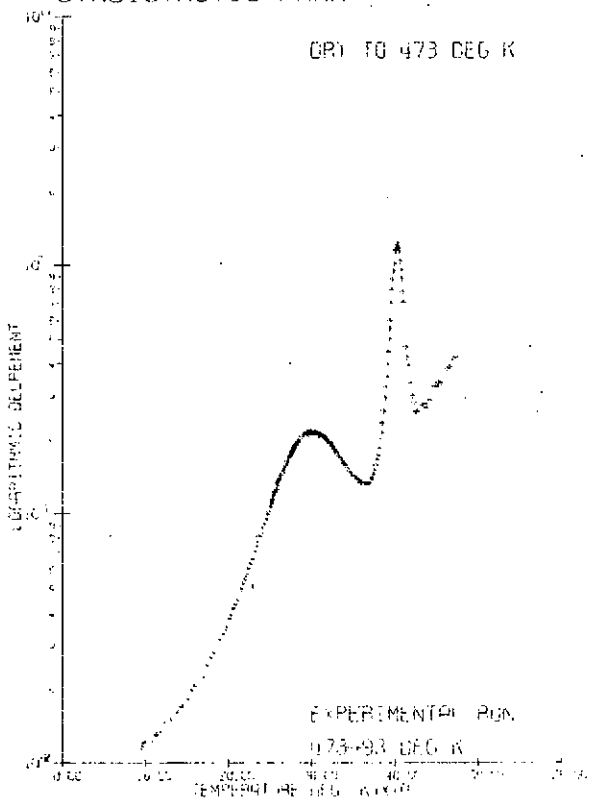
SYNDIOTACTIC PMMA

FIGURE 2



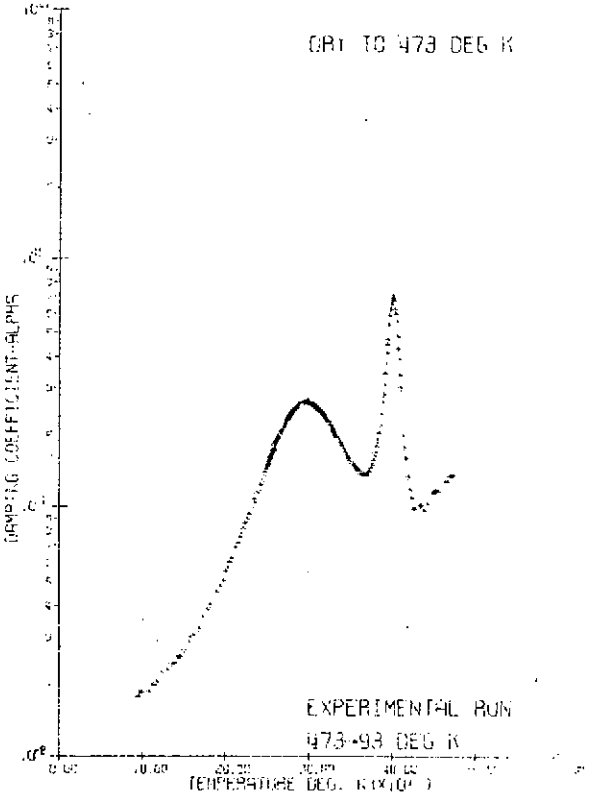
SYNDIOTACTIC PMMA

FIGURE 3



SYNDIOTACTIC PMMA

FIGURE 5



SYNDIOTACTIC PMMA

FIGURE 4

LOW FREQUENCY THERMOMECHANICAL SPECTROMETRY OF POLYMERIC MATERIALS: COMPUTERIZED TORSIONAL BRAID EXPERIMENTS - II. DATA PROCESSING. S. J. Stadnicki and J. K. Gillham, Polymer Materials Program, Department of Chemical Engineering and Y. Hazony, Computer Center, Princeton University, Princeton, N. J. 08540.

INTRODUCTION. The effectiveness of torsional pendulum studies has been limited due to difficulties in processing large amounts of data. Manual data reduction techniques, to determine the rigidity and damping for each damped wave, using a stopwatch and graduated scale, or a strip-chart recorder, are slow and limited in accuracy. An overview of the Hierarchical Computer System used with a Torsional Braid Analysis (TBA) apparatus for fully automated data acquisition, reduction, and presentation has been described in Part I (1-3).The present manuscript deals with data processing.

On-line data acquisition and preprocessing are performed by a computer which is situated in the experimental laboratory. The data reduction program which employs a linear least mean squares fit of the data to the differential form of the equation of motion, is written in Fortran and is processed in a batch computer. An intermediate computer is employed for data buffering and for matching the time requirements of the batch computer. Evolution of the data reduction scheme is outlined.

INSTRUMENTATION. An IBM System/7 computer is employed in conjunction with a torsional braid apparatus for on-line data acquisition and preprocessing. At the time of this work, an Hierarchical Computer System was used with the data transmitted through an IBM 1800 computer (employed for data buffering) and then onto an IBM 360/91 batch computer for data reduction. The final presentation of the thermomechanical parameters as a function of temperature is obtained on a Calcomp Plotter. Presently,the data are sent by telecommunication from the System/7 directly to an IBM 370/155 computer which is attached to the IBM 360/91.

The capabilities of the present preprocessing facility are as follows:

1. Four digit analog to digital conversion.
2. Maximum scan rate of 20,000 samplings per second.
3. Running several simultaneous experiments.
4. Reduced data transmission directly to the laboratory.
5. Real time local control functions.

A summary of the data acquisition and preprocessing characteristics of the present procedure are as follows:

1. A data acquisition rate of 100 points per second (3). This scan rate is automatically adjusted to acquire a minimum of two complete cycles.
2. Acquisition of approximately 600 raw data points from each damped wave. (The reduction program at the batch computer utilizes all of these to obtain one reduced data point for each of the frequency and damping parameters.)
3. Standardization of phase angle and amplitude boundary conditions of the data to be acquired.

Figures 1A and 1B show typical preprocessed digital data (damped waves) obtained in the glassy state and glass transition regions, respectively.

THEORY OF DATA REDUCTION. The basic equation of motion for a "simple" torsional pendulum is given in Eq. (1), where θ is the angle of displacement from the neutral position (or the amplitude of the electrical analog), I is an inertial constant, η_{dym} is the dynamic viscosity,and G_{dym} is the dynamic modulus (4,5).

$$I \frac{d^2\theta}{dt^2} + \eta_{dym} \frac{d\theta}{dt} + G_{dym}\theta = 0 \qquad (1)$$

Equation (2) contains the same information in terms of the complex shear modulus.

$$I \frac{d^2\theta}{dt^2} + (G' + iG'')\theta = 0 \qquad (2)$$

The solution to Eq. (1) has the form of an exponentially damped cosine function

$$\theta = \theta_o e^{-\alpha t}\cos(\omega t + \phi) \tag{3}$$

with

$$\alpha = \eta_{dym}/2I$$

and

$$\omega = [G_{dym}/I - (\eta_{dym}/2I)^2]^{1/2}$$

where α is the damping coefficient and ω is the frequency in radians per second. A phase angle term, ϕ, has been introduced because of the timing of the initiation of data acquisition. Because the TBA specimen has a tendency to twist, especially during a transition, causing a drift in the baseline, the equation describing the actual amount of deflection at any point in time is more closely represented by Eq. (4).

