UNIVERSITY OF ILLINOIS

May 15 1987

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Janice L. Musfeldt

ENTITLED Thermal History and Aging Effects in J-2 Polymer

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

Instructor in Charge
Prof. P.H. Geil

APPROVED: C. Marvin Wayman, Acting Head

HEAD OF DEPARTMENT OF Metallurgical and Mining Engineering

O-1364

THERMAL HISTORY AND AGING EFFECTS ON
THE PHYSICAL PROPERTIES OF J2-POLYMER

BY

JANICE L. MUSFELDT

THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

College of Liberal Arts and Sciences
University of Illinois at Urbana-Champaign
1987

ABSTRACT

This report details the results of an investigation into the affect of thermal history and aging time on the physical properties of Du Pont's thermoplastic (PACM-n) J2-copolymer.

Both glass transition temperature and dynamic mechanical properties were examined as a function of thermal history and aging time. Tensile Properties were characterized at room temperature, 100 °C, and 160 °C.

The position and shape of the glass transition endotherm was found to be a slight function of cooling rate (as well as the extent of T_g overshoot). These trends are discussed in terms of the Free Volume vs. Temperature Curve. Thermal History has a more pronounced affect on the tensile properties; the affect of processing temperature on entanglement networks contributes to these observed properties.

The glass transition temperature of J2-polymer exhibits a significant decrease as a function of aging time. These effects are observable via DSC, viscoelastic spectra, and tensile measurements. Several possible explanations are outlined, but more work is needed to ascertain the true mechanism of aging.

ACKNOWLEDGEMENTS

I would like to take this opportunity to acknowledge and thank the people who advised and helped me during my work on this project. I would especially like to thank:

- Professor P.H. Geil, for his guidance and advice.
- Professor S.S. Wang, for use of equipment in the Composites Center.
- P. Desoutter and D. Phillips, whose assistance was greatly appreciated.
- Materials Research Laboratory, for use of equipment.
- Du Pont, for the generous supply of J2-polymer.

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INTRODUCTION

Because the physical properties of polymers are extremely structure dependent, it is important to characterize them accurately with respect to temperature and time. This report details the results of an investigation into the effect of thermal history and aging on the physical properties of Du Pont's experimental J2-polymer. Both glass transition temperature and dynamic mechanical properties were examined as a function of thermal history and aging time. Tensile properties were characterized at room temperature, 100 °C, and 160 °C. Based upon these results, recommendations for future work are discussed.

SURVEY OF LITERATURE

An amorphous (or glassy) polymer does not have a geometrically regular structure like a crystal. Instead, its structure is more like a liquid: not entirely random, but lacking in long range order.

There are many reasons why the chains in a glassy polymer prefer to be in a less stable disordered state rather than a regularly packed arrangement. One reason is that many structural irregularities are incompatible with the formation of a crystalline lattice. Examples of these irregularities include the presence of bulky side groups, cross linking or an irregular ordering of the repeat unit (tacticity or random co-polymerization). In addition, strong intermolecular forces may interfere with the freedom of motion of the chains by chemically associating certain functional groups in the melt. These factors, plus the loss of mobility associated with the glassy state, prevent the chains from rearranging into a more ordered state.

For any amorphous polymer, the transition from the rubber to glassy state (and vice versa) is called the α relaxation. (For crystalline polymers, the α transition is above T_g.) It is a second order phase transition (as defined by the Ehrenfest criterion) and occurs at a temperature which is called the glass transition temperature (T_g). The position of this change in specific heat (as represented by the DSC curve) is a very important material property.

Although there is no change in the average geometric arrangement (conformation) of the molecules at the glass transition, there is a significant change in the state of molecular motion. Below T_g, chains are frozen in the disordered state. At T_g (and slightly before), thermal energy starts to excite chain mobility, thus inducing bond rotation and vibration, as well as segmental chain movement.

The properties of a polymer are affected by the number of chain entanglements, which is a function of sample thermal history. The temperature of melt, the length of time in the melt, and rate of cooling all contribute to the rate each sample progresses toward the state of an equilibrium number of entanglements.

