

Dynamic Spring Analysis and Its Application to the Polystyrene Melt Relaxation

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Synopsis

The technique of dynamic spring analysis (DSA) was employed to obtain the storage and loss moduli of polystyrene samples in the glassy and rubbery regions of viscoelastic response. These results were compared with dynamic shear moduli from eccentric rotating disc experiments by time-temperature superposition to determine the degree and range of applicability of DSA. The storage moduli gave semiquantitative agreement over the rubbery region, while the loss moduli agreed over a narrower region of response. An apparent relaxation above the glass transition temperature of polystyrene was attributed to the evolution of solvent from the polymer-spring composite samples studied.

INTRODUCTION

The study of the viscoelastic properties of materials with insufficient strength to be analyzed in the tensile mode of the Rheovibron dynamic viscoelastometer has presented experimental problems to those studying elastomeric materials, crosslinking reactions, low molecular weight polymers, and other systems of low modulus. Several techniques have been developed which are capable of aiding the experimenter in such a viscoelastic analysis. A brief discussion of three techniques will be given here.

A technique which has been extensively applied is torsional braid analysis (TBA), developed by Gillham and co-workers.¹⁻³ By this technique, studies have been made of viscoelastic behavior of many polymers at high temperatures, curing reactions of numerous types, and the effect of additives and aging upon polymer viscoelastic properties. In a recent investigation of a liquid-liquid relaxation in atactic polystyrene, TBA was employed extensively to determine the effect of molecular weight and polydispersity on the temperature at which this transition occurred.^{4,5} This method of analysis suffers from several disadvantages, the principal ones being a lack of quantitative information about the complex modulus and its loss and storage components, the inability of frequency to be varied over a wide range, the variability of the frequency during a test.

Other attempts to obtain information on dynamic viscoelastic properties of rubbery polymers and polymer melts have focused upon modification of the Rheovibron. A study of the rheological properties of styrene-ethylene oxide block copolymers by Erhardt and co-workers⁶ included a modification of the Rheovibron DDV-II which produced a shearing mode of deformation. More recently, Shah and Darby⁷ have employed the Rheovibron DDV-III in a study of dynamic moduli of polymer melts, again by modification to give a shear deformation.

An interesting approach to monitoring the curing reaction of a thermosetting resin was described by Naganuma and co-workers.^{8,9} In this method, termed dynamic spring analysis (DSA), the hardening reaction was followed by application of a small oscillating displacement to a spiral spring used to contain the sample, and the change in modulus with temperature was characterized. This technique was subsequently employed in a study of commercial adhesive curing, radical polymerization, and solvent evaporation from a polymer solution.¹⁰ The authors also compared the viscoelastic response of polycarbonate obtained by DSA to that resulting from a thin film analyzed in the tensile mode on the Rheovibron, and obtained the dynamic viscoelastic response of polystyrene and high-density polyethylene in a demonstration of the versatility of this method of analysis.

In previously published treatments of DSA data, no attempt to obtain the complex modulus or its storage and loss components was made. The relative modulus of the polymer-spring sample to the spring alone was the only measure of strength discussed. This quantity is similar to the relative rigidity parameter defined as a measure of strength in TBA in that neither variable is an absolute measure of the modulus of a material. This work will show how the storage and loss modulus can be obtained from DSA by the assumption of a model for the deformation. With the aid of the time-temperature superposition principle, moduli obtained in this manner from polystyrene test samples will be compared to those available from an analysis with the Rheometrics mechanical spectrometer to show the validity of this method of data reduction. An interesting phenomenon observed during comparison of these polystyrene data, an apparent relaxation in the liquid state above T_g , will be discussed in light of recent work on the liquid-liquid transition and studies of solvent evolution.

EXPERIMENTAL

Materials

The atactic polystyrene used throughout this work, unless otherwise noted, was supplied by the Monsanto Company. The molecular weight characteristics of this polymer were as follows: $\bar{M}_n = 9.0-9.5 \times 10^4$, $\bar{M}_w = 2.6-2.8 \times 10^5$, $\bar{M}_z = 4.7-5.0 \times 10^5$ g/mole. To ensure purity of the polymer, the polystyrene pellets were first dissolved in toluene, then precipitated with an amount of methanol eight to ten times the initial volume and dried under vacuum for three days at 90°C. Atactic polystyrene of narrow molecular weight distribution, obtained from the Pressure Chemical Company, was also employed in this study. Two molecular weights were used without further purification, 37,000 and 233,000 g/mole.

Rheometrics Mechanical Spectrometer Analysis

Samples were prepared in the form of 1-in.-diameter discs by compression molding at 220°C and 7×10^8 dynes/cm². Polystyrene discs 2.4 and 3.2 mm thick were prepared in this manner, as were samples 0.8 mm thick. The latter samples were kept under vacuum at 175°C for 42 hr to ensure thorough drying, while the former samples were removed from the press and quenched to room temperature.

Three discs 0.8 mm thick were required to obtain the minimum samples thickness.

The Rheometrics mechanical spectrometer,¹¹ a refinement of the orthogonal rheometer,¹² was used in the eccentric rotating disc (ERD) mode to obtain the shear modulus of the polystyrene discs. A platten diameter of 25 mm and sample thickness of 2.0–2.5 mm were employed throughout. A temperature range of 120–180°C inclusive was examined. Strains within the range of 0.2%–35% were used, depending upon the temperature and rotational speed, but operation was always maintained within the linear range of stress–strain response. Three or more determinations of the stress as a function of strain at a given temperature and frequency were conducted to verify that the range of strains examined was within the linear region. Nominal rotational speeds of 0.1, 0.4, 1, 4, and 10 rads/sec in both directions of upper platten rotation were employed. A theoretical treatment of the ERD mode of the Rheometrics mechanical spectrometer, a discussion of reduction of data, and an outline of the procedure to correct the data for instrument compliance has been given by Macosko and Davis.¹³

Rheovibron Dynamic Viscoelastometer Analysis

The helical springs used in dynamic spring analysis were made of either steel music wire or copper. The former were obtained from the National Camera Supply Corporation, while the latter were wound from 26-gauge armature wire about a rod of appropriate diameter. The ends were formed in a right-angle bend so that they could be inserted into small holes drilled in the center of the gripping surfaces of the Rheovibron DDV-II clamps to minimize possible slippage effects. In preparation of a sample for DSA, the spring was first immersed in a chromic acid solution, then stretched to achieve a pitch, P , of 0.05 or 0.1 mm. A solution of polystyrene in toluene, typically 0.04 g/ml, was applied dropwise, with the solvent allowed to evaporate before another drop was added. As this procedure progressed, the polymer formed a thin, continuous film between turns of the helically coiled spring. Application at a temperature of 55°C over a 3-hr period was found to be convenient, after which the samples were dried under vacuum. A schematic representation of a sample prepared in this manner is shown in Figure 1. This film samples tested were compression molded at 160°C and 7×10^8 dynes/cm² and allowed to cool slowly to room temperature. An appropriate length of a 0.3-mm-thick polystyrene film was also evaluated in the tensile mode on the Rheovibron.