$$\theta = \theta_o e^{-\alpha t}\cos(\omega t + \phi) + \beta t + C \tag{4}$$

The differential equation corresponding to Eq. (4) is used in the linear least mean squares analysis of the digitized data,

$$\frac{d^2\theta}{dt^2} + 2\alpha\frac{d\theta}{dt} + (\alpha^2 + \omega^2)\,\theta - C(\alpha^2 + \omega^2) - 2\alpha\beta - \beta(\alpha^2 + \omega^2)t = 0 \tag{5}$$

which may be simplified to

$$D = \frac{d^2\theta}{dt^2} + A_1\frac{d\theta}{dt} + A_2\,\theta + A_3 t + A_4 = 0 \tag{6}$$

where A_i are the parameters fitted by the analysis, and

$$\alpha = A_1/2$$

$$\omega = [A_2 - (A_1/2)^2]^{1/2}$$

(The significance of D will be discussed below.) The derivative values of θ at any point n were calculated numerically from an extension of Newton's Forward Formula, which utilizes 5 consecutive points to obtain the first and second derivatives (6). These derivative formulae are refinements of the expressions used in Part I of this paper (3) and are given by

$$\frac{d\theta_n}{dt} = (-\theta_{n+2} + 8\theta_{n+1} - 8\theta_{n-1} + \theta_{n-2})/12h \tag{7}$$

$$\frac{d^2\theta_n}{dt^2} = (-\theta_{n+2} + 16\theta_{n+1} - 30\theta_n + 16\theta_{n-1} - \theta_{n-2})/12h^2 \tag{8}$$

where h is the step size.

LINEAR LEAST MEANS SQUARES ANALYSIS. The linear least mean squares fitting of N experimental data to the differential form of the equation of motion involves minimization of the summation,

$$S = \sum_{n=3}^{N-2} v_n^{\,2} = \sum_{n-3}^{N-2} (f_n - D_n)^2 \tag{9}$$

where $v_n^{\,2}$ are the squares of the approximation errors and f_n is derived from the experimental data,

$$f_n = \frac{d^2\theta}{dt_n^{\,2}} + A_1\frac{d\theta_n}{dt_n} + A_2\theta_n + A_3 t_n + A_4 \tag{10}$$

The respective derivatives are defined by Eqns. 7 and 8. t_n is n divided by the scan rate. D_n is identically zero by definition (Eqn. 6). The limits of the summation (n = 3 to N - 2) have been dictated by the method for obtaining the derivatives. From the requirement that S is minimized, it follows that,

$$\frac{\partial S}{\partial A_i} = 2 \sum_n v_n \frac{\partial v_n}{\partial A_i} = 0 \qquad (i = 1 \text{ to } 4) \qquad (11)$$

This results in four simultaneous linear equations which may be presented in matrix notation:

$$\begin{bmatrix} \sum_n \dot{\theta}_n^2 & \sum_n \dot{\theta}_n \theta_n & \sum_n \dot{\theta}_n & \sum_n \dot{\theta}_n t_n \\ \sum_n \dot{\theta}_n \theta_n & \sum_n \theta_n^2 & \sum_n \theta_n & \sum_n \theta_n t_n \\ \sum_n \dot{\theta}_n & \sum_n \theta_n & \sum_n 1 & \sum_n t_n \\ \sum_n \dot{\theta}_n t_n & \sum_n \theta_n t_n & \sum_n t_n & \sum_n t_n^2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{bmatrix} = \begin{bmatrix} -\sum_n \ddot{\theta}_n \dot{\theta}_n \\ -\sum_n \ddot{\theta}_n \theta_n \\ -\sum_n \ddot{\theta}_n \\ -\sum_n \ddot{\theta}_n t_n \end{bmatrix}$$

The above expression can be solved by a matrix inversion procedure to determine the values of the coefficients A_i. A_1 and A_2 contain the damping and frequency parameters (see above).

REFINEMENT OF DATA REDUCTION TECHNIQUE. Even with the use of low pass signal filters (cut-off frequency of 2 Hz), the initial automatic data reduction technique was found to produce data with unacceptable scatter in the damping, although the frequency data was acceptable (Figure 2). (The two rigidity curves in Figure 2 are the consequence of thermohysteresis - see below.) The first refinement involved truncation of the data so that an integral number of cycles was analyzed. The excess points were eliminated from further computation. Effectively this is a digital filtering technique which was empirically found to improve the signal-to-noise ratio. Frequency, damping, and the number of points comprising the maximum number of integral cycles are determined by an iterative process which typically converges after 3 cycles. Computer simulations have demonstrated that this operation is theoretically unnecessary for noise-free data.

Once this change had been incorporated into the data reduction program, the reduced data for the damping appeared to be on two distinct levels (Figure 3). This phenomenon was traced back to the fact that the incoming data at the initiation of data storage had either a zero degree or 180 degree phase angle associated with it, corresponding to a maximum and a minimum in the oscillations of the analog damped wave. After the data acquisition program was modified to accept data only at a phase angle of zero degrees, the reduced data were on a single curve (Figure 4). Upon even closer examination, the damping curve showed signs of small discontinuities which were traced back to the procedure used to adjust for the baseline drift due to specimen twisting. This corrective action is employed to compensate for the non-linearity of the response curve of the optical transducer. This instrumentation problem has been solved manually (Figure 5) and a technique for automatic drift compensation is being developed (7). Alternatively, the computer itself can be programmed to compensate for non-linearities which can be incorporated into the equation of motion. With the increased sensitivity of the system, it is now essential to control precisely the temperature programming as fluctuations in the data are observable in regions in which there are non-constant rates of temperature change. As an example of the resolution of the experimental results, a linear expansion of the modulus data through a secondary transition is presented in Figure 6. The two different sets of data for decreasing and increasing temperature (thermohysteresis) are attributed to properties of the polymeric specimen *per se*, and not to the methods used in processing the data. This phenomenon will be discussed elsewhere (8).

COMMENT. The present system provides a powerful tool for the study of thermomechanical properties of polymeric materials and its flexibility allows

for extensive conceptual evolution of the experimental design. While this report presents preliminary data, further refinements of the system are in progress. These include upgrading of the TBA instrumentation, refinement of the data reduction procedure, optimization of the data acquisition parameters, as well as development of data analysis techniques for more quantitative interpretations of the thermomechanical spectra.

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ACKNOWLEDGMENT. This work was supported in part by the National Aeronautics and Space Administration (Grants NGR 31-001-200 and NGR 31-001-221), by the Chemistry Branch of the Office of Naval Research (Contract N00014-67-A-0151-0024, Task No. NR 356-504) and by the Air Force Materials Laboratory (Contract F33615-72-C-1590). It is our pleasure to thank Messrs. Robert Cassidy and Peter Olenick of the Princeton University Computer Center for the development of the necessary system software and Mr. Colin Bell of the Natural Rubber Research Products Association, U.K., for his contributions in the early stages of this work.

FIGURE CAPTIONS

Figure 1A - Digitized damped wave for polymer specimen in the glassy region.
Figure 1B - Digitized damped wave for the same polymer specimen in a transition region.
Figure 2 - Syndiotactic PMMA. Unacceptable scatter in the data. Logarithmic decrement and relative rigidity vs. T. Prehistory: heat to 423°K. Experiment: 423 → 93 → 423°K. Rate: 2°K/min.
Figure 3 - Polyethylenecarbonate (β-peak). Corrections made for an integral number of cycles. Logarithmic decrement and relative rigidity vs. T. Prehistory: heat to 393°K. Data: 236→93→247°K. Rate: 2°K/min. Reference: Udipi, K., Gillham, J. K., and Tsuruta, T., "Poly(ethylene carbonate) and Poly(propylene carbonate): Transitions and Thermomechanical Spectra", J. Appl. Polym. Sci., (in press).
Figure 4 - Same experiment as for Figure 3. Corrections made for phase angle.
Figure 5 - Syndiotactic PMMA (new specimen). Corrections made manually for non-linearity of optical transducer. Logarithmic decrement and relative rigidity vs. T. Prehistory: heat to 473°K. Experiment: 473 → 93 → 473°K. Rate: 2°K/min.
Figure 6 - Same experiment as for Figure 5. Expanded scale - relative rigidity vs. T.

