TECHNICAL REPORT NO 7

MONITORING THE CURE OF A COMPOSITE MATRIX RESIN WITH MICRODIELECTROMETRY

by

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November 15, 1986

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2 GOVT ACCESSION NO. ADA177490	3 RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) Monitoring the Cure of a Composite Matrix Resin with Microdielectrometry	5. TYPE OF REPORT & PERIOD COVERED Technical 10/84-10/86
	6. PERFORMING ORG. REPORT NUMBER Technical Report No. 7

7. AUTHOR(s) Wayne W. Bidstrup and Stephen D. Senturia	8. CONTRACT OR GRANT NUMBER(s) N00014-K-0274

9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology 77 Massachusetts Avenue Cambridge, MA 02139	10. PROGRAM ELEMENT PROJECT, AREA & WORK UNIT NUMBERS Work Unit 4313260

11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA	12 REPORT DATE November 15, 1986
	13. NUMBER OF PAGES 13

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

conductivity, thermosetting polymers, Williams-Landel-Ferry equation, glass transition temperature, epoxy resins, amine hardener, network structure, microdielectrometry, differential scanning calorimetry, loss factor

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Solvent free resin was prepared from a MY720-DDS prepreg solution by evaporation in a vacuum oven. This material was cured under vacuum by a ramp-hold-ramp to cure temperature cycle and the temperature and dielectric loss factor at 5 frequencies were measured every four minutes for the duration of the cure cycle. At selected times during the cure, small samples of the reacting mixture are removed and quenched and subsequently analyzed for Tg. At frequencies of 1 and 10 Hz, the ionic

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S/N 0102-LF-014-6601

20. Abstract

conductivity dominates the loss factor and the logarithmic derivative
of the loss factor with respect to time equals the logarithmic derivative
of the conductivity with respect to time. This derivative is then related
to the derivative of Tg with respect to time by a WLF equation.

INTRODUCTION

Dielectric monitoring of thermoset cure is an old technique (1) which is receiving new interest through improved instrumentation, such as microdielectrometry (2-6). This paper reports initial results from a program of dielectric cure studies in glass and graphite fiber composites made from a common MY720-based matrix resin. The present work addresses only the neat resin, and the relation between the changing conductivity of the resin and the corresponding increase in the glass transition temperature during cure.

EQUIPMENT AND PROCEDURES

Samples of MY720-based prepreg solution, and of glass-reinforced and graphite-reinforced prepregs made from this solution, were obtained from Lockheed. The MY720 resin consists of ~80% TGDDM (7) (see Figure 1) plus other by-product epoxies and impurities. The prepreg solution contains the MY720 resin, the DDS curing agent (see Figure 1), and other proprietary ingredients dissolved in a mixed methyl ethyl ketone-acetone solvent. For the studies of the neat resin, the bulk of the solvent was removed by evaporation in a vacuum oven at ~29" Hg vacuum and ~100° C. The sample was then cured by placing the microdielectrometer sensor (Micromet Instruments Model S10), covered with a small quantity of the vacuum dried prepreg solution, in a small chamber to which a vacuum could be applied. This chamber was placed in an electrically heated hydraulic press (Carver Model 2518 with 12" platens) controlled by a Wizard Model 1600 temperature controller. The press was used at a small applied load to assist in sealing the vacuum chamber. A series of Differential Scanning Calorimetry (DSC) pans were filled with 8-20 mg. of the vacuum dried prepreg solution and placed in holders carrying up to 4 pans which were then inserted in the press external to the vacuum chamber. The press was then ramped at 3°C per minute to 116°C, and the temperature was held until the dielectric loss factor (see following section for definitions of the permittivity and loss factor) as measured by the microdielectrometer had stabilized. Then ~28" Hg vacuum was applied to the chamber to remove residual solvent from the prepreg solution, and was maintained for the remainder of the cure. When the loss factor had again stabilized after the vacuum application, the temperature was ramped at 3°C per minute to the final cure temperature of 177°C and held for the remainder of the cure. The dielectric permittivity, ε', and loss factor, ε'', were measured by the microdielectrometer at five frequencies (1, 10, 100, 1000, and 10000 Hz) every four minutes from the beginning at room temperature until the completion of the cure cycle. The various holders containing the DSC pans were removed at different times beginning shortly after the press temperature reached 177°C and continuing through the remainder of the cure, and the pans were quenched rapidly to -20°C. The glass transition temperature of each quenched DSC sample was subsequently determined using a Perkin-Elmer Model 4 DSC. Typical cure cycles were ~14 hours.

Typical results for the loss factor vs. time for the curing MY720 resin are shown in Figure 2. During the initial ramp to and hold at 116°C, the ionic conductivity is very high and, at low frequencies, often exceeds the capability of the microdielectrometer. This results in a default value which makes interpretation of the results difficult. This occurs in this plot in the time period between 20 and 200 minutes at 1, 10, and 100 Hz, and the default data has not been plotted. ε'' initially increases with the increasing temperature and then stabilizes when the temperature reaches 116°C (point A in Figure 2). It remains approximately constant until the vacuum is applied (point B in Figure 2) at which time an abrupt adjustment occurs. The loss factor then continues at an approximately constant value until the ramp to 177°C begins (point C in Figure 2). The irregular order of the data in relationship to the frequency that occurs in these times and the difference in the response of the various frequencies at vacuum application are the result of polarization effects (8), which are greater when the conductivity is high, and vary with the frequency.