Polymer conformation and glass transition temperature are directly related to many engineering properties. At T_g, many properties such as Young's and tensile modulus, hardness, elasticity, coefficient of expansion and the dielectric constant exhibit a discontinuity. In both the glassy and rubbery states, the material behaves elastically, although with significantly different modulus. In the vicinity of the relaxation temperature, deformation under applied stress occurs with a loss of energy; this represents the resistance to internal molecular rearrangement. Thus, a polymer is said to exhibit a viscoelastic response.

The glass transition temperature is not a constant for any given polymer--even for a given frequency of applied stress. It can be affected by many things: molecular weight, the amount of chain branching and cross linking, the presence of additive, water adsorption, physical aging, and thermal history.

EXPERIMENTAL

A thermoplastic polymer, J2-polymer (Du Pont's PACM-n polyamide copolymer), was chosen for this study. It is thought to be a completely amorphous polymer with at least two different values of n for the repeat units, the units being randomly arranged within the molecules. The chemical structure of PACM-n is shown in Figure 1. The variation in the number of $-CH_2-$ units for polymers with a single value of n has a major effect on the crystallisability of the polymer (1).

The polymer was supplied in the form of a powder, presumably in the as polymerized state. It was dried in a vacuum oven at 110 °C for 3 hours and stored in a desiccator prior to and after molding.

Samples were prepared by compression molding with various processing conditions. Pressures employed were approximately 800 lb/in^2. Time in the melt was 20 minutes. Variation of sample thermal history was achieved using two different processing temperatures (225 °C and 260 °C). Different rates of cooling were used as well. Samples were slow- cooled in the press (0.5 °C/min), water-cooled in the press (30 °C/min) or quenched in a bucket of water.

The thermal analysis of J2-polymer was done with a Perkin Elmer DSC-4. A heating and cooling rate of 20 °C/min was used for all studies. Each sample was scanned from 70 °C to 220 °C. Several runs were made to higher temperatures. Thus, the effect of thermal history and aging on the glass transition region of compression molded neat resin samples was studied.

X-ray diffraction scans were obtained on a Rigaku D-Max diffractometer with appropriate counting and recording equipment. Measurements were made with CuKα radiation. Scans were done in both transmission and reflection mode over an angular range of $2° \leq 2\theta \leq 52°$. In transmission mode, each sample was scanned at a rate of 10° 2θ/min and added five times to give better peak resolution of the final profile. In reflection mode, each sample was scanned only once at the rate of 4° 2θ/min.

Dynamic mechanical properties (G', G'' and tan δ) were measured using the Rheometrics System-IV in torsion rectangular mode at about 1 Hz frequency and 5 °C temperature increments. Samples were machined into a rectangular shape approximately 2.5 inches long, 0.5 inches wide and 0.032 inches thick.

Melt viscosity as a function of time (at a constant temperature) was measured using the Rheometrics System-IV in dynamic oscillatory shear using parallel plate geometry. Measurements were taken at five minute intervals at a frequency of 1 Hz, the samples being maintained stationary between measurements. The material was machined into one inch diameter disks for testing.

Tensile tests were performed on an MTS testing system (equipped with an oven) under stroke control at a 2%/min strain rate. Local axial displacement was measured with a one inch gauge length MTS extensometer. Load/displacement data was recorded and converted to engineering stress/strain curves. The standard dog-bone sample geometry (ASTM D638, thickness = 0.32 inches) was used to insure a uniform stress distribution along the gauge length. When tests were performed at elevated temperatures, samples were given 15-20 minutes to come to thermal equilibrium in the oven.

RESULTS AND DISCUSSION

Thermal History Effects

Differential Scanning Calorimetry (DSC) was used to examine the glass transition temperature as a function of thermal history. These results are shown in Figures 2-5, and summarized in Table 1. (also see later discussion on aging affect) The position of T_g is only a slight function of the rate of cooling; for both processing temperatures, the water-cooled samples have a higher T_g, but a factor of 60 increase in the cooling rate increases T_g only approximately 2.5 °C. The effect of the processing temperature is less clear. However, aging times are not identical (see later discussion on aging), so no good comparison can be made.