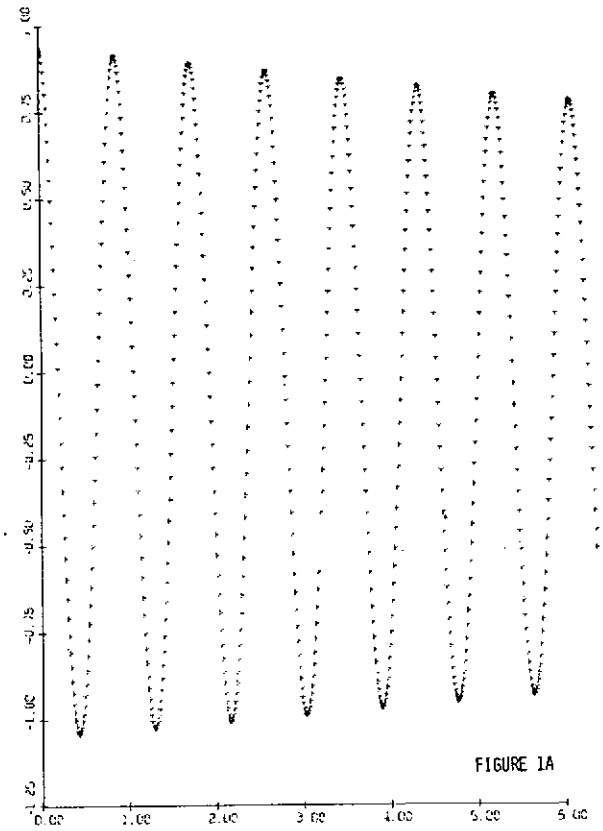
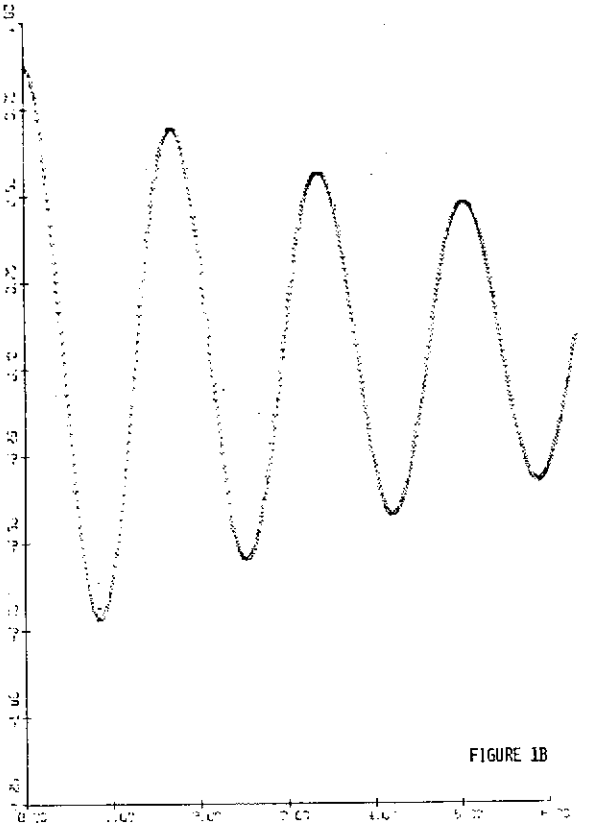


FIGURE 1A



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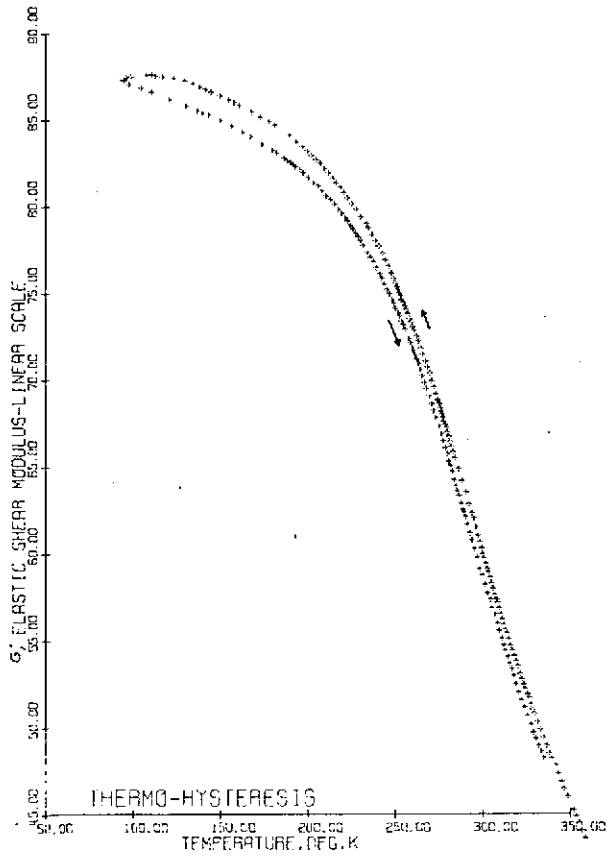
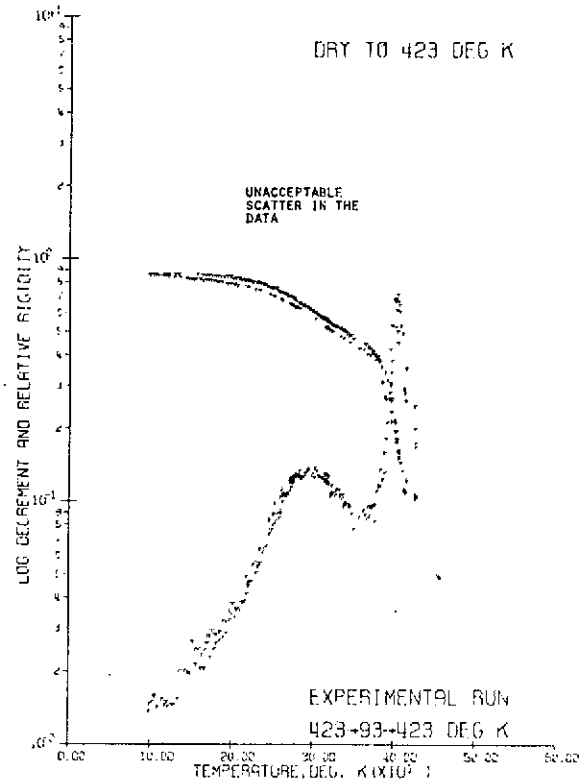