The Rheovibron DDV-II, with a slight modification to the clamps as previously described, was employed in all DSA experiments as well as in the tensile mode for thin films. Samples were analyzed in a nitrogen atmosphere from ambient to about 240°C at a heating rate of 1.5°–2.0°C/min and at frequencies of 3.5, 11, and 110 Hz. Some samples were also studied while cooling from elevated temperatures, again at a nominal rate of 2.0°C/min. The DSA data were corrected for instrument compliance as discussed by Massa.¹⁴ This correction should be applicable at all temperatures since deformation of the sample in the clamps does not occur in this system. Inertial corrections were found to be small even at 110 Hz, and they were neglected in this analysis.

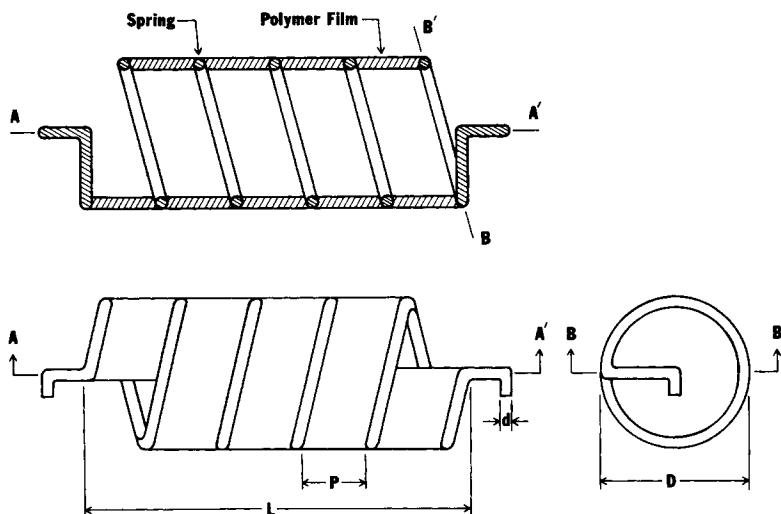


Fig. 1. Schematic representation of a DSA composite sample.

Thermal Analysis

A comprehensive interfaced pyrolysis–gas chromatographic peak identification system was employed to detect the evolution of solvent vapors during heating. Samples were prepared in the same manner as for DSA analysis. A length of 1.6 mm outer diameter aluminum tube was used to support the ends of the spring in the extended position. Samples were placed in a Spex MP-3 multipurpose thermal analyzer and heated at a rate of 4°–8°C/min to 250°C under a flowing helium atmosphere. The evolved gases were passed through a thermal conductivity detector (TCD) and a flame ionization detector (FID), then trapped on a glass bead column maintained at 77°K. Upon completion of heating, the trapped gases were back-flushed into a Varian 2700 gas chromatograph and passed through a 153-cm-long column of 1.5% OV-101 on Chromosorb G, 100–120 mesh. A Norcon 201 infrared prism spectrometer was used to record spectra of substances which gave rise to peaks on the GC trace. Uden and co-workers¹⁵ have given a thorough description of the entire system and its capabilities.

RESULTS AND DISCUSSION

A Quantitative Treatment of DSA

In previous work by Naganuma et al.,⁸ an attempt was made to outline a method of analysis for the behavior of the polymer–spring composite in order to obtain the modulus of the polymer as a function of temperature at a given frequency. It was found necessary to expand upon this analysis in order to obtain the storage and loss components of the polymer modulus. The central feature of the analysis by Naganuma, the assumption of a parallel model to describe the behavior of the composite under an applied strain, was retained.

For the two-component system of the spring S and the polymer P, the modulus of the composite C can be expressed as

$$M_C^* = \phi_S M_S^* + \phi_P M_P^* \quad (1)$$

where M_k^* denotes the complex modulus and ϕ_k , the volume fraction of each component k .

If this equation is solved for the polymer complex modulus M_P^* and since the sum of the volume fractions is unity, the following relation is obtained:

$$M_P^* = \frac{M_C^*}{\phi_P} + \frac{(\phi_P - 1)M_S^*}{\phi_P} \quad (2)$$

The complex modulus can be expressed as the product of two terms, the magnitude and the phase information, allowing eq. (2) to be rewritten as

$$|M_P^*| \exp(i\delta_P) = \frac{1}{\phi_P} |M_C^*| \exp(i\delta_C) + \frac{\phi_P - 1}{\phi_P} |M_S^*| \exp(i\delta_S) \quad (3)$$

The real and imaginary terms can be separately equated to yield expressions for the storage and loss moduli. An additional quantity, the relative modulus M_r , can be defined as the ratio of the magnitude of the composite modulus to that of the spring modulus, or in terms of an equation:

$$M_r = \frac{|M_C^*|}{|M_S^*|} \quad (4)$$

If the contribution of the spring to the composite loss behavior is small, the storage and loss moduli can be obtained from the following expressions:

$$M_P' = \frac{|M_S^*|}{\phi_P} [M_r \cos(\delta_C) + \phi_P - 1] \quad (5)$$

$$M_P'' = \frac{|M_S^*|}{\phi_P} M_r \sin(\delta_C) \quad (6)$$

The response of the spring can be seen to be totally elastic in nature by noting the low values of the loss tangent given in Figure 2.