These observed trends are explainable in terms of the Free Volume vs. Temperature curve, shown in Figure 6. It is proposed that the faster cooled samples "quenched in" a greater degree of disorder, i.e. a higher free volume, whereas, in slow-cooled samples, the volume shrinks along the equilibrium liquidus line to a lower value before molecular motion ceases. When reheated in the DSC, the position of T_g and the presence of an endothermic T_g-overshoot peak will depend on the rate of heating in the DSC relative to the initial rate of cooling (as well as the length of time and the temperature at which the sample is stored below T_g, see next section on aging effects). If heated more slowly than cooled or at the same rate, the volume will increase along the appropriate glassy state volume expansion line until it meets the equilibrium liquidus line; thus, T_g will be lower for a slow cooled sample, and only a base line shift will be observed at T_g. If heated more rapidly than cooled, it is observed that the sample overshoots the equilibrium line and then rises rapidly to that line, as shown by the dotted line in Figure 6. In this case, T_g for the slow cooled sample can be either lower or higher than for a quenched sample depending on the amount of overshoot.

The shape of the T_g endotherm is also a function of thermal history. At slow cooling rates, an endothermic hump is observed at T_g, in addition to the typical baseline shift. The endothermic peak (T_g overshoot) corresponds to the heat absorbed as the sample free volume rises to the equilibrium line, and it results in an error in measurement of T_g. The presence of a small endothermic hump on the second heating runs suggests that the heating and cooling processes are not completely reversible. This endothermic hump is not seen in the more rapidly cooled samples.

The effect of annealing below T_g was also examined by DSC. After annealing only two days at 145 °C, the shape of the T_g endotherm changed significantly for both slow-cooled and water-cooled samples. In both specimens, a large endothermic hump appeared in addition to the typical baseline shift. This is (possibly) indicative of a more ordered hydrogen bond structure which formed upon annealing and is broken up by the molecular motion at T_g. Such an explanation has been used in the literature to explain similar effects in a number of nylons (2). However, it is noted that infrared (IR) spectroscopy in that paper and in our laboratory on J1 (a PACM-n homopolymer) (3) indicate that the hydrogen bonding network is gradually broken up with increasing temperature. No significant change occurs at T_g. Instead, we propose the endothermic hump may again be related to the T_g overshoot. Annealing below T_g results in a slow decrease in density (and thus, free volume) for all samples, quenched or slow cooled. When heated rapidly, these samples will show a higher T_g and a larger endothermic peak. (Note the T_g of this sample can not be compared with those of the other samples; this sample was 'aged' at room temperature prior to annealing, see below.)

Both X-ray reflection and transmission were used to examine the diffraction pattern of J2-polymer as a function of thermal history. Scans for three different thermal histories are shown in Figures 7 and 8. A comparison of these scans indicates that three amorphous peaks are present in each sample, one strong peak at ~19° similar to that found in many other amorphous polymers and two peaks at 7° and 42°. Values of 2θ, d, and full width at half maximum are listed in Table 2.

The small peak at 2θ ≈ 7° corresponds to an intra-molecular spacing of between 12-13 Å. This is about half the length of the chemical repeat unit. The main scattering peak (2θ ≈ 19°) corresponds to inter-molecular spacings.

As evidenced by the increased half width of the main peak, the quenched samples appear to have a larger distribution of inter-molecular spacings than the slow-cooled samples. This indicates that quenched samples have a more irregular structure. However, in both reflection and transmission, faster cooling increases 2θ (decreases d) of the main peak, which suggests that the slow-cooled sample should have a larger free volume than the quenched sample. This is opposite to the explanation described above. We have no explanation for this discrepancy at present.

By measuring the mechanical response of a material as it is deformed under periodic stress, the viscoelastic behavior of a polymer can be characterized. Dynamic mechanical properties were studied using the Rheometrics System-IV in torsion rectangular mode. As shown in Figures 9-11, the magnitudes of the storage modulus, loss modulus and tan delta (G', G'', Tan δ) are only a slight function of thermal history. For example, the elastic modulus of J2 is $9.9\times10^9 \pm 0.1\times10^9$. Thus, J2 has good stiffness for all processing conditions tested, until reaching T_g.