DIELECTRIC PROPERTIES

The microdielectrometer measures both ε', the real part of the complex dielectric constant called the permittivity, and ε'', the imaginary part named the loss factor. In this work, only the loss factor will be discussed. The loss factor is a measure of energy dissipation by the dipole motion and by the ion movement under the influence of an alternating electric field and may be expressed in the following form:

$$\varepsilon'' = \varepsilon''_{Dipoles} + \sigma/\varepsilon_0 \omega \qquad (1)$$

where
σ = the ionic conductivity
ε_0 = the permittivity of free space
ω = 2π times the frequency

The measured loss factor is also influenced by electrode polarization particularly when the ionic conductivity is high and/or the frequency is low (8). A typical frequency scan of an epoxy material is shown in Figure 3 with the various regions of dipole contribution, conductivity dominance, and polarization effects noted. While the location of these regions within the frequency spectrum will vary with the particular sample of epoxy, frequencies where conductivity dominates (when the loss factor is a linear function of the reciprocal of the frequency) can usually be found. This is the region on which we will concentrate our attention.

A typical plot, at six frequencies of the applied electric field, of the loss factor vs. time for the isothermal cure of the neat epoxy system, DGEBA-DDS (see Figure 1), is shown in Figure 4. Sheppard (9), in his studies of this system, was able to relate the time to reach the dipole peak in a plot of loss factor vs. time to the vitrification or glass transition temperature of the resin. The dipole peaks are prominent, particularly at the higher frequencies, starting at about 150 minutes into the cure. Sheppard in subsequent work (10,11) related the ionic conductivity to the glass transition temperature by a WLF (12) type formulation. This is not a surprising development considering the well-known dependency of the ionic conductivity on the media viscosity and the fact that the WLF equation was originally developed as a viscosity relationship. Shepppard did report with theoretical support that the WLF "constant" in the denominator of this equation has some material dependence which is expressed in terms of the glass transition temperature, T_g, as shown by the expression in parentheses in the denominator of his equation

$$\log \frac{\sigma(T_c)}{\sigma(T_g)} = \frac{C_1 (T_c - T_g)}{(C_3 + C_4 T_g) + T_c - T_g} \qquad (2)$$

where T_c and T_g are respectively the cure temperature and the glass transition temperature and C_1-C_4 are constants.

Sheppard also developed the empirical equation,

$$\log (\sigma(T_g)) = C_5 + C_6 T_g \qquad (3)$$

where C_5 and C_6 are constants to relate the ionic conductivity at the glass transition temperature to the glass transition temperature.

RESULTS AND DISCUSSION

Ramped cures of the concentrated prepreg solution give results typified by Figure 2. The first 200 minutes were occupied by the ramp to and hold at $116^{\circ}C$ followed by the ramp to $177^{\circ}C$ as described in the experimental procedures

section. After the temperature reaches 177°C, the loss factor shows the usual rapid decrease as the ionic conductivity decreases due to epoxy cure. However, the dipole peaks observed by Sheppard in the cures of the DGEBA-DDS system are essentially absent in the MY720-DDS system and so cannot be used as an indication of the glass transition.

It would be expected that the ionic conductivity which decreased after reaching the cure temperature would stabilize at a constant value when the epoxy is fully cured and so the derivative of the conductivity with respect to time would be *independent of the absolute ion concentration and could be used as a cure monitor*. This derivative can be related to the glass transition by Sheppard's WLF equation and his empirical relation between T_g and the conductivity at T_g as shown in the following equation:

$$\frac{d(\log \sigma(T_c))}{d(t)} = \left\{ C_6 - \frac{C_1 C_3 + C_1 T_c C_4}{[(C_3 + C_4 T_g) + T_c - T_g]^2} \right\} \frac{d(T_g)}{d(t)} \quad (4)$$

This assumes that the conductivity at T_g for the MY720-DDS has a linear relationship to T_g similar to that for the DGEBA-DDS system. This is further simplified if the frequency of measurement is chosen so that the ionic conductivity is the dominant contributor to the loss factor. In this case the proportionality between ε'' and σ leads to

$$d(\log \varepsilon'')/d(t) = d(\log \sigma)/d(t) \quad (5)$$

independent of the frequency.

Figure 5 is a plot of the term $(1/\varepsilon'')d(\varepsilon'')/d(t)$ vs. time for the two frequencies in the conductivity dominated regime for the cure of a concentrated MY720-DDS *prepreg solution. The $d(\varepsilon'')/d(t)$ value was determined by subtracting the two sequential values of ε'' obtained during the cure and dividing by the time interval between measurements. This value was then assigned to the time at the midpoint of the time interval. The ε'' values at the midpoint was taken to be the arithmatic average of the two nearest ε'' values. These results are independent of frequency in the region of interest (times greater than 210 minutes when $T_g = 77°C$, which is within 100°C of the cure temperature, the range of applicability of the WLF equation) and follow the expected path by approaching zero at long cure times.

The reproducibility of the derivative of the log of the conductivity is demonstrated by comparing the results of two separate cures of the vacuum dried MY720-DDS prepreg solution in Figure 6.