The relative modulus and loss tangent behavior of the composite can be readily observed from the Rheovibron analysis. The equation used to calculate the

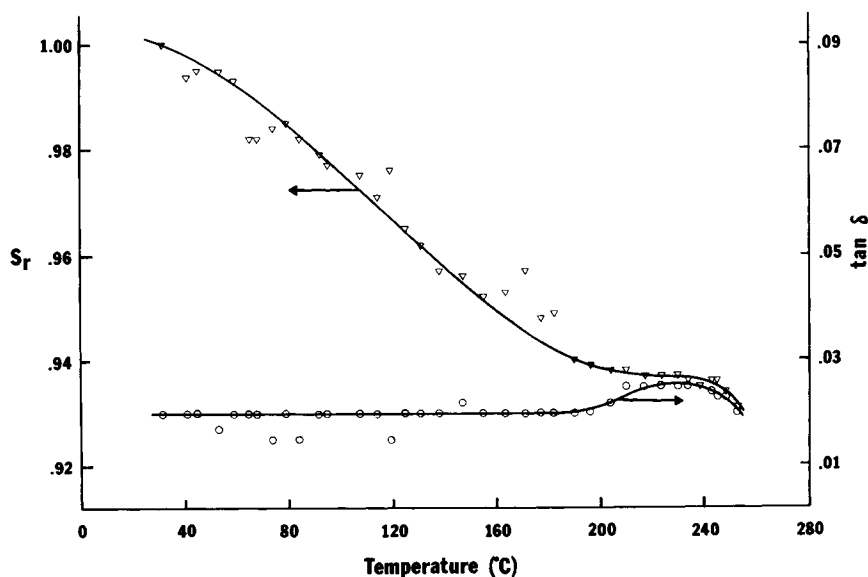


Fig. 2. Variation in relative spring modulus and loss tangent as function of temperature for the spring of sample C-1.

complex modulus from the rheovibron data can be found in the instruction manual for the instrument¹⁶ and is shown below:

$$|E^*| = \frac{2L \times 10^9 \text{ dynes/cm}^2}{A(DF - K) \times S} \quad (7)$$

where E^* is the dynamic complex modulus, L is the sample length, S is the sample cross-sectional area, A is the amplitude of the deformation, DF is the resultant force, and K is the instrument compliance correction. Provided that the spring and composite have the same length and cross-sectional area, the relative modulus can be expressed as

$$M_r = \frac{A_S(DF_S - K)}{A_C(DF_C - K)} \quad (8)$$

The composite and spring length and cross-sectional area will be equal if a spring evaluated alone at a length identical to the final composite length is used in preparation of the polymer-spring composite sample.

The modulus of the supporting spring can be calculated from eq. (7) if the length and the sample cross-sectional area are known. The length under consideration should involve only the coil or active segment of the spring, not the ends, which merely provide a means to secure the coil to the instrument clamps. The sample length is then the distance between the ends of the stretched coil. The cross-sectional area can be found by consideration of the total area of contact between the spring and the polymer sample. Provided that the film thickness and wire diameter are comparable, the cross-sectional area can be approximated by the area of an annulus having an inner diameter equal to the coil diameter less twice the wire diameter d and an outer diameter equal to the coil diameter D . The actual area of contact extends over a helix of n turns so that the total area of polymer-spring contact can be approximated by the area of the annulus multiplied by the number of turns of the spring. The length L and cross-sectional area S , expressed in terms of measurable dimensions of the spring, are given in eqs. (9) and (10), respectively:

$$L = n(P + d) \quad (9)$$

$$S = n\pi d(D - d) \quad (10)$$

A sample calculation for sample C-2 from Table I showed that the wire diameter and film thickness were indeed comparable. From geometrical considerations and the volume fraction of polystyrene, a film thickness of 0.32 mm was calculated, almost identical to the wire diameter for the spring in this sample, 0.30 mm.

A check of the measured spring constant as compared to that calculated from theory is desirable to ensure that the technique can be correctly applied. The force applied to a helical spring, F , can be related to the deformation x by the relation

$$F = kx \quad (11)$$

where k represents the spring constant. From an experiment conducted on the Rheovibron, both the dynamic force ΔF and the oscillating displacement ΔL were determined for a spring. The spring used in sample C-1 gave a resultant spring constant of $k = 4.72 \times 10^5$ dynes/cm. For helical extension or compression

TABLE I
Characteristics of Composite Samples

Sample code	Spring material	Wire diameter, mm	Outer diameter, mm	Number of turns	Pitch, mm	ϕ_p	Molecular weight $\bar{M}_n \times 10^{-3}$, g/mole	\bar{M}_w/\bar{M}_n	Drying history
C-1	copper	0.39	2.75	20	0.05	0.406	90-95	2.9	48 hr at 55°C
C-2	steel	0.30	3.30	23	0.10	0.278	90-95	2.9	24 hr at 90°C under vacuum
C-3	steel	0.30	3.30	21	0.10	0.431	90-95	2.9	17 hr at 170°C under vacuum
C-4	steel	0.30	3.30	22	0.10	0.352	37	1.06	10 hr at 90°C under vacuum
C-5	steel	0.30	3.30	23	0.10	0.350	233	1.06	10 hr at 90°C under vacuum
TA-6	steel	0.30	3.30	25	0.10	—	90-95	2.9	18 hr at 95°C under vacuum
TA-7	steel	0.30	3.30	20	0.10	—	90-95	2.9	22 hr at 95°C under vacuum
TA-8	copper	0.39	2.75	23	0.10	—	90-95	2.9	14 hr at 93°C under vacuum

springs, the spring constant can be calculated from an equation given by Faulpel¹⁷:

$$k = Gd^4/8nD^3 \quad (12)$$

where G is the shear modulus of the material which forms the spring. Substitution of the appropriate geometric variables and the shear modulus of copper into eq. (12) led to a value for the spring constant of $k = 4.34 \times 10^5$ dynes/cm. The experimentally determined and theoretically calculated values of the spring constant can be seen to differ by about 8%. This discrepancy could have arisen from variations in wire and coil diameter and effects of the spring ends upon the uniform distribution of the applied displacement. These effects were not taken into account in the analysis, but the agreement between theory and experiment is reasonable nevertheless.

Variation of the spring modulus and loss tangent with temperature is an important consideration, as it is desirable that the spring respond elastically at all temperatures with minimal change in strength. To characterize the temperature dependence of these spring properties, the spring from sample C-4 was evaluated from 30° to 250°C on the Rheovibron at 110 Hz. As an aid in the interpretation of these results, a relative spring modulus S_r can be defined as the ratio of the spring modulus at any temperature to the spring modulus at the initial temperature. A plot of the variation of S_r and the loss tangent with temperature for this spring is given in Figure 2. It is evident that the loss tangent was small and virtually independent of temperature while the relative spring modulus decreased slightly with increasing temperature. Since S_r at 253°C showed less than a 7% drop from the initial value, the spring modulus was assumed to remain constant during a composite test. Identical results were obtained when the experiment was repeated, an indication that these properties were not dependent upon the thermal history of the spring.