Much of this stiffness is lost during the relaxation at the glass transition temperature. There is no change in the size, shape or position of this relaxation in the dynamic mechanical spectra as a function of thermal history. The scattered data points approximately 15 °C above T_g are due to sample slumping, stretching (and finally, flow). In glassy polymers, not only can this range of the scan not be properly measured in the chosen mode of operation of the equipment, but it is anticipated that the dynamic mechanical properties will not be function of thermal history above T_g.

It was expected that the samples processed at 260 °C would have a different number of chain entanglements than those processed at 225 °C (under constant cooling rate), the number increasing with increasing coil size. Following solidification, the mechanical properties may be dependent on this entanglement network

Melt viscosity as a function of time (at a constant temperature) was examined on the Rheometrics System-IV in dynamic mode under oscillatory shear. A comparison of Figures 12 & 13 shows the effect of melt temperature on the melt viscosity of a sample of J2-polymer that was initially rapidly molded at 225 °C. The appearance of the powder suggests that it was precipitated from solution during polymerization. The melt viscosity at 260 °C is constant with respect to time, whereas the melt viscosity of the sample tested at 225 °C increases --and then reaches a plateau-- as a function of time. (Both specimens were equilibrated at the appropriate temperature for 15 minutes prior to measurement.) Since the entanglement network is dependent on the viscosity (4), this behavior suggests that it takes time for the molecules to attain an equilibrium entanglement state from the presumably less entangled original (solution precipitated?) state. Following solidification, the mechanical properties are dependent on this entanglement network.

Tensile properties of J2-polymer as a function of thermal history were studied at three different temperatures. Tensile curves are shown in Figures 14-16, and values of tensile modulus, 2% offset yield stress, the yield point (if present) and the ultimate tensile strength are summarized in Table 3. As shown in the Figures, the engineering stress/strain curves show the classical cold-drawing behavior. This is characterized by non-linear strain softening in the first region, yielding, and stress decreasing to a constant value as the neck propagates.

Tensile properties of J2-polymer at room temperature are shown in Figure 14. Tensile modulus is very similar for all samples tested. Both specimens processed at 260 °C exhibit ductile failure, with the slow cooled sample possessing a somewhat higher yield point than the water cooled sample. Both samples processed at 225 °C exhibit brittle failure.

These observations can be explained in terms of variations in the degree of chain entanglements. As shown in the melt viscosity studies, the number of chain entanglements are directly related to temperature and time in the melt. In addition, in hydrogen bonding polymers, there can be significant entanglement coupling as a result of strong interactions at specific sites along the chain (5). Thus, specimens processed at 225 °C may possess fewer than the equilibrium number of chain entanglements due to insufficient time in the melt. The rate of cooling can have a similar effect. A slower cooling rate will enable a more stable (entangled) structure to form.

When tested at 100 °C, J2-polymer is a softer material, and all tensile samples exhibit ductile failure upon deformation. This is shown in Figure 15. At both processing temperatures, the slow cooled samples exhibit a greater ultimate tensile strength than the water cooled samples. This verifies results obtained at room temperature--that slow cooled samples have a greater number of chain entanglements than their more rapidly cooled counterparts. However, samples processed at 225 °C exhibit greater strength at the yield point than the corresponding sample processed at 260 °C. More work should be done to investigate the reproducibility of this result.

Tensile specimens tested at 160 °C will be discussed in terms of aging time, in the next section.

Aging

While examining T_g on the DSC as a function of thermal history, severe 'aging' effects were observed. The glass transition temperature as a function of thermal history and aging is shown in Table 1. A plot of T_g vs. time (for the three different thermal histories) shows that T_g decreases rapidly from about 170 °C at short times, reaching a plateau of approximately 140 °C at longer times (see Figure 17). This unexpectedly large decrease in T_g should play a significant role in potential practical applications of this polymer. Thus, the origin is very important.

In addition to the change in position of T_g, the shape of the T_g endotherm changed significantly with increasing sample 'age'. At short times, an endothermic hump was observed at T_g in slow-cooled samples; at longer times, this hump was replaced by a typical baseline shift, as in the original water-cooled samples. These observations argue against the idea that the peak height may be the result of the breakup of a hydrogen bonding network, since the network would be expected to strengthen with 'aging' time.