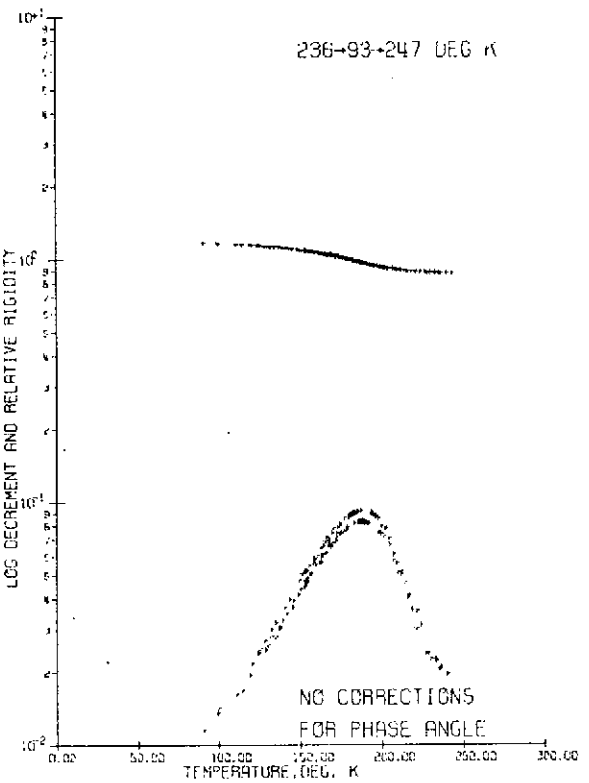
SYNDIOTACTIC PMMA

FIGURE 6



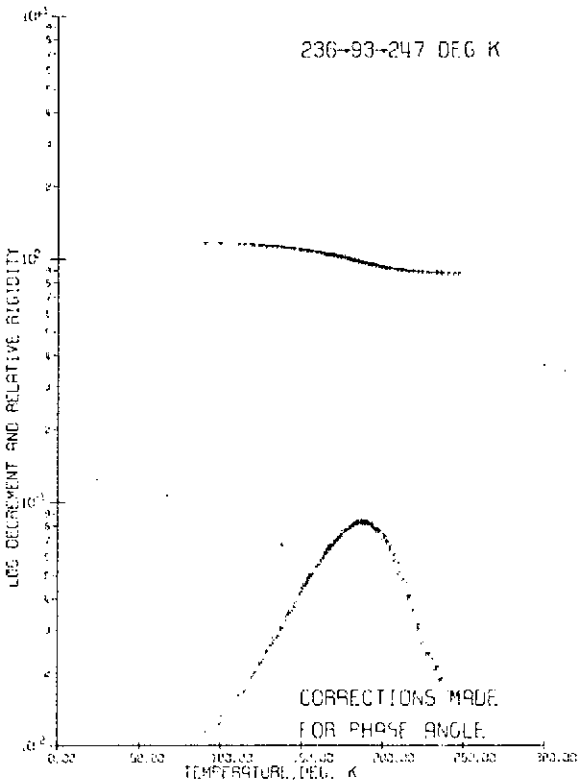
SYNDIOTACTIC PMMA

FIGURE 2



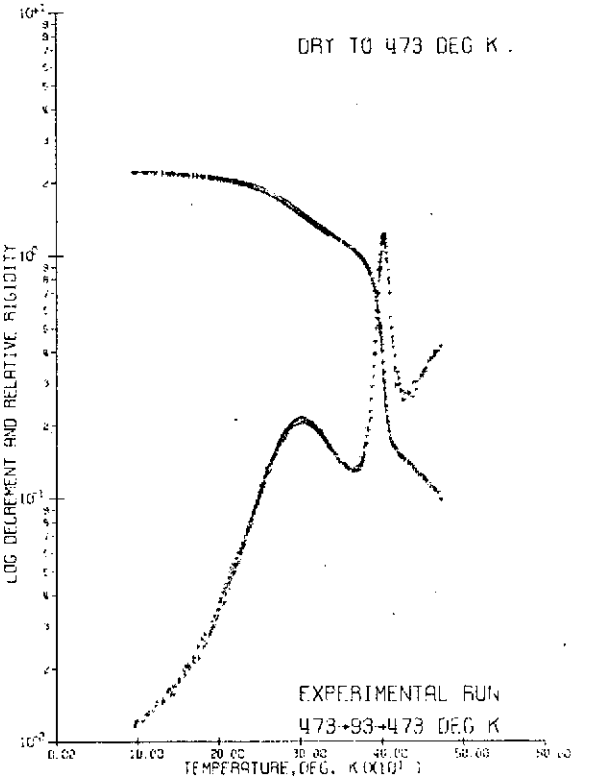
POLYETHYLENE CARBONATE (BETA PEAK)

FIGURE 3



POLYETHYLENE CARBONATE (BETA PEAK)

FIGURE 4



SYNDIOTACTIC PMMA

FIGURE 5

LOW FREQUENCY THERMOMECHANICAL SPECTROMETRY OF POLYMERIC MATERIALS: COMPUTERIZED TORSIONAL BRAID EXPERIMENTS. III. TACTIC POLYMETHYLMETHA - CRYLATES. J. K. Gillham, and S. J. Stadnicki, Polymer Materials Program, Department of Chemical Engineering, and Y. Hazony, Computer Center, Princeton University, Princeton, N. J. 08540

INTRODUCTION. An automated instrument for torsional braid analysis (TBA), which includes on-line reduction of data (1,2), was used to characterize amorphous syndiotactic, atactic and isotactic polymethylmethacrylates at about 1 Hz in the temperature range 473 → 93°K. Manually reduced TBA data for the same polymers, together with documentation of the synthesis of the polymers, their average molecular weights ($\bar{M}w$ and $\bar{M}n$), and tactic contents (syndio-, hetero-, and iso-) have been reported previously (3). Characteristics of the stereoregular polymethylmethacrylates are summarized in Table I which includes assignments for the Tg and Tβ transitions made on the basis of the present data.

Polymer-braid composite specimens were prepared by impregnating multifilamented glass braids in 10 percent solutions of the polymers in tetrahydrofuran (THF, b.p. 66°C). Solvent was removed by heating the composite specimens to 473°K at the rate of 2°K/min. in flowing dry nitrogen gas (obtained from a Dewar of liquid nitrogen). The thermomechanical spectra were then obtained in a nitrogen atmosphere while cooling the solvent-free braid composites to 93°K and then heating to 473°K at a rate of 2°K/min. The spectra for the syndiotactic, atactic, and isotactic polymethylmethacrylates on cooling are presented in Figures 1, 2 and 3, respectively, in terms of the temperature dependence of the relative rigidity (∿ elastic shear modulus, G') and logarithmic decrement (Δ). This is the conventional mode for presentation of torsional pendulum data.

MODES OF DATA PRESENTATION. Whereas logarithmic decrement and relative rigidity as a function of temperature are presented in Figures 1-3, Figures 4-6 illustrate the same data in terms of G" and dG'/dT. This latter mode of data presentation has been found (1) to be the most consistent in the assignment of transition temperatures. A summary of the transition temperatures for all three PMMA samples as determined from the maxima of the various modes of data exposition is found in Table II. The assignment of transition temperatures appears to conform to the following trend:

$$T(\tan\delta) = T(\Delta) \geq T(\alpha) \geq T(G'') \approx T(dG'/dT).$$

EFFECT OF TACTICITY ON TRANSITIONS. The general characteristics of the TBA spectra compare well with published work (4), exhibiting two distinct loss peaks above 93°K. Temperatures below 93°K are not accessible with the present apparatus. The glass transition temperatures (as determined from G" and dG'/dT data) are assigned using the sharp loss peaks at 399°K (0.68 Hz), 384°K (0.67Hz), and 334°K (0.81 Hz) in syndiotactic, atactic, and isotactic PMMA, respectively. Each loss peak is accompanied by a large rise in rigidity with decreasing temperature. The glassy-state loss peaks (β-peaks) in syndiotactic and atactic PMMA are broad and centered at 294°K (1.25 Hz) and 297°K (1.24 Hz), respectively. The β relaxation in isotactic PMMA is ill-defined and appears as a shoulder at around 280°K (1. 4 Hz). The β-peak for each of these polymers is accompanied by a small but distinct rise in the rigidity with decreasing temperature. It should be noted that the absolute value of the relative rigidity at low temperatures (∿ 93°K) is about the same for all specimens, indicating an approximately equal amount of polymer in each composite specimen.

The secondary transitions appearing below Tg have been attributed to the motion of ester side groups which may include localized motions of the main polymer chain (3,4,5,6).