The type of modulus that can be obtained from dynamic spring analysis has not yet been specified. An examination of the degree of deformation expected from a typical spring can prove to be useful for this purpose. The oscillating displacement in the direction of the spring axis can be calculated for tensile deformation. Using data obtained for the spring of sample C-3, a value of $\Delta L = 1.58 \times 10^{-3}$ cm was obtained the total dynamic tensile displacement. The total angular deflection of one end of the spring with respect to the other, θ , can be calculated from a method given by Wahl¹⁸ for an elementary analysis as

$$\theta = 8nFD^3/Gd^4 \quad (13)$$

provided the shear modulus of the spring material, the applied load F , and certain geometric characteristics of a given spring are available. Again, for the spring of C-3, a total angular deflection of $\theta = 2.22 \times 10^{-3}$ cm was obtained. These results indicate that both tensile and shear deformation take place in the Rheovibron so the modulus obtained will be mixed in character, neither pure tensile nor shear. As can be seen from a comparison of eqs. (12) and (13), any attempt to reduce the amount of shear deformation will result in an increase in the spring constant and a resulting loss in sensitivity to variation of the polymer modulus in the composite sample. The values of moduli obtainable by DSA should lie somewhere between shear moduli obtained from ERD analysis in the Rheometrics mechanical spectrometer and tensile moduli determined with a thin film sample on the Rheovibron dynamic viscoelastometer.

Comparison of DSA and ERD Results

Several samples for DSA were prepared by the technique outlined in the experimental section. Table I contains sample composition and drying information. A sample dried at high temperature under vacuum, composite C-3, displayed the viscoelastic behavior shown in Figure 3 when heated to well above the glass transition temperature. The glass transition relaxation was found to occur over the range of 110°–120°C, as determined from the loss modulus maxima. An apparent activation energy of 94 kcal/mole was determined for this transition, in reasonable agreement with that reported by Baker and co-workers¹⁹ in a dielectric relaxation study of polystyrene, 86 kcal/mole.

The agreement of the magnitude of the storage and loss moduli between DSA and a tensile mode test on the Rheovibron was found to be rather poor at ambient temperature. The storage modulus of a polystyrene sample analyzed in the tensile mode of the Rheovibron at 25°C was found to be about 10^{10} dynes/cm². The same polymer evaluated by DSA yielded a storage modulus of about 3×10^7 dynes/cm². Part of this discrepancy can be accounted for by the mixed nature of the storage modulus obtained from DSA, this modulus being intermediate between the tensile and shear modulus values. At most, however, the mixed

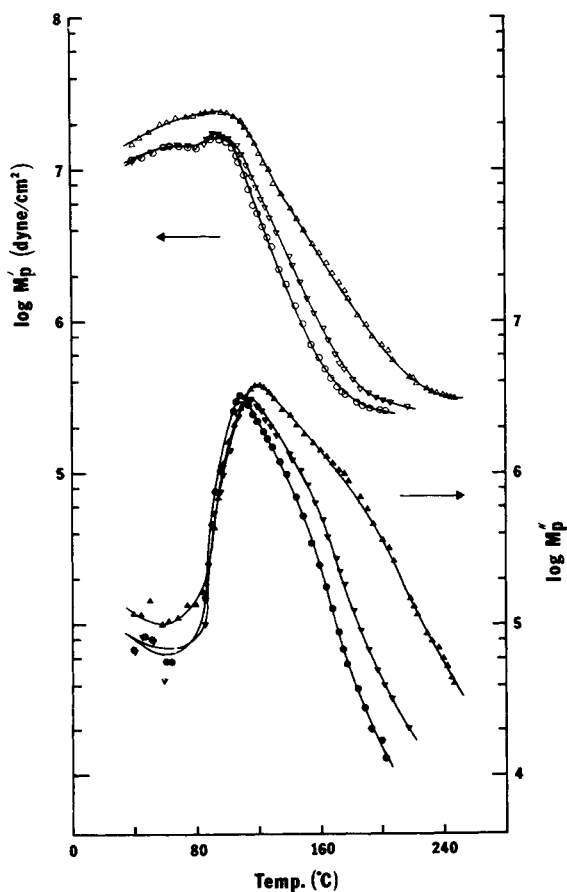


Fig. 3. Storage and loss modulus of polystyrene DSA sample C-3 as function of temperature: (O)(●) 3.5 Hz; (▽)(▼) 11 Hz; (Δ)(▲) 110 Hz.

nature of the DSA storage modulus could account for a factor of 3 difference between the DSA and tensile storage moduli. A similar disparity in the loss modulus values was also apparent.

A possible explanation for the hundredfold discrepancy remaining is a change in the nature of the deformation which occurs in a polymer-spring composite when the polymer can be characterized as glasslike in behavior. The high-modulus glassy polymer can cause the applied oscillating deformation to act on the spring ends rather than on the coil. The shape of the spring ends can change by small deformations at bends in the wire, accommodating the small displacement with less expenditure of energy than would be necessary to deform the coil and the polymer film between its turns. This type of behavior was not taken into account in the previous analysis outlined, as the spring ends were assumed to be rigid supports. As the glass transition temperature of the polymer is approached, the polymer modulus will decline and the oscillating deformation will then act on the coil and the polymer film. The lack of rigidity of the spring ends precludes the quantitative use of DSA to determine the moduli of glassy materials. This is not a serious problem, as glassy polymers can be routinely analyzed on the Rheovibron in the tensile mode. The agreement of modulus data available from DSA above the glass transition region with shear moduli available from Rheometrics ERD analysis will be considered in a subsequent discussion of time-temperature superposition.

In order to obtain the storage and loss components of the shear modulus of polystyrene at various temperatures and frequencies, a study of the material in the ERD mode of the Rheometrics mechanical spectrometer was undertaken. Two orthogonal stresses can be determined from an ERD analysis. The stress in the direction of the platten offset, σ_y , results from elastic forces which act in a direction opposite to the centerline displacement. A plot of σ_y versus strain will yield the storage modulus as its slope. The x direction stress σ_x results from forces of viscous dissipation. The loss modulus can be obtained from a plot of this stress versus strain.