The glass transition temperatures of these curing materials as determined by DSC of the quenched samples are shown plotted vs. cure time in Figure 7 for the same two cures reported in Figure 6. Again the results are reproducible when curing the same material. The solid line on the plot is a least squares fit of a polynomial equation to the T_g data. This was determined to provide the derivative of T_g with respect to time needed for solution of the above equation. The derivative of the glass transition temperature with respect to time for the curing MY720 becomes very small but remains positive at times where the glass transition temperature is more than 30°C greater than the cure temperature. This indicates cure proceeds in the glassy state which is in qualitative agreement with the findings of Pang and Gillham (13).

Figure 8 shows the relationship between the measured value of $d(\log \sigma)/d(t)$ and that calculated from the equation (4) using a least squares analysis to determine the values of the constants. The good fit is expected considering the simple form of the curve and the number of constants involved. The "universal" constants in the WLF equation (C_1, C_3, and C_4) for the DGEBA-DDS system as obtained by Sheppard and Bidstrup (14) were within a factor of two of those obtained here for the MY720-DDS system (see Table 1). This discrepancy is not surprising considering the relative

insensitivity of the least squares fitting procedure to simultaneous variations in the various parameters.

The logarithmic derivative of the loss factor with respect to time at frequencies selected to be in a region of ionic conductivity dominance correlates through a WLF type equation with the increase in the glass transition temperature in curing neat MY720-DDS epoxies. Additional data, particularly at other cure temperatures, should provide tighter bounds on the WLF constants.

TABLE 1

	PURE DGEBA RESIN	DGEBA-DDS CURE	MY-720-DDS CURE
C_1	10.5	9.0	10.0
C_3	-109	-194	-438
C_4	.58	.73	1.12
C_6	.013	.013	.14

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EPOXY RESINS:

Diglycidyl Ether of Bisphenol A
(DGEBA)

Tetraglycidyl Diamino Diphenyl Methane
(TGDDM)

AMINE CROSSLINKER:
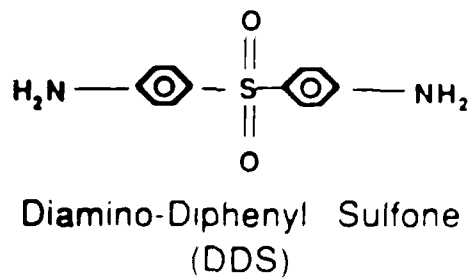

Diamino-Diphenyl Sulfone
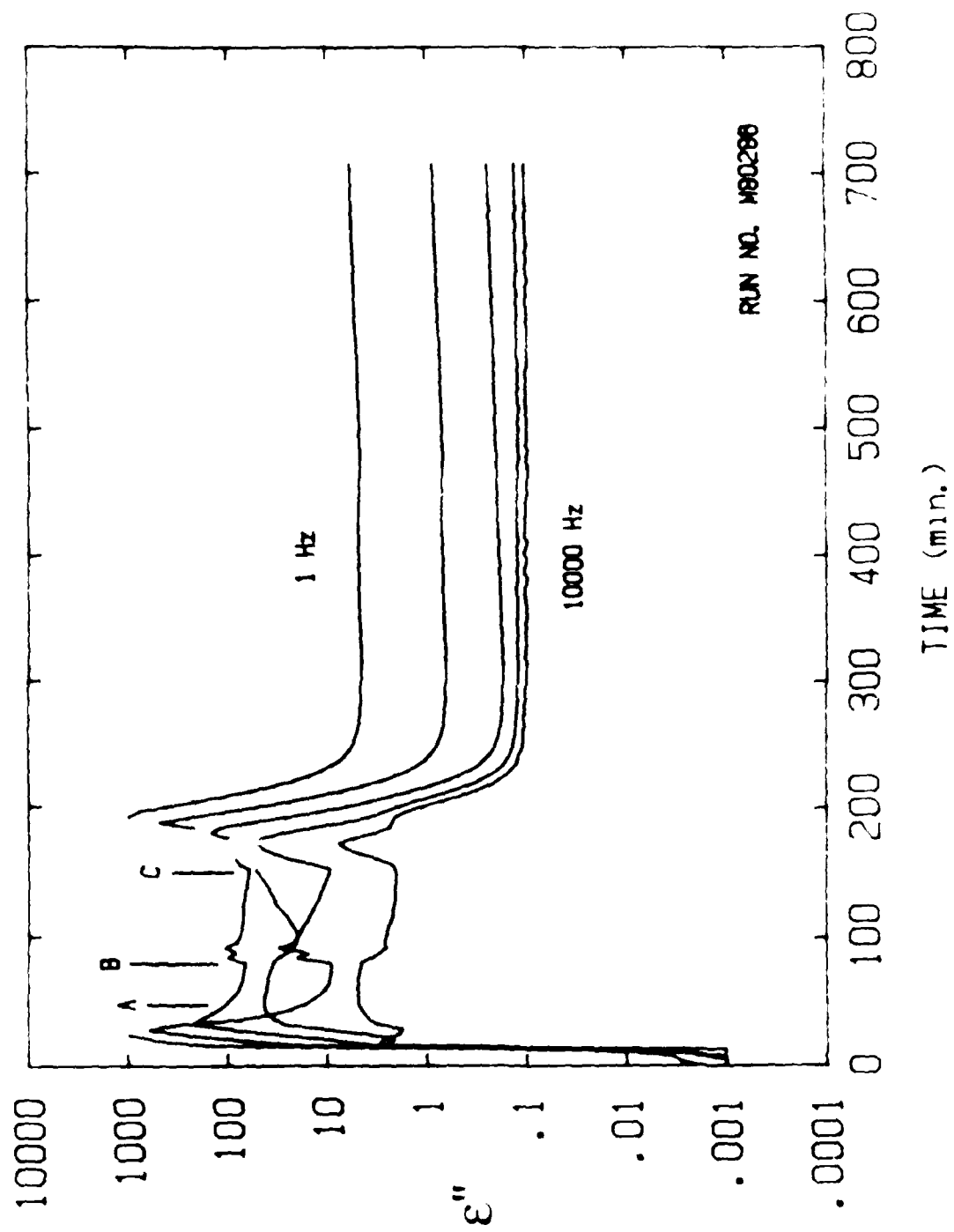(DDS)
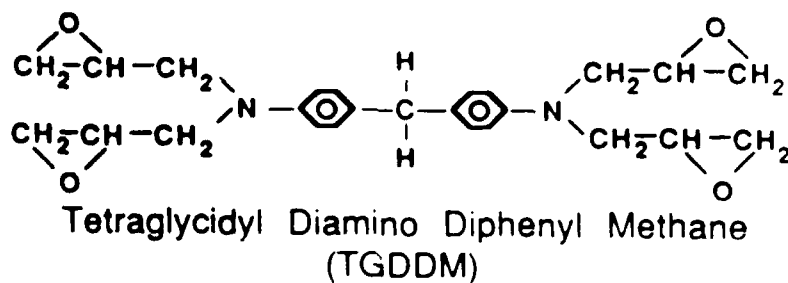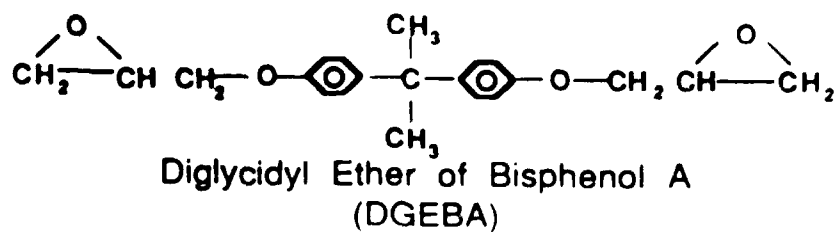
Figure 1   Chemical structure of materials