The fact that the glass transition temperature of syndiotactic PMMA is some 65°K higher than that of isotactic PMMA, despite a higher density for the latter in the glassy state, has been considered to be due to intermolecular geometrical interlocking of the syndiotactic chains (3,7), or alterna-

tively to differences in intramolecular chain stiffness (4). It should be noted that the molecular weight of the isotactic sample is some 30 times that of both the syndiotactic and atactic forms which, if anything, should have the effect of raising the glass transition temperature. The influence of molecular weight on the intensity of the β-peak is not known. The similarity of the thermomechanical spectra of atactic and syndiotactic PMMA was not unexpected due to the small difference between them in microtacticity content (50% versus 70% syndiotacticity).

EFFECT OF PREHISTORY. A problem of concern to the mechanical spectroscopist is the determination of the most suitable conditioning variables for specimen preparation. To obtain the relaxation spectrum of a polymer *per se*, it is necessary to prepare the specimen in a manner which removes all occluded volatiles (e.g., solvent and absorbed moisture) without causing crosslinking or degradation. Thermogravimetric analysis (TGA), often used to complement thermomechanical spectroscopy, is employed to determine temperature regions in which weight loss occurs. A more informative approach determines the volatile components upon heating by employing a pyrolyzer in series with a mass chromatograph (8) and an "on-the-fly" infrared spectrophotometer .

Thermogravimetric analysis of isotactic PMMA showed a 1-2% weight loss in heating to 473°K after predrying to 423°K. Mass chromatographic analysis of the volatile products of heating in the 433 to 473°K range indicated one major volatile component having a molecular weight of about 93. Monomer was not detected until above 523°K. A check of the synthesis procedure (3) indicated that petroleum ether (C_5s and C_6s) was used as one of the solvents for purification and was probably the volatile component in question.

Figure 7 shows the thermomechanical spectra (logarithmic decrement vs. temperature) of a single specimen of syndiotactic PMMA after preheating first to 423°K and then to 473°K, respectively, at the rate of 2°K/min. Plasticization by bound solvent is apparent. The glass transition temperature of the specimen dried more thoroughly is some 11 degrees higher. The secondary transition (298°K) does not appear to have been affected, but the observed differences in the loss levels at temperatures between Tβ and Tg and also at ∿100°K are attributed to the presence of the small amount of diluent.

EFFECT OF THERMAL CYCLING. Figure 8 presents the thermomechanical spectra, G" and G' versus temperature for syndiotactic PMMA preheated to 473°K. Experimental data is displayed during cooling to 93°K and subsequent heating to 473°K at 2°K/min. The thermohysteresis in the G" loss data at low temperatures may be due either to inaccurate temperature assignment (thermal lag between the thermocouples and specimen) or to microcracking of the composite specimen. Correct temperature assignment is indicated at higher temperatures since the data lie on one curve. Figure 9 illustrates a portion of the elastic shear modulus curve, G', (shown in Figure 8) on an expanded linear scale. The irreversibility in the rigidity, upon first cooling to 93°K and then heating, is attributed to microcracking of the composite specimen. The mechanism leading to these cracks may involve the thermal stresses which arise from the different coefficients of contraction of the two phases of the specimen. Polymers with bulky side groups are observed to be susceptible to cracking (3) probably because there are weaker cohesive forces between chains, per unit cross-sectional area, than for more compact molecules (9, 10). The fracture mechanism may also involve penetration of trace amounts of water into small pores and its subsequent expansion upon freezing. The moisture content of the "dry" nitrogen atmosphere was measured to be about 5 PPM which corresponds to a frost point of about 207°K. In a similar manner, occluded solvent could form voids upon freezing which could be sites for initiation of cracks. Alternatively, cracks may originate from the stress applied to initiate pendulum oscillations, particularly at low temperatures where the side group motions are frozen out. In any case, the loss level would be expected to be higher after a crack, reflecting an increase in the ability of the composite specimen to dissipate energy on deformation. In a like manner, the elastic modulus curve would be expected to be at a lower level on heating after cracking, indicating a less rigid structure. Indeed,

this is what is found.

EFFECT OF H_2O. Atactic PMMA was conditioned overnight at RT in a flowing N_2 atmosphere containing 300 PPM H_2O (~1.2% R.H.). A hygrometer (Panametrics Model 2000), capable of measuring to less than 1 PPM, was used to monitor the water content continuously at the exit port of the TBA apparatus. The specimen was then taken through the temperature cycle, RT → 473 → 93 → 473°K at 2°K/min (Figure 10). The "wet" conditioning atmosphere was changed to a flowing dry atmosphere containing less than 5 PPM H_2O at 303°K during the cooling mode. The presence of this small amount of water had no effect on Tg, but a small γ-peak centered around 170°K had developed. The derivative form of the logarithmic decrement, $d\Delta/dT$, illustrates the presence of the γ-transition in another way (Figure 11).

DISCUSSION. Use of G" as the measure of loss in dynamic mechanical experiments has been shown herein to give values for transitions which are identical with those obtained from the maxima of the derivative of G' with respect to temperature. Use of G" rather than other loss parameters appears to be particularly effective for investigating secondary transitions by reducing the response of the Tg relaxation. The G" mode would also appear to be the logical function to use in comparing dynamic mechanical and dielectric loss (ε") data. A further advantage in its use appears to lie in the flat baseline of G" vs. temperature curves which could provide opportunities for comparing peak shapes and for resolving peaks quantitatively.

For example, the data of Figure 12, which compares G" vs. T plots for the syndiotactic, atactic and isotactic polymers, shows that the relative intensity of the β-peak decreases drastically with increasing isotactic content. The speculation could be made that completely isotactic polymer would not display a β-peak. The similar shape of the G" vs. T curves for the three polymers (Figure 12) indicates that the basic mechanism of the β-process is the same for the three polymers and supports the validity of extrapolating in this fashion. The absence of a β-peak is noted for polyisobutylene (11) which also has an anomalously low glass transition temperature. The latter has been ascribed to a lack of spacial sites for geometrical intermolecular interlocking along the molecule (7) and this reason has also been suggested to explain the low Tg of isotactic PMMA (3).

The data presented above are preliminary. Nevertheless the power of the computerized experiment and the scope of the investigation which may be undertaken have been demonstrated.

ACKNOWLEDGMENT. This work was supported in part by the National Aeronautics and Space Administration (Grants NGR 31-001-200 and NGR 31-001-221), by the Chemistry Branch of the Office of Naval Research (Contract N00014-67-A-0151-0024, Task No. NR 356-504), and by the Air Force Materials Laboratory (Contract F33615-72-C-1590). Gratitude is expressed also to Dr. E. Gipstein for providing the characterized polymers.

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Table I
Characteristics of Stereoregular Polymethylmethacrylates

Molecular Weight (3)	Syndiotactic	Atactic*	Isotactic
$\overline{M}w$	83,200	105,000	2,780,000
$\overline{M}n$	62,700	48,000	1,200,000
$\overline{M}w/\overline{M}n$	1.33	2.15	2.29
Tactic Content (%) (3)			
syndio-	70.1	50.6	0
hetero-	26.1	41.7	8.5
iso	3.8	7.7	91.5
Transition Data			
Tg, °K†	399 (0.68)	384 (0.67)	334 (0.81)
T_β, °K (Hz)#	294 (1.25)	297 (1.24)	∿ 280 (1.4)
T_β/Tg	0.74	0.77	> 0.84
Ratio of Peak Heights of the T_β to Tg Transition#	0.73	0.60	0.19
Synthesis (3)			
initiator	fluorenyl lithium	*	phenylmagnesium bromide
$T_{synthesis}$, °C	-70		0

†Determined from G" and dG'/dT loss data (decreasing temperature).
#Determined from G" loss data (decreasing temperature).
*Source: Cellamer Associates (3).