Macosko and Davis¹³ have favorably compared results from ERD studies to three other dynamic shear techniques. A typical plot of σ_y versus strain at several frequencies as a function of temperature is shown in Figure 4. The linear relationship between stress and strain over the region of strain examined is confirmed by this data. It is evident that an increase in rotational speed or frequency at constant temperature, or a decrease in the test temperature at constant frequency, caused an increase in the elastic modulus. Similar behavior was observed for the corresponding loss modulus data obtained from σ_x -versus-strain plots.

Information about the storage and loss modulus as a function of temperature for polystyrene samples analyzed by ERD and DSA cannot be directly compared, owing to the different frequency range covered and the mode of operation of the two techniques. The DSA experiments were conducted at three constant frequencies, 3.5, 11, and 110 Hz, as a function of temperature. ERD experiments were performed at a constant temperature between 120° and 180°C and with varying rotational speeds from 0.1 to 10 rad/sec, corresponding to frequencies in the range of 0.016–1.6 Hz. As the frequency ranges studied for each technique did not overlap, it was not possible to compare the modulus information obtained from the two techniques without resorting to the time-temperature superposition

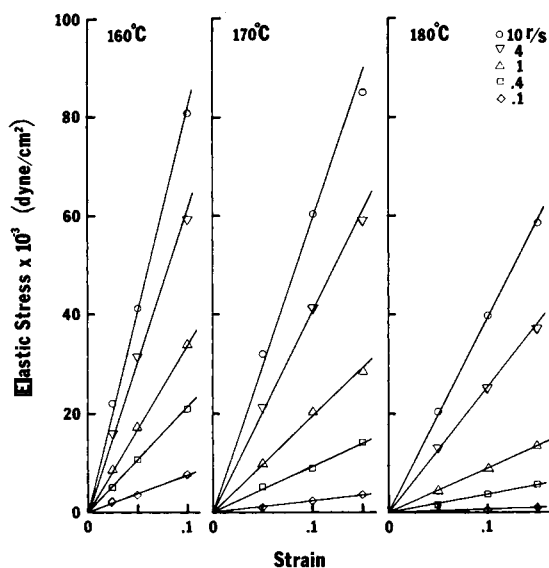


Fig. 4. Typical elastic stress-strain characteristics of polystyrene samples analyzed by ERD at several temperatures.

principle. The shift factors a_T can be determined from the temperature of the experiment by the WLF equation:

$$\log a_T = \frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (14)$$

For polystyrene, the WLF constants were determined by Plazek²⁰ to be $C_1 = 13.3$ and $C_2 = 47.5$, while 100°C was taken for the long-time T_g . An additional correction for the temperature dependence of entropy elasticity was included to normalize the modulus values at any temperature to those at the reference temperature.

The storage modulus data obtained from both techniques were shifted with the WLF equation to produce the plot of reduced storage modulus versus shifted frequency, shown in Figure 5. The storage modulus obtained from DSA is a mixed modulus, since both tensile and shear deformation occur, but should at most be a factor of 3 greater than the shear modulus for the polymer in the rubbery region. Figure 5 shows that good agreement between DSA and ERD storage moduli was obtained over the shifted frequency range of about 2×10^{-8} to 2×10^{-4} Hz. Below 2×10^{-8} Hz, the composite sample began to approach the modulus of the spring alone and the DSA technique became insensitive to changes in the polystyrene storage modulus. The DSA data points show some scatter when compared to the ERD results, which clearly lie on a single curve. It is evident that the storage modulus obtained from DSA is a reasonable approximation of the shear modulus of the polymer in the region above T_g .

The agreement between loss moduli obtained from the two techniques was not as good, as can be noted from Figure 6, a plot of loss modulus as a function of shifted frequency. A smaller region of concurrence of the moduli occurred in the range of shifted frequency from 2×10^{-7} to 4×10^{-6} Hz. At lower shifted frequencies, the DSA loss modulus data declined rapidly while the ERD data decreased at a much slower rate.

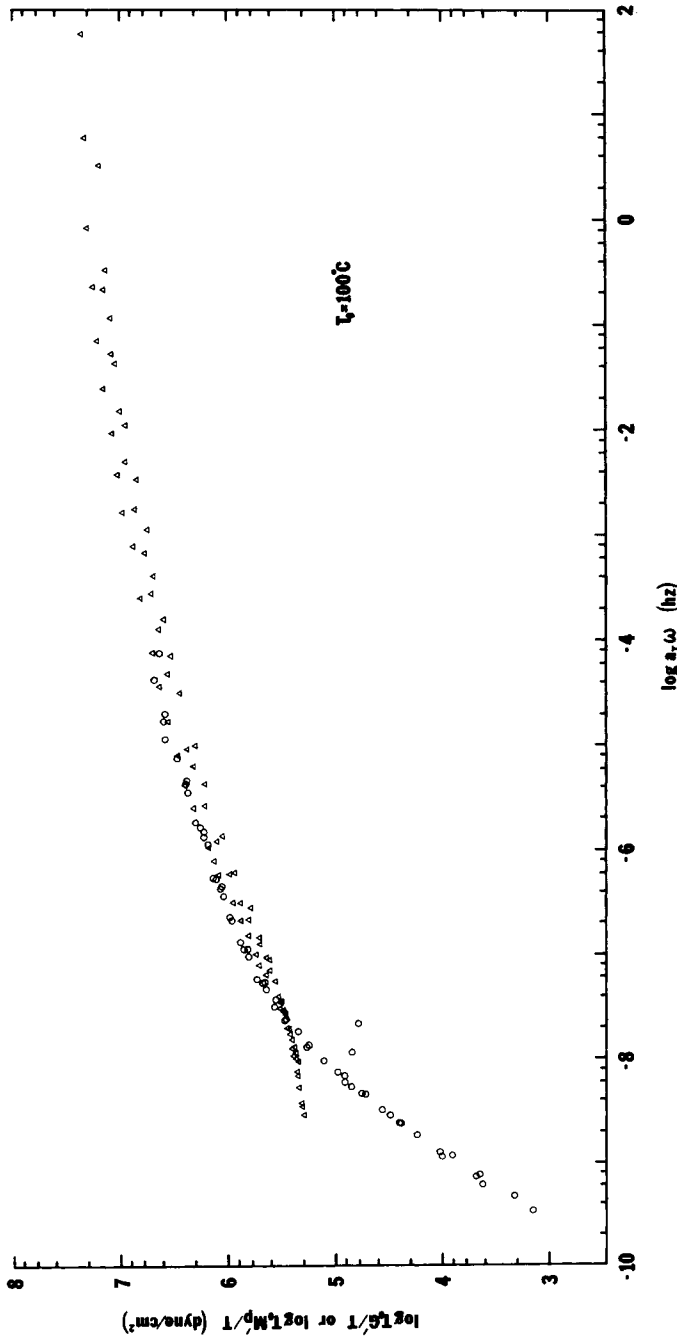


Fig. 5. Time-temperature superposition of storage moduli obtained from (Δ) DSA and (O) ERD response of polystyrene.