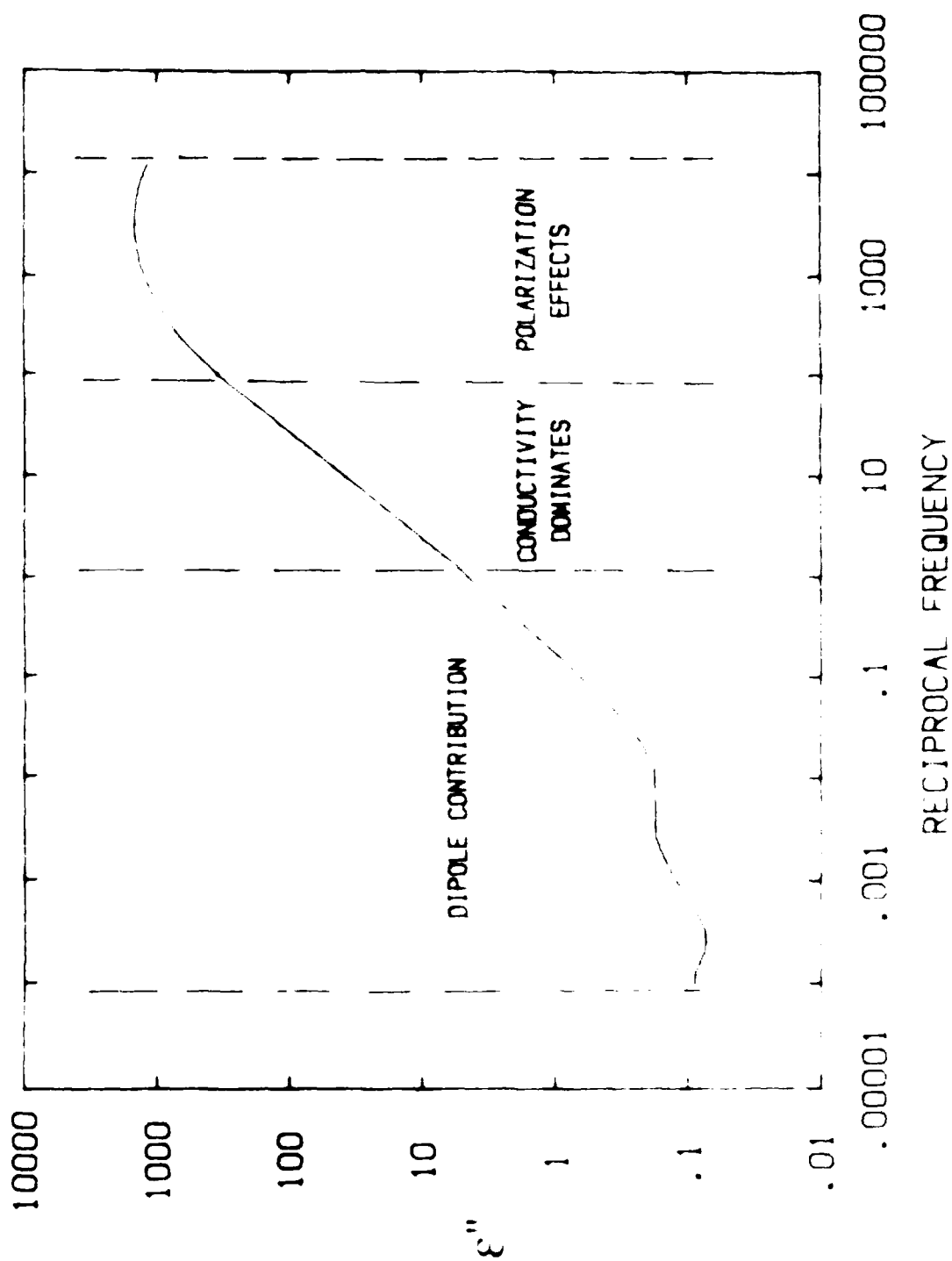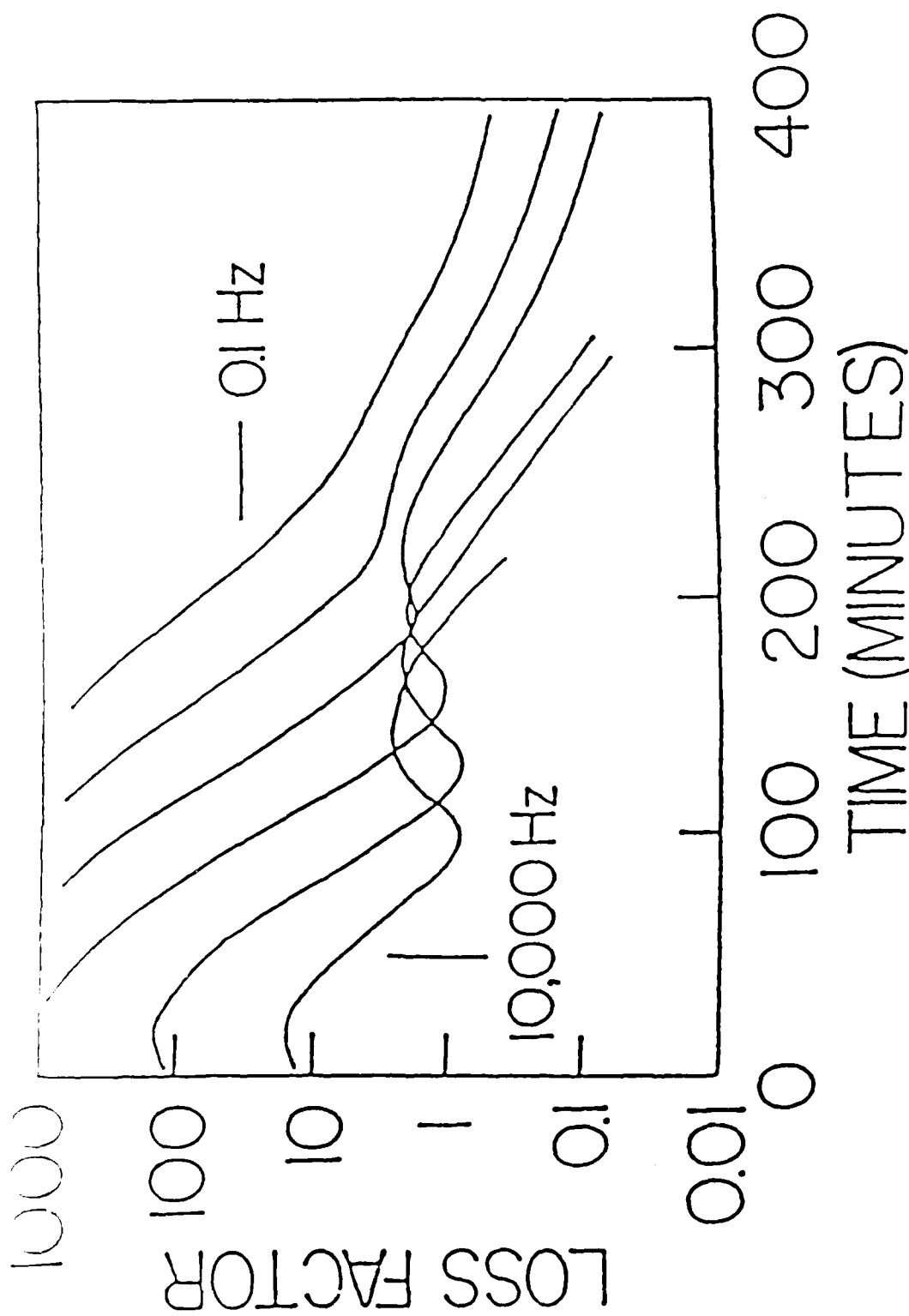Figure 2. Typical loss factor versus cure time results for MY 720 resin cured with DDS.