Table II
Transition Data of Stereoregular Polymethylmethacrylates*

PMMA	dG'/dT	G"		Δ		tanδ		α	
	Tg	Tg	Tβ	Tg	Tβ	Tg	Tβ	Tg	Tβ
Syndiotactic	399	399	294	403	298	403	298	400	298
Atactic	384	384	297	388	297	388	297	384	297
Isotactic	334	334	∿280	336	∿285	336	∿285	336	∿285

*Loss maxima in °K (decreasing temperature data).

FIGURE CAPTIONS

Figure 1. Syndiotactic PMMA.
Figure 2. Atactic PMMA.
Figure 3. Isotactic PMMA.

Logarithmic decrement and relative rigidity vs. T. Prehisotry: heat to 473°K. Experiment: 473 → 93°K. Rate: 2°K/min.

Figure 4. Syndiotactic PMMA.
Figure 5. Atactic PMMA.
Figure 6. Isotactic PMMA.

G" (upper) and dG'/dT (lower) vs. T. Same experiments as for Figures 1, 2 and 3, respectively.

Figure 7. Syndiotactic PMMA. Effect of thermal prehistory.

Logarithmic decrement vs. T.
Prehistory: heat to 423°K (x) and 473°K (+), (same specimen).
Experiment: cool to 93°K. Rate: 2°K/min.

Figure 8. Syndiotactic PMMA. Thermohysteresis.

G" and G' vs. T. Prehistory: heat to 473°K. Experiment: 473 → 93 → 473°K. Rate: 2°K/min.

Figure 9. Syndiotactic PMMA. Thermohysteresis.

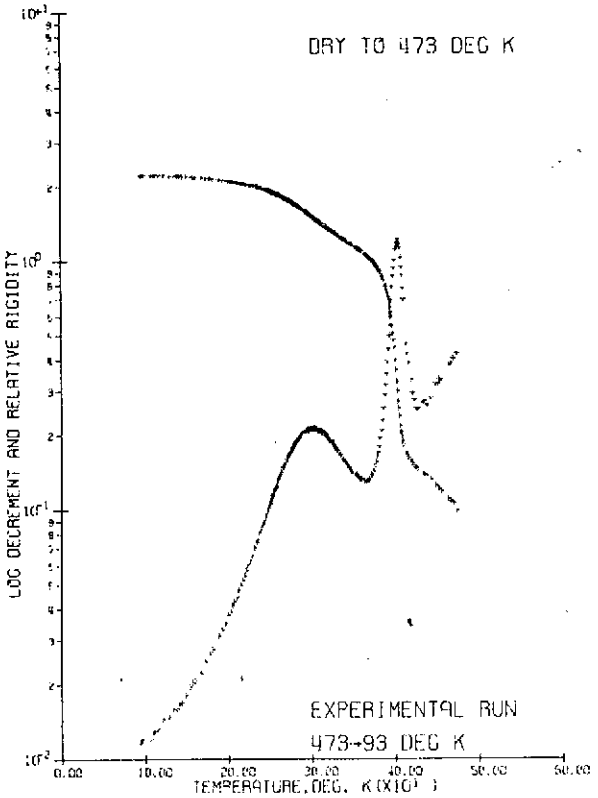
G' vs. T (linear scale). Same experiment as for Figure 8.

Figure 10. Atactic PMMA. Effect of H_2O (300 PPM).

Logarithmic decrement and relative rigidity vs. T. Prehistory: see text. Experiment: 473 → 93 → 473°K. Rate: 2°K/min.

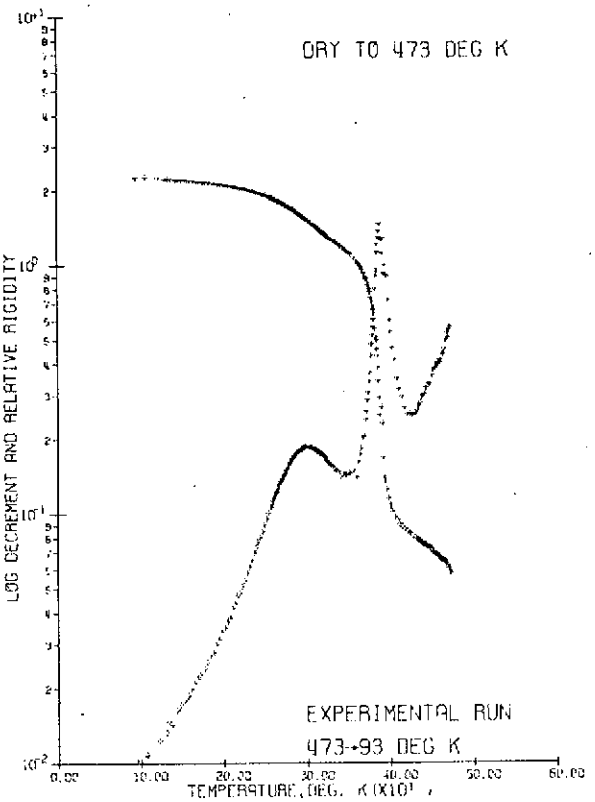
Figure 11. Atactic PMMA. Effect of H_2O (300 PPM). Derivative of logarithmic decrement vs. T. Same experiment as for Figure 10 using data for 93 → 473°K.

Figure 12. Syndiotactic, Atactic and Isotactic PMMA. G" vs. T.
Prehistory: RT → 473. Experiment: 473 → 93°K.
Rate: 2°K/min.