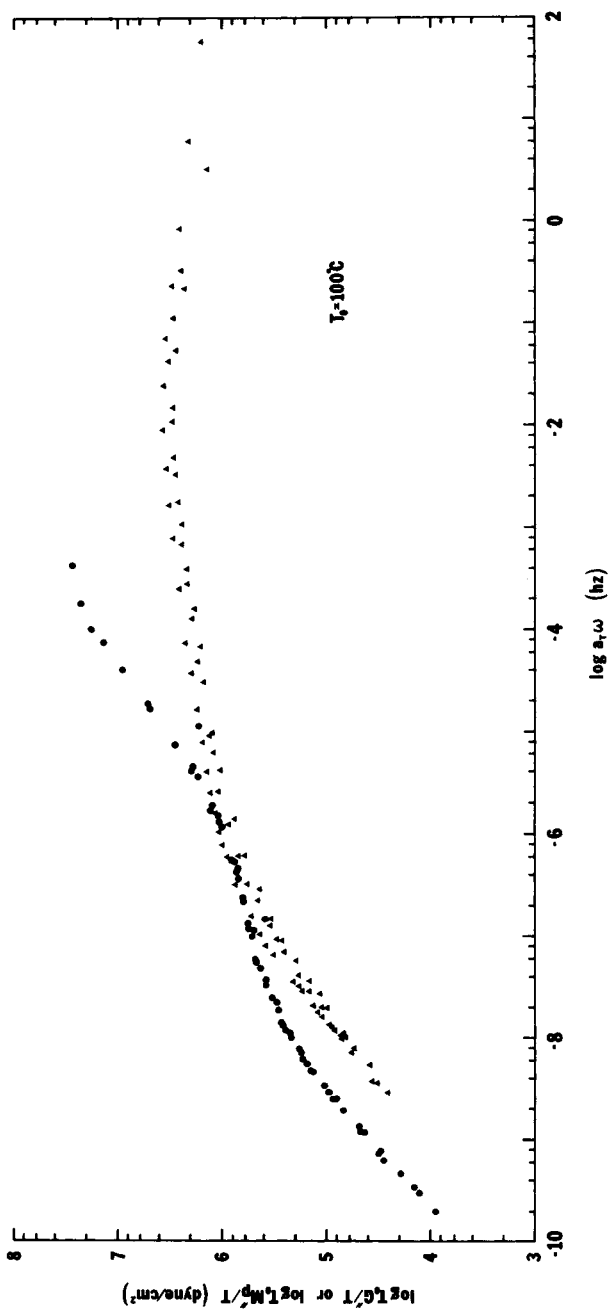


Fig. 6. Time-temperature superposition of loss moduli obtained from (\blacktriangle) DSA and (\bullet) ERD response of polystyrene.

Several problems are inherent in the comparison of DSA and ERD data with the aid of the time-temperature superposition principle. At low shifted frequencies the DSA data becomes less accurate as the composite modulus closely approaches that of the spring and as the temperature of measurement exceeds the limit of applicability of the WLF equation. At high shifted frequencies, the ERD analysis becomes less accurate owing to difficulties in maintaining the no-slip condition at the platten surfaces for a glassy sample.

Additional simplifications due to the assumption of a parallel model that neglects any interfacial effects, and complications which arise out of the mixed character of the modulus obtainable by DSA, further reduces the possibility for exact agreement between the two techniques. However, the method of DSA can clearly be used to obtain semiquantitative predictions of the dynamic storage and loss moduli of polymers above the glass transition temperature in addition to providing information on loss processes and their frequency dependence.

Liquid-State Relaxation of Polystyrene

Several samples prepared for DSA studies exhibited an apparent relaxation in the molten state above the glass transition. Figure 7 shows the loss tangent behavior of sample C-2 during the first heating. The plot shows a T_g relaxation

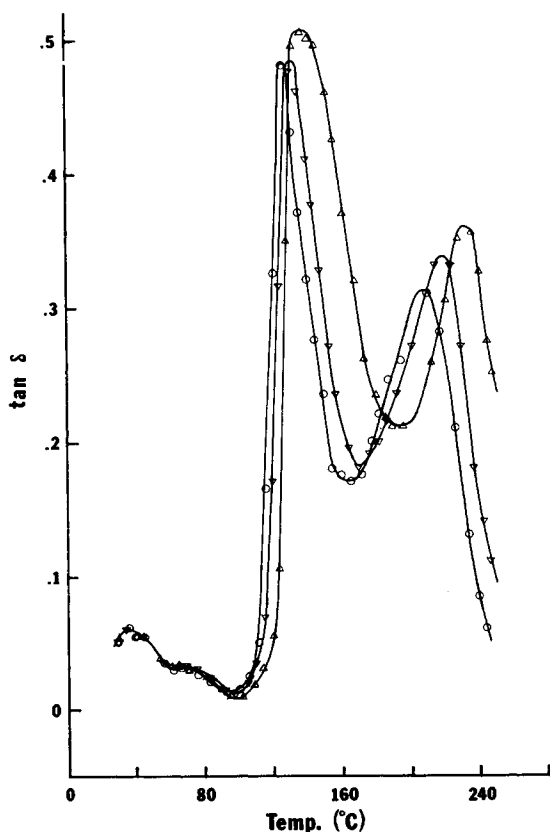


Fig. 7. Loss tangent of DSA sample C-2 as a function of temperature upon first heating: (O) 3.5 Hz; (∇) 11 Hz; (Δ) 110 Hz.