Figure. Typical loss factor versus frequency results for a cured MY750 DDS resin system showing regions of dipole contribution, conductivity dominance, and polarization effects.

ε"

10000

1000

100

10

1

.1

.01

.00001   .001   .1   10   1000   100000

RECIPROCAL FREQUENCY

DIPOLE CONTRIBUTION

CONDUCTIVITY DOMINATES

POLARIZATION EFFECTS

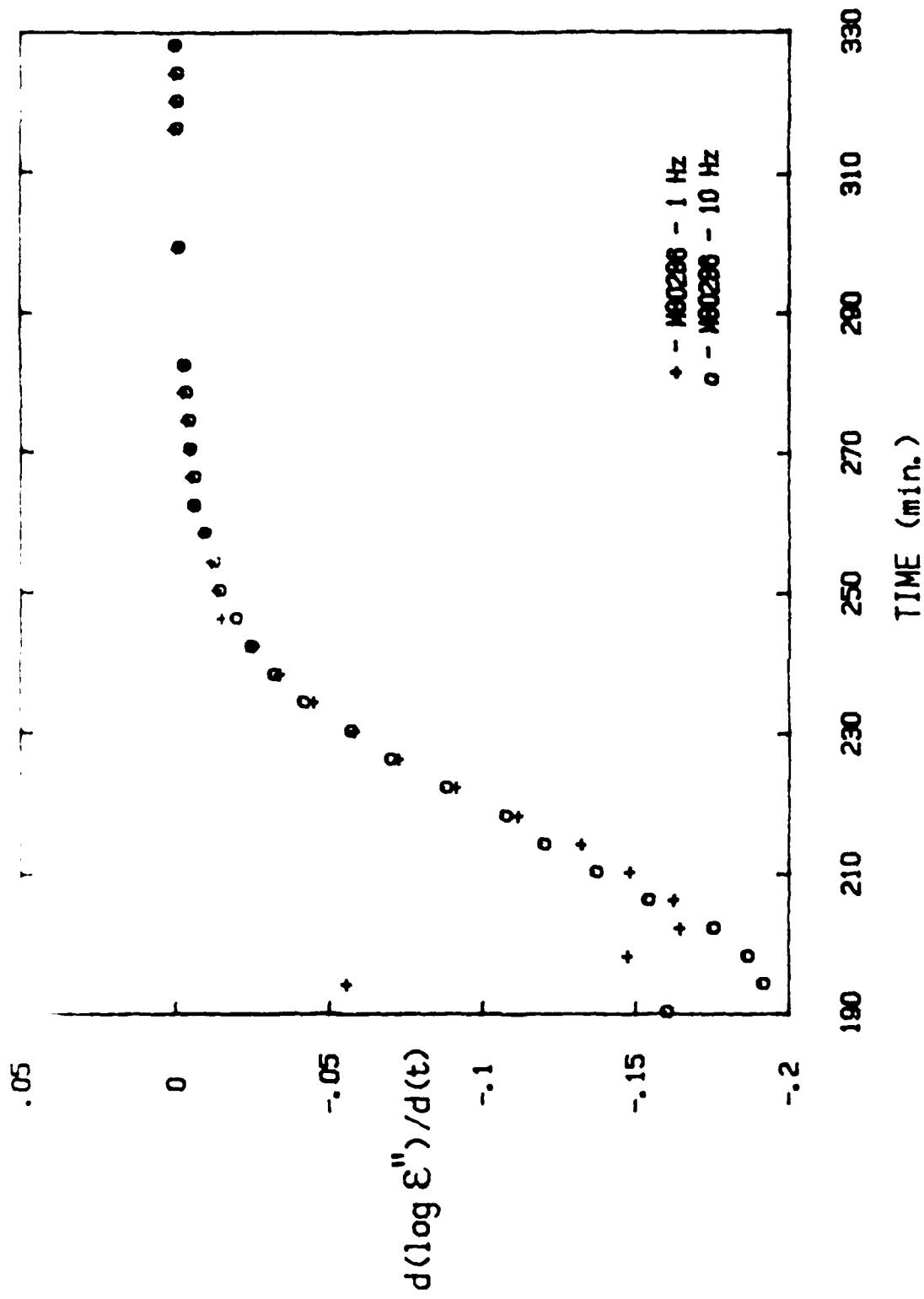Figure 4.   Typical loss factor versus cure time for DGEBA cured with DDS showing the dipole peaks.