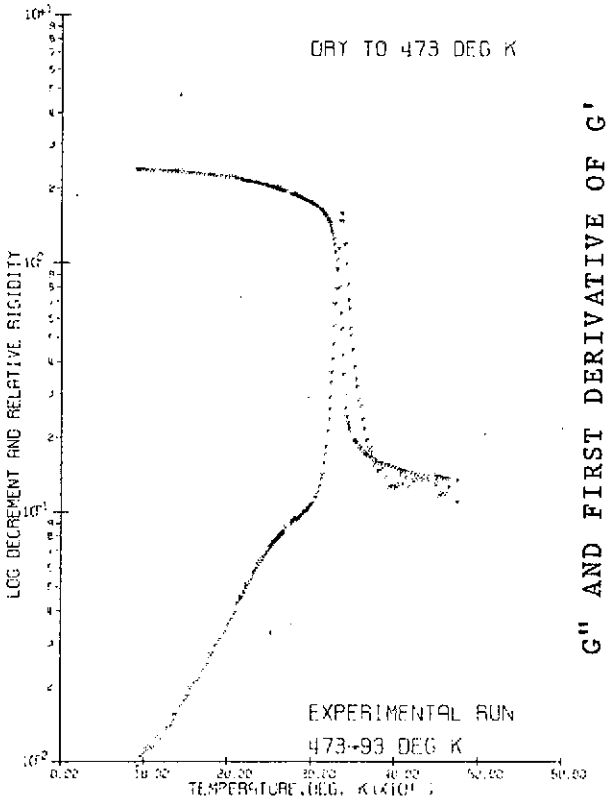
SYNDIOTACTIC PMMA

FIGURE 1



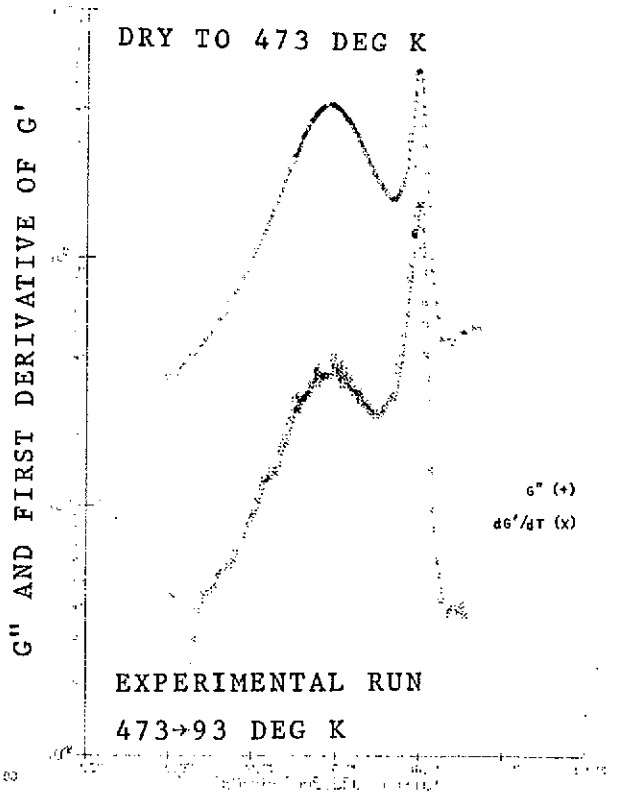
ATACTIC PMMA

FIGURE 2



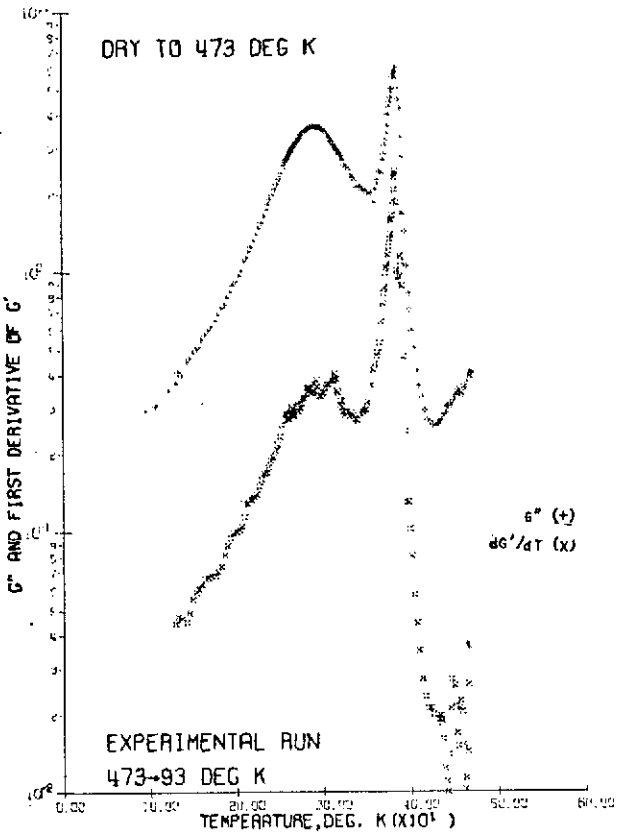
ISOTACTIC PMMA

FIGURE 3



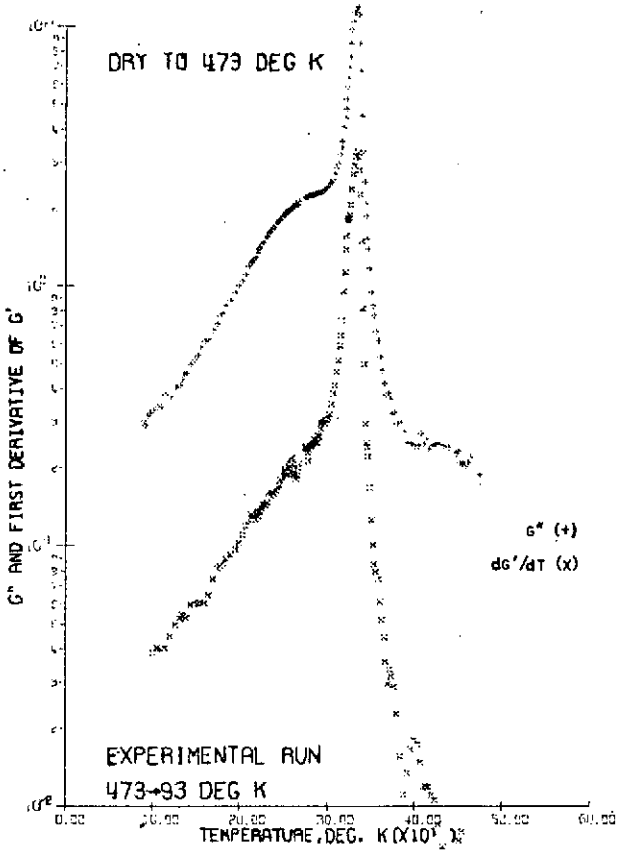
SYNDIOTACTIC PMMA

FIGURE 4



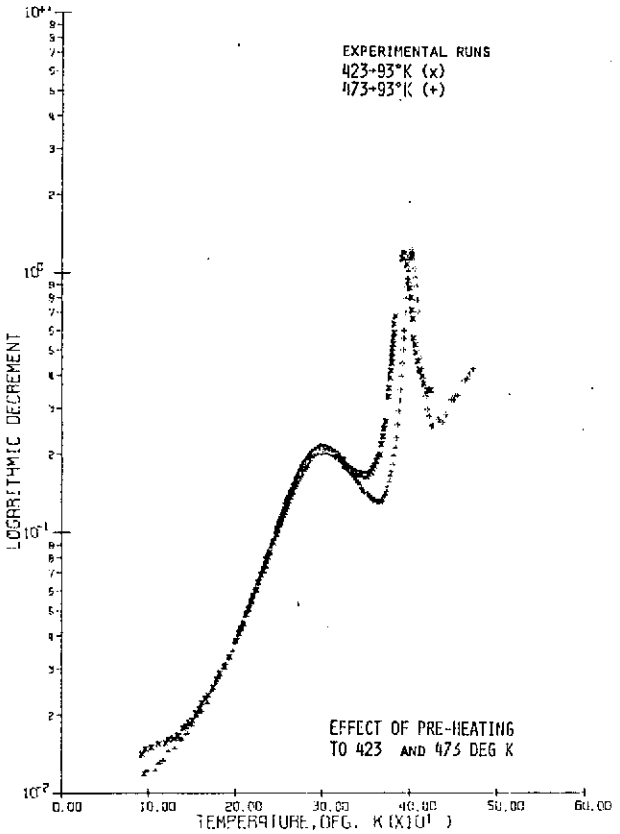
ATACTIC PMMA

FIGURE 5



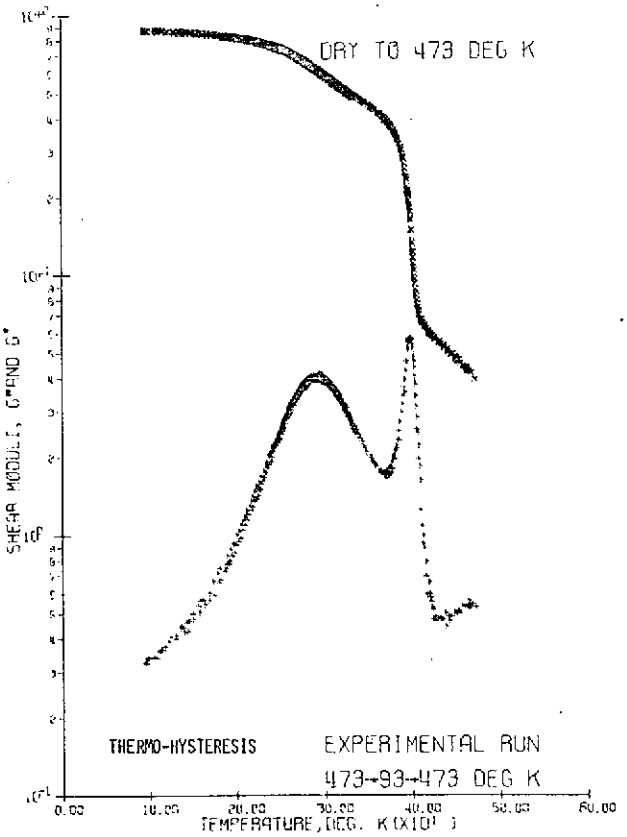