near 130°C and a second broad loss peak well above the glass transition region. Apparent activation energies were determined to be 161 and 61 kcal/mole, respectively, for the two transitions from the position of the loss modulus maxima. Further analysis of sample C-2 revealed that the transition above T_g could not be reproduced upon reheating, as shown by the loss tangent response in Figure 8. The loss tangent plot revealed a single broad T_g relaxation with no evidence of a second relaxation. As a comparison, loss tangent data obtained from analysis of a thin film of the same polystyrene in the tensile mode of the Rheovibron is also shown in Figure 8. Thin film results gave an abrupt rise in $\tan \delta$ as the sample softened above T_g until the applied tensile deformation could no longer be supported. The advantage of using a supported sample in the DSA technique becomes evident, as it was possible to observe the behavior of the loss tangent during the entire T_g relaxation. The loss modulus behavior was similar to that of the loss tangent in that only a single relaxation attributable to the glass transition was present. This relaxation occurred about 8°C lower than the position observed during the first heating. An activation energy of 79 kcal/mole was calculated from the loss modulus peak, in good agreement with the results of Baker.¹⁹ Similar results were obtained from a composite prepared with polystyrene of molecular weight 233,000 and narrow molecular weight distri-

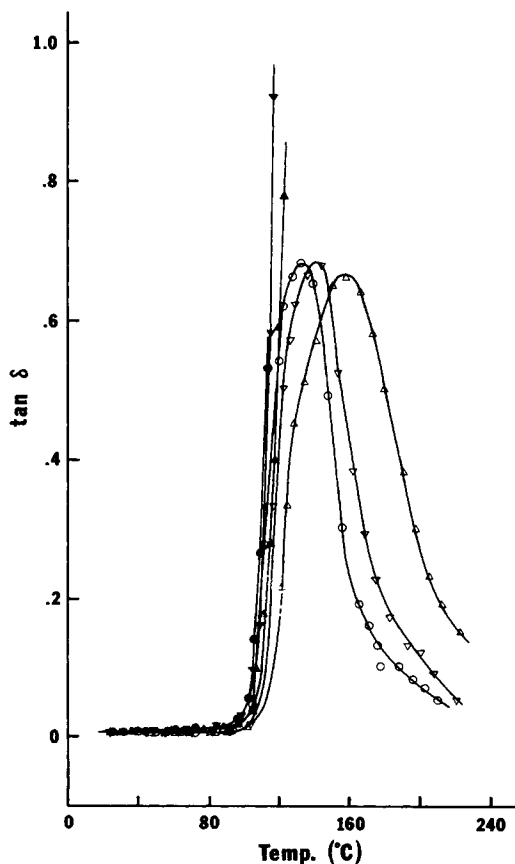


Fig. 8. Loss tangent of DSA sample C-2 as function of temperature upon second heating (open points) compared to that of a thin film in tension (filled points): (●)(○) 3.5 Hz; (▼)(▽) 11 Hz; (▲)(△) 110 Hz.

bution, sample C-5. Upon first heating, a T_g transition in the neighborhood of 109°–119°C was observed in a loss modulus-versus-temperature plot as well as a transition above T_g , again very broad, occurring at 210°–222°C. When the sample was rerun, the position of the T_g transition had dropped by 2° to 3°C, and no higher temperature transition was evident. Sample C-4 exhibited a loss process above T_g which appeared as a broad shoulder on the high-temperature side of the T_g relaxation peak for the loss modulus during the first heating of the sample. Data subsequently collected while cooling sample C-4 until ambient temperature was reached showed the T_g transition at the same position observed upon heating and no evidence of a higher temperature transition.

The results obtained from DSA evaluation of samples C-2 through C-5 are summarized in Table II. It can be seen that T_g values are several degrees lower by the second analysis than values obtained from the first run. The glass transition temperature did not show a significant variation between samples owing to the relatively high molecular weight of all the polymers studied. The glass transition temperature determined from a polystyrene thin film sample in the tensile mode agreed very well with the values obtained from DSA. Samples C-2, 4, and 5 displayed a relaxation above T_g only during the first analysis. Subsequent DSA evaluations upon either cooling from the first run or reheating after the sample had cooled to ambient temperature revealed no higher temperature transitions.

It is interesting to consider the variation of this high-temperature relaxation phenomenon with polymer molecular weight. Sample C-4, composed of polystyrene of lowest molecular weight studied, showed the earliest onset of the phenomenon, while sample C-5, of highest molecular weight, gave the highest onset of the pseudorelaxation. Sample C-2, of intermediate number-average molecular weight, exhibited a transition between that of the two narrow-distribution polystyrenes analyzed. This variation is similar to the dependence of the liquid–liquid transition temperature T_{ll} on number-average molecular weight reported by Stadnicki and Gillham.⁴ The T_{ll} transition was found to be present above the glass transition temperature for monodisperse atactic polystyrene by TBA and was postulated to represent a relaxation from a fixed liquid to a true liquid state. The T_{ll} transition was found to be both reversible and reproducible and exhibited a proportionality to $\log \bar{M}_n$.

The unusual viscoelastic behavior displayed by some of the polystyrene DSA samples above T_g was thought to be attributable to the loss of monomer or solvent from the polymer. This seemed likely for several reasons. The high-temperature loss peak could not be reproduced upon reheating, indicating that a unique event had occurred. The complete evolution of solvent vapors upon heating during the first analysis could explain why the relaxation was not observed when the experiment was repeated. The only sample which did not display irregular behavior above T_g was sample C-3. From Table I it can be noted that this sample was dried under vacuum at 170°C, while the other samples were all dried below the glass transition temperature of polystyrene. As the drying procedure was the only significant difference in the preparation of these DSA samples, incomplete drying of samples C-2, 4, and 5 could have caused irregular behavior of these samples.

Consideration of the diffusion of small molecules through amorphous polymers as a function of temperature was useful in determining the efficiency of sample

TABLE II
Summary of Polystyrene Relaxations as Determined from Loss Modulus Maxima

Sample	Molecular weight $\bar{M}_n \times 10^{-3}$, g/mole	Analysis ^a	T_g Transition, °C			Above T_g transition, ^b °C		
			3.5 Hz	11 Hz	110 Hz	3.5 Hz	11 Hz	110 Hz
C-4	37	1H	117	121	132	140	150	168
C-2	90-95	1C	115	119	134	NO	NO	NO
		1H	124	128	133	188	202	211
C-5	233	2H	116	119	126	NO	NO	NO
		1H	109	113	119	210	215	222
C-3	90-95	2H	106	109	117	NO	NO	NO
		1H	110	114	120	NO	NO	NO
Thin film	90-95	1H	110	114	121	NO	NO	NO

^a 1H = First heating; 1C = cooling after first heating; 2H = second heating.