Ref: Sheppard, MIT Thesis, 1985

Figure 5. Experimentally measured values of d(log ε'')/d(t) versus time for curing MY720-DDS system at two frequencies, demonstrating frequency independence in regions of conductivity dominance
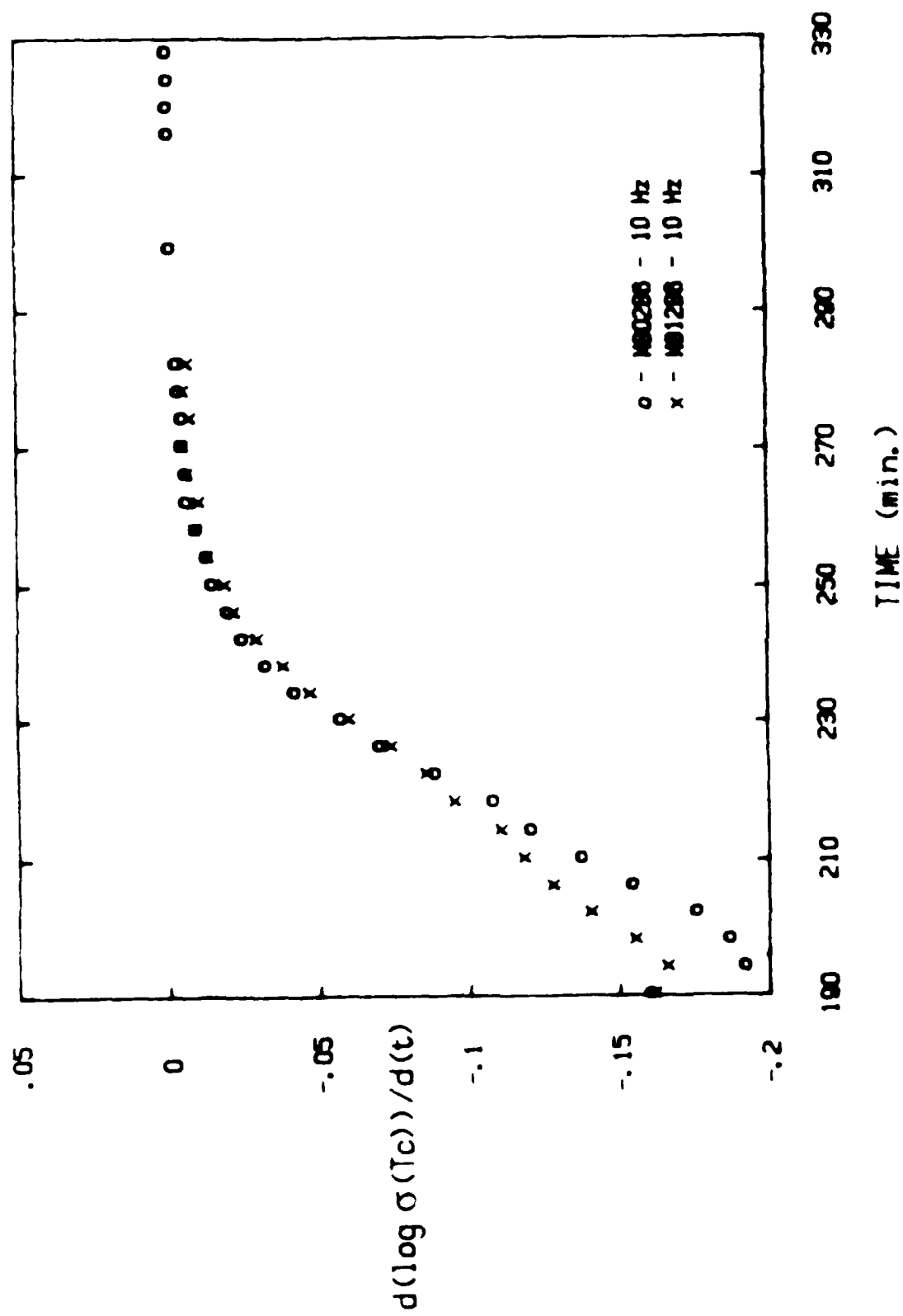
Figure 6   Experimentally measured values of d(log σ)/d(t) versus time for two separate
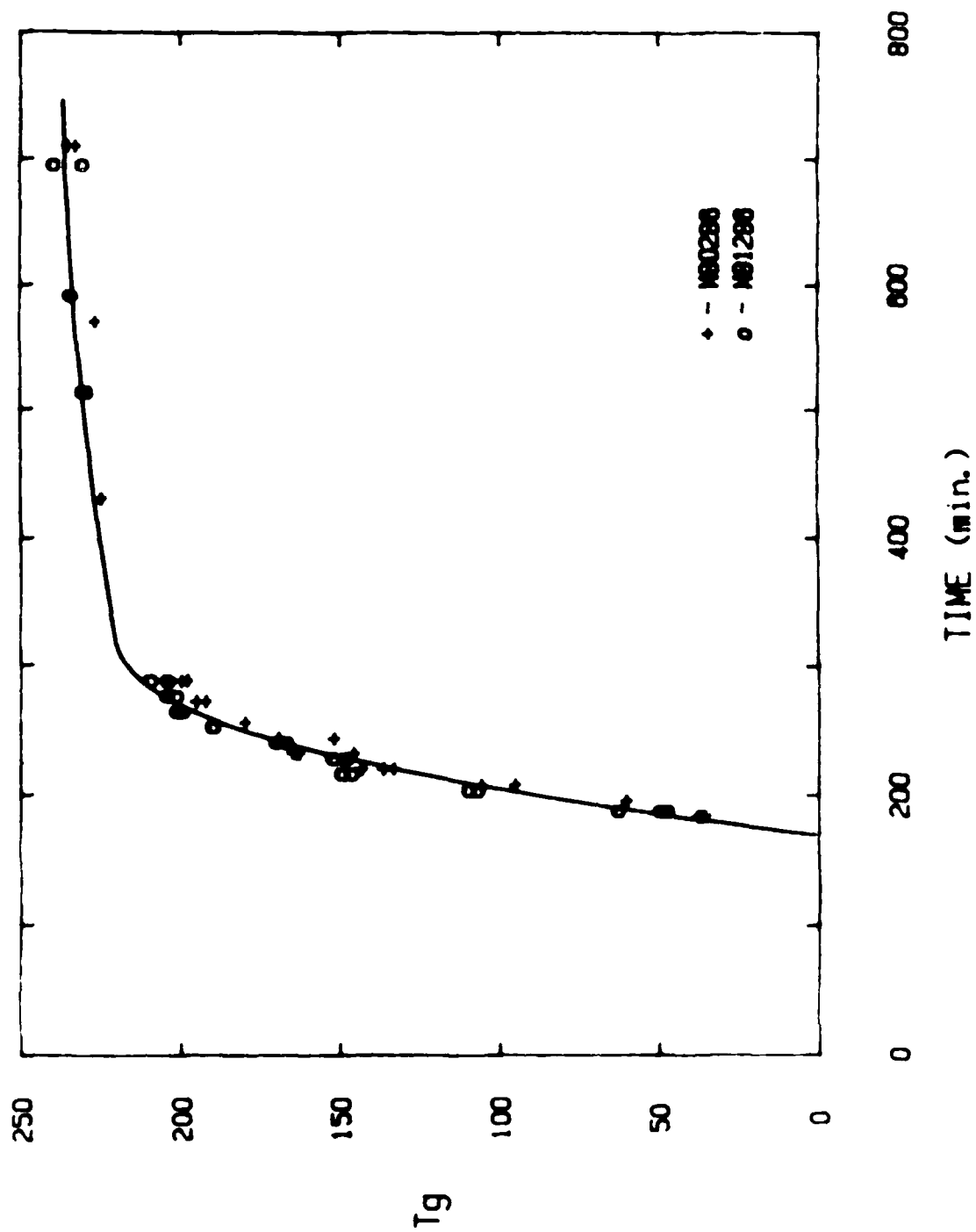cures of a MY720 DDS system demonstrating reproducibility of this parameter