Another phenomena (associated with sample 'aging') is the appearance of several large, sharp endothermic peaks approximately 50 °C above T_g. A representative scan is shown in Figure 18. These peaks do not appear on 'unaged' samples--even when scanned to 270 °C. This indicates that the appearance of these peaks is associated with the passage of time. In addition, this phenomena has only been observed in the water-cooled samples. One line of speculation as to the origin of these peaks is that they are caused by the recoil of residual stresses and strains in the sample. Since the slowly cooled samples stay in the melt long enough to relieve much of the stress, this explains the absence of the large peaks in scans of slow-cooled samples. However, we might expect residual stresses to be relieved closer to T_g than 50 °C; possibly the pressense of the hydrogen bond network superimposed on a relatively rapid heating rate causes the 50 °C shift in temperature. Another possible explanation is degradation. However, more work needs to be done to ascertain the true explanation.

The thermal history effect on the rate of 'aging' is not clear. As shown in Figure 17, there is a slight difference in T_g for similar 'aging' times. More work should be done to characterize this effect.

'Aging' effects in dynamic mechanical properties can be seen via comparison between Figures 9-11 (2 day old samples) and Figures 19-21 (2 week old samples). Because the glass transition temperature occurs approximately 25 °C lower in the two week old samples, the mechanical properties (G', G", Tan δ) undergo the corresponding α transition earlier. However, little change in the magnitude of these properties was noted before or after the transition as a function of 'aging time'. In addition, the size and shape of the relaxation did not change with 'aging time'.

Tensile properties (measured at 160 °C) are a clear example of the effect of 'aging'. As shown in Figure 16, the newest sample has the greatest tensile modulus and yield point. The two oldest samples support minimal stress at 160 °C, and consequently, no value of tensile modulus was obtained; no yielding or necking was observed. This indicates that T_g in these 'aged' samples has decreased below 160 °C. This trend supports earlier evidence (obtained by DSC) that 'aging' is occurring, and T_g is decreasing with time.

Possible explanations of the observed 'aging' in J2-polymer include: physical aging, hydrogen bond network formation, degradation with light/O_2, relaxation of residual stress incurred durring the compression molding process and moisture adsorption. Each possibility will be considered and discussed in terms of its effect on T_g.

The gradual approach to an equilibrium state with increasing time (with respect to volume, enthalpy and entropy) is called physical aging (6). Physical aging can strongly affect the behavior of a glassy polymer, particularly if T_g is greater than room temperature. It persists for long periods of time (occuring more slowly at lower temperatures) and is completely thermoreversible if the sample is heated above T_g. Physical aging is best explained qualitatively in terms of free volume effects.

In an attempt to establish equilibrium, glassy materials undergo a very free slow free volume relaxation along the dotted vertical line shown in Figure 22. The extent of this decrease (which is small, but finite below T_g) is proportional to aging time, as well as the temperature at which it occurs. Thus, physical aging affects physical properties primarily through the decrease in free volume and the corresponding changes in relaxation times.

The Free Volume vs. Temperature graph (Figure 22) shows the affect of physical aging on the glass transition temperature. As the free volume decreases during 'aging' (following the dotted line), T_g increases if heated rapidly, as the result of T_g overshoot. Therefore, a heating/cooling rate of 20 °C/min causes T_g to increase with the passage of time. Thus, the normal trend in physical aging is directly opposed to the trend observed in J2-polymer, and it is not usually so large. In addition, the rate of physical aging for J2-polymer should not be appreciable at room temperature, 120-150 °C below T_g. Consequently, physical aging is not a viable explanation.

Because J2-polymer is a polyamide, intermolecular hydrogen bonding is potentially very important. Each monomer unit has two sites where hydrogen bonding could potentially take place. However, the molecular rearrangements which occur with time would tend to strengthen the hydrogen bonding network between the chains, thus increasing T_g. This trend is directly opposite to the trend observed in J2-polymer.

Sample degradation (by O_2 or light) is another possible explanation for the observed decrease in T_g with time. However, the degradation process is continuous; it occurs at a constant rate, and no plateau is reached at longer times. In addition, this effect would not be reversible. Running an aged sample in the DSC results in an increase in T_g of 17 °C upon reheating. For these reasons, degradation is an unlikely cause of the observed 'aging' effects.