^b NO = None observed.

drying techniques. In a study by Rhee,²¹ a polymer film was used to adsorb a small volume of a radioactive liquid at a given temperature. The time required for the liquid to diffuse through the film and reach an equilibrium distribution was determined as a function of temperature. From these data, the diffusion coefficient D of the polymer as a function of temperature could be determined. The equilibrium time t_e was found to be related to the diffusion coefficient by the following equation:

$$Dt_e = \gamma h^2 \quad (15)$$

where h is the film thickness and γ is a parameter dependent upon the system polarity and compatibility. For a nonpolar and compatible system, such as polystyrene and toluene or styrene monomer, $\gamma = 1$. Several rubbers at about 75°C above the glass transition temperature were found to have a diffusion coefficient of about 10^{-7} cm²/sec. In a study of diffusion of benzene in polystyrene at 25°C by Park,²² the diffusion coefficients determined were of the order of 10^{-12} cm²/sec.

The drying process can be viewed as the reverse of the adsorption process since the uniformly distributed solvent molecules must be removed from the interior of the polymer film and brought to the surface where they are volatilized with the aid of a vacuum. The equilibrium time can be seen to be applicable to a process of desorption as well as for adsorption and can provide an estimate of the length of time required to remove an organic solvent from a polymer film. Since approximate values of the diffusion coefficient were available, it was possible to estimate the equilibrium time for a known thickness of polystyrene from eq. (15). At 175°C the equilibrium time for polystyrene was found to be 2×10^3 sec, while at room temperature it was estimated to be about 2×10^8 sec. The equilibrium time at 90°C should be of the same order of magnitude as that at room temperature, since molecular motions of the polymer chains remain restricted below the glass transition temperature. As evident from Table I, sample C-3 was dried for 17 hr at 170°C, well in excess of the theoretically estimated time. Samples C-2, 4, and 5 were all dried at temperatures slightly below 100°C for only 24 hr at most. This evidence supports the possibility that solvent or monomer evolution could have given rise to the high-temperature loss phenomenon observed when samples not thoroughly dried were examined by the DSA technique. Sample C-3, shown to be the only DSA sample dried completely, was the only sample to give no evidence of a high-temperature loss process.

A test for evolution of volatile organic compounds was undertaken with the Spex MP-3 thermal analyzer. Table I gives details on several samples prepared for testing with this system. All samples were dried near T_g in a procedure similar to that used in preparation of samples C-2, 4, and 5. The samples were evaluated *in situ*, as the sample chamber of the MP-3 proved to be of adequate diameter.

A preliminary experiment conducted with sample TA-6 indicated the presence of an organic material in the helium gas stream passed over the heated sample. Sample TA-7 was evaluated by heating at a rate of 8°C/min from 35° to 220°C. The detectors showed the first presence of organic vapors at 70°C. The highest concentration was observed at 138°C, but a small amount of material could still be detected at 200°C. A gas chromatograph of the material collected over the course of the run showed that several small peaks and one major component were

present. An infrared spectrum of the most abundant compound showed prominent bands at 3.3, 3.4, 6.7, 9.4, 9.7, 13.5, and 14.7 μ . These positions are similar to the locations of major absorptions in the IR spectrum of toluene. No absorption could be noted at 10.1, 11.1, and 12.9 μ , the most intense absorptions in the IR spectrum of styrene. A comparison of band intensity and exact position was complicated by the background subtraction procedure, which produced several "negative peaks" in the difference spectrum.

Sample TA-8 was analyzed in order to make a quantitative determination of the amount of material evolved during heating. The sample was heated at 4°C/min from 40° to 215°C, then cooled to ambient temperature and reheated from 40° to 180°C at the same rate. During the first run, the detectors recorded the presence of organic material from about 60°–190°C, with the highest concentration at 125°C. No organic compounds were detected in the inert gas stream during the second heating. A sample of neat toluene injected into the GC gave a peak with the same position as the major peak in the GC of the evolved gases, which confirmed the identification of the major component of the GC spectrum as toluene. Several injections were used to obtain a calibration curve for peak height as a function of the amount of toluene. From this curve it was estimated that about 1.7 μ toluene was released during the first heating. This amount was approximate but was used to estimate the concentration of solvent that remained in the dried sample to be about 8% by weight.

The evolution of solvent during heating of polystyrene samples dried at temperatures near T_g for less than 24 hr has been clearly shown by thermal analysis. It is likely that this release of solvent caused a loss phenomenon above T_g to be observed when similarly prepared samples were analyzed by DSA. The absence of solvent evolution upon reheating during thermal analysis is consistent with the failure of the high-temperature loss peak to be reproduced upon repetition of the DSA experiments. The mechanism of the loss process above T_g is not certain but could be envisioned as a conversion of the mechanical energy input into heat necessary to volatilize the solvent. A process requiring the formation of a new surface area, in the form of small solvent bubbles and their transportation to the surface of the polymer, could also account for a one-time expenditure of energy.

The variation of the high-temperature loss peak with molecular weight, as described previously, can be explained by the high sensitivity of melt viscosity to molecular weight. Above the critical molecular weight, about $\bar{M}_w = 38,000$ for polystyrene, the zero-shear melt viscosity has been found by many laboratories to be dependent upon the weight-average molecular weight raised to the 3.4 power.²³ The rate of diffusion of an organic solvent in a molten polymer should be higher and the temperature at which evolution is complete should be lower for a lower molecular weight polymer, as the ease of diffusion depends on the viscosity of the polymer melt. This relation was found to hold for the loss phenomenon above T_g , which showed an onset temperature proportional to the molecular weight of the polymer sample.

CONCLUSIONS

Dynamic spring analysis, a technique of supported dynamic viscoelastic testing, has been shown to be a valuable tool for evaluation of polymer properties

in the rubbery region of behavior. From an assumption of a simple parallel model for the composite deformation, the storage and loss moduli and the loss tangent as a function of temperature can be derived from a straightforward treatment of the Rheovibron data. The deformation was shown to be both tensile and shear in nature, but the loss and storage moduli agreed reasonably well with shear modulus data, as compared by time-temperature superposition. DSA provides a method for obtaining the loss tangent and, semiquantitatively, the moduli of a polymeric material above the glass transition temperature. A loss phenomenon observed at temperatures above T_g was found to be irreversible and was attributed to solvent evolution from incompletely dried polymer samples.

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