ISOTACTIC PMMA

FIGURE 6



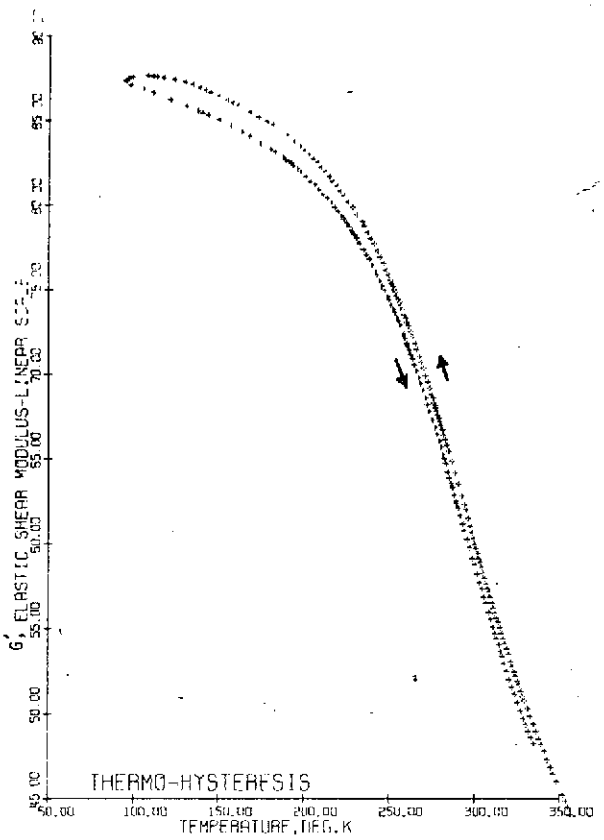
SYNDIOTACTIC PMMA

FIGURE 7



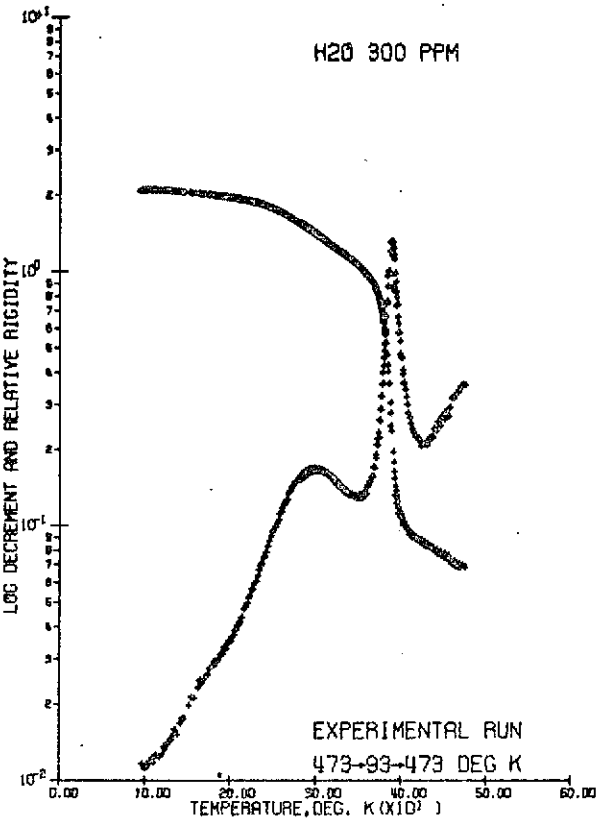
SYNDIOTACTIC PMMA

FIGURE 8



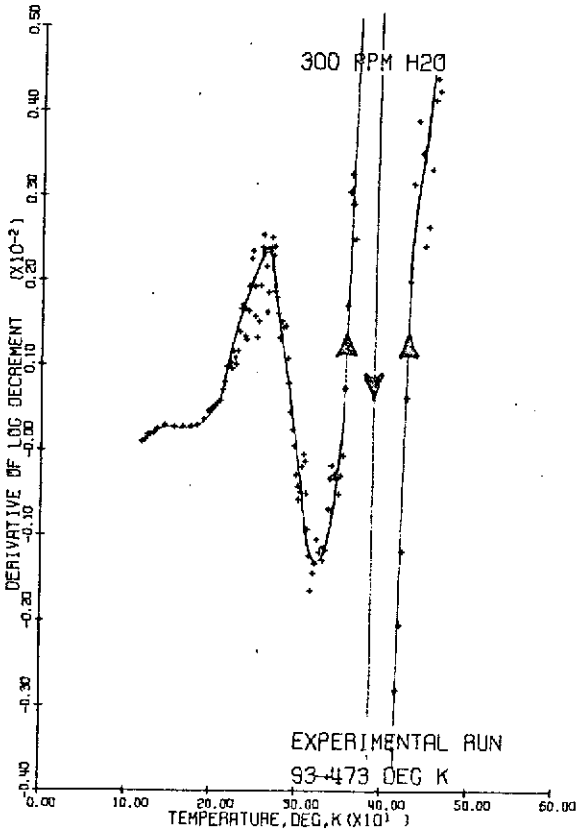
SYNDIOTACTIC PMMA

FIGURE 9



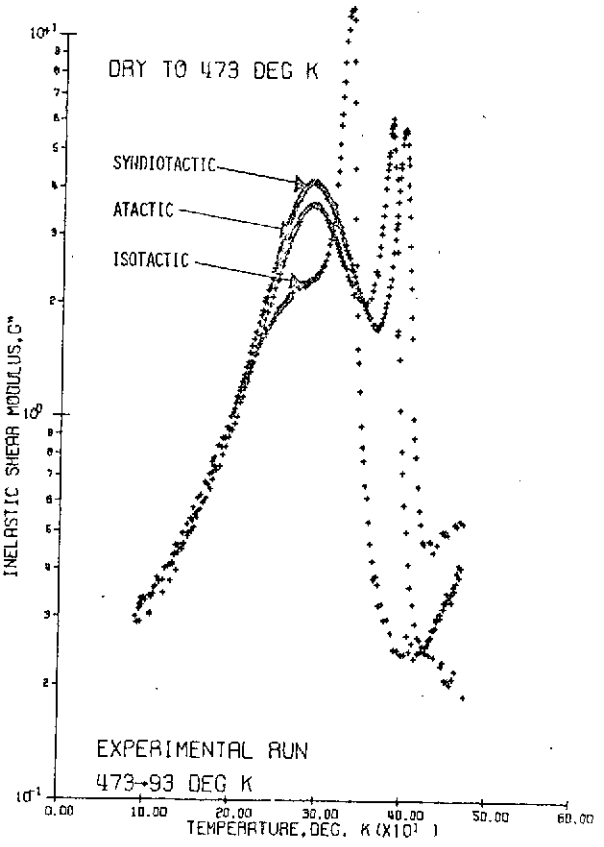
ATACTIC PMMA

FIGURE 10



ATACTIC PMMA

FIGURE 11



TACTIC PMMAS

FIGURE 12