Figure 7   Glass transition temperature versus time in a curing MY720 DDS system The points are the experimentally measured values and the line is a least squares fitted curve through the data
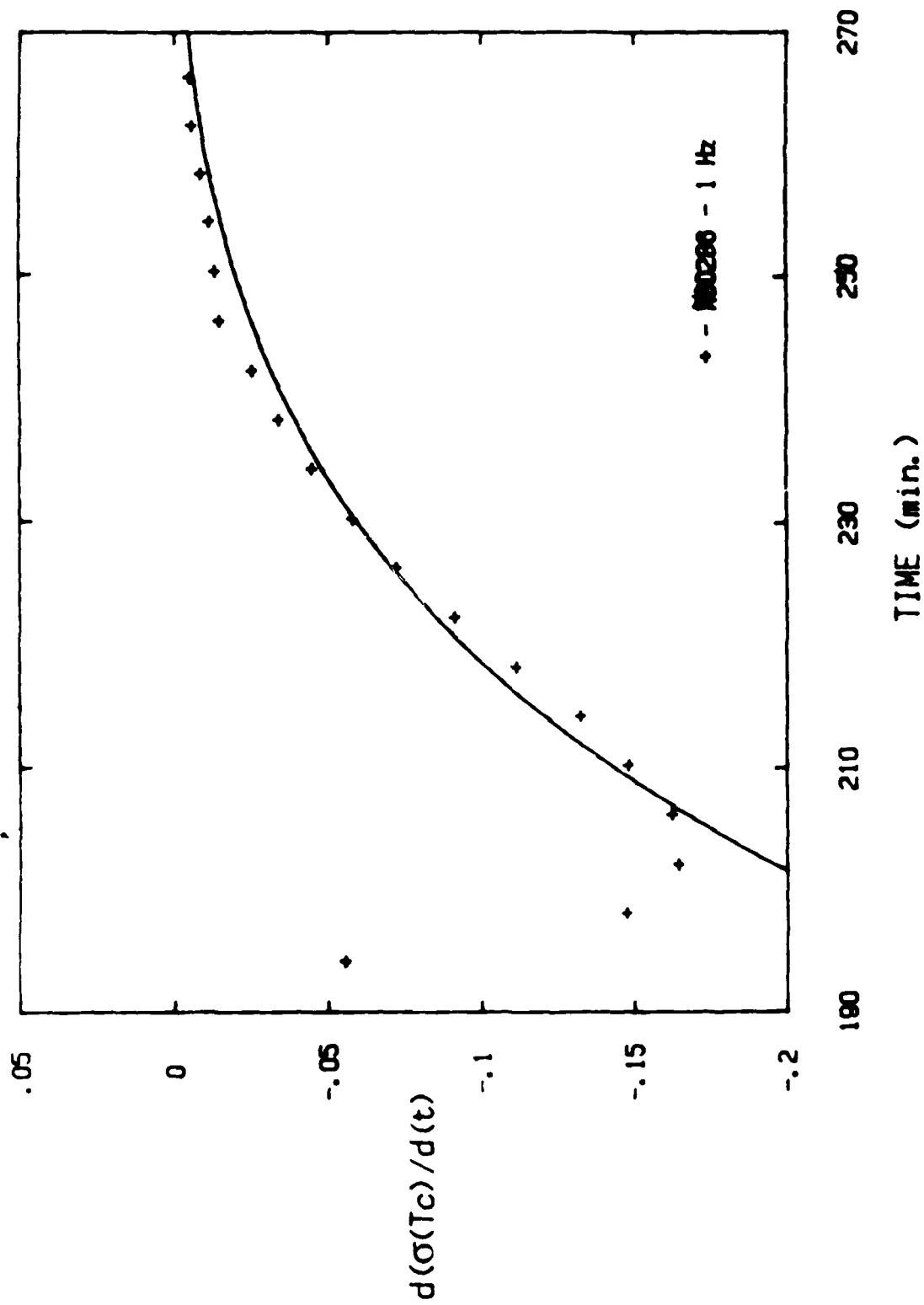
Figure 8   d(log σ)/d(t) versus time. The points represent the data measured by the microdielectrometer and the line is the calculated values determined from the model equation.

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