A more plausible explanation for the observed 'aging' effects in J2-polymer is the relaxation of residual stresses incurred in the compression molding process. Samples are molded under extreme compression, causing the free volume of the chains in the melt to decrease. Cooling the sample freezes in this conformational stress. The greater the cooling rate the lower the density (greater free volume) for a given applied pressure (7). Although the affect of cooling rate under pressure on T_g has not been reported, an increase in T_g with molding pressure has been reported for glassy polymers (8). The presence of this residual stress lowers the free volume and induces an artificial increase in T_g, which one would expect to relax (decrease) with time. At longer times, the sample reaches an equilibrium plateau.

This is the trend which is observed in J2-polymer. It accounts for the observation that $T_{g,water\ cool} > T_{g,slow\ cool}$. However, the magnitude of ΔT_g (between water cooled and slow cooled samples) in unaged samples is only 3 °C. Since the slow-cooled sample would be expected to have minimum residual stress but has a T_g in an unaged sample only 3 °C below that of a quenched sample, the 30 °C drop in T_g with 'aging' appears to large to interpret solely in terms of relaxation of residual stresses. Thus, residual stress relaxation may be a partial explanation for the observed decrease in T_g with 'aging', but it is only part of a larger contribution.

The most realistic explanation for the magnitude of the decrease in T_g with increasing sample age appears to be the adsorption of water. Baer et al. (9) claim a 40 °C drop in T_g with only 1.2 wt. % water for nylon 6 corresponding to slightly fewer than one water molecule bridging each carbonyl-amino group. For longer repeat units (such as Nylon 12), 20 °C drops in T_g have been reported (for samples conditioned in 100% relative humidity) by Prevorsek, Butler, and Reimschuessel (5). As J2-polymer is also a polyamide, these figures may be indicative of the size of drop in T_g that could be expected with the absorption of only one water molecule per repeat unit, i.e. bridging all carbonyl and amino functional groups.

Water absorption and incorporation procedes by a mechanism involving aqueous hydrogen bonding. According to Baer et al, the water molecule spans the intermolecular gap between the carbonyl and amino functional groups, thus decreasing intermolecular adhesion (9). This reduces the steric restrictions for motion which were previously associated with the hydrogen bonding between segments.

Since the absorption of water occurs gradually, this explains the decrease (and gradual approach to a plateau) in T_g with respect to time. However, this explanation has several flaws. Kolarik and Janacek (10) claim that upon water absorption there is a change in the size and shape of the α-relaxation peak (in addition to position). With increased water absorption, the loss maximum becomes significantly higher and narrower with increasing absorption. Comparison of Figures 10 & 20 shows that in J2-polymer, the shape of the loss maxima does not change with 'aging time'. Thus, this theory does not explain the observed viscoelastic behavior. In addition, all samples were kept in a desiccator. If this is to be a plausible explanation, one must assume that J2-polymer has a greater affinity for water complexation than the desiccant.

In conclusion, the observed 'aging' phenomena in J2-polymer has a number of possible origins. The final explanation may involve a combination of these mechanisms. More work should be done to ascertain the complete explanation.

CONCLUSIONS AND RECOMMENDATIONS

Results of this study can be summarized as follows:

1 - faster cooling rates result in a slightly higher T_g due to decreased free volume.

2 - melt temperature (with a constant time in the melt) affects the rate of approach to the equilibrium number of chain entanglements.

3 · the observed endothermic hump at T_g in both the slow-cooled and annealed samples is probably due to T_g overshoot. Water-cooled samples do not exhibit this additional increase in specific heat.

4 - at short times, T_g decreases rapidly with increasing 'age', reaching a plateau of approximately 140 °C at longer times.

5 - sample 'aging' is evidenced by the position of T_g using DSC and the position of the α relaxation in the dynamic mechanical properties, as well as in the tensile properties when tested at 160 °C.

Therefore, I recommend:

1 - closely examining the effects of annealing on T_g, the dynamic mechanical properties, and the tensile properties.

2 - investigation of the origin of the large, sharp endothermic peaks observed at higher temperatures in DSC scans of water-cooled samples.

3 - clarifying the effect of processing thermal history on 'aging'.

4 - examining the effect of water absorption more closely by testing samples with known moisture content to ascertain the rate that J2-polymer incorporates water, as well as its saturation limit. The effect of moisture on the shape and position of T_g must also be studied.

5 - determine the origin and exact mechanism of the observed 'aging' phenomenon.

6 - review all mechanical testing of J2-polymer in terms of 'aging time' prior to testing.

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ATTACHMENTS

TABLE 1

GLASS TRA N TEMPERATURE AS A FUNCTION
OF T HISTORY AND AGING TIME

THERMAL HISTO	AGING TIME (days)	T_g
Water Cooled from C	1	170.3
	3	164.0
	7	157.5
	45	143.0
	49	141.0
Slow cooled from 225 °C	1	167.0
	35	153.0
Water cooled from 260 °C	1	169.0
Slow cooled from 260 °C	0	169.5
	1	164.4
	34	148.4

TABLE 2

X-RAY PARAMETERS AS A FUNCTION OF THERMAL HISTORY

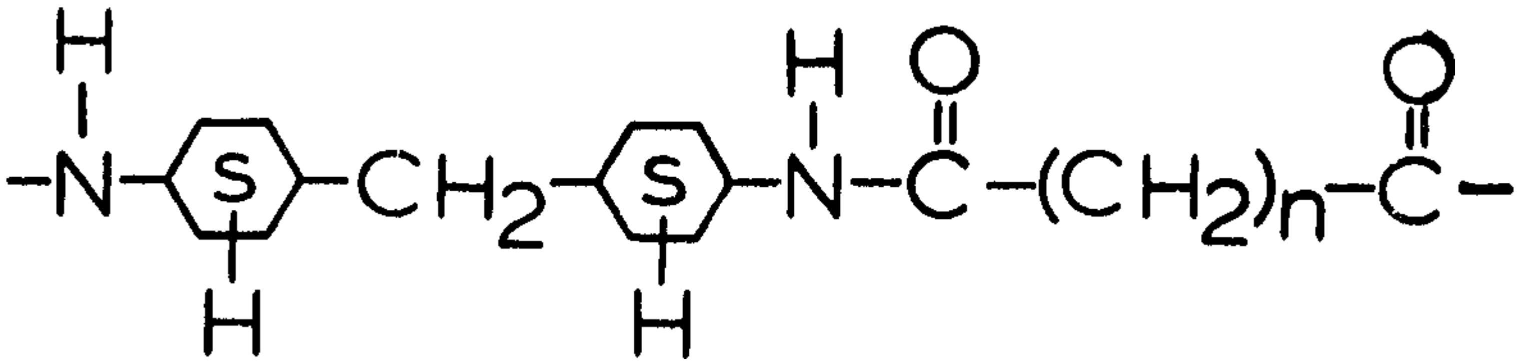
$T_{PROCESS}$	COOL RATE	MODE	2θ	d	FWHM
260 °C	0.5 °C/min	reflect.	6.9(est.)	12.8(est.)	-
			20.46	4.34	7.16
			42.88	2.11	5.40
		transmi.	7.2(est.)	12.3(est.)	-
			20.54	4.32	7.24
			42.71	2.11	5.40
260 °C	QUENCH	reflect.	7.7(est.)	11.5(est)	-
			20.92	4.24	7.34
			43.27	2.09	5.69
		transmi.	7.7(est.)	11.5(est.)	-
			21.00	4.23	7.51
			42.15	2.14	5.42
225 °C	QUENCH	reflect.	7.5(est.)	11.8(est.)	-
			21.06	4.21	7.57
			42.62	2.12	2.91
		transmi.	7.0(est.)	12.6(est.)	-
			20.25	4.38	7.58
			42.64	2.11	7.06

TABLE 3

TENSILE PROPERTIES OF J2 AS A FUNCTION OF THERMAL HISTORY

T_{TENS}	$T_{PROCESS}$	COOL RATE	E(ksi)	YIELD PT	2% OFF	σ_{TS}(ksi)
26°C	260°C	0.5°C/min	394.6	14.9	7.0	10.3
		30°C/min	433.3	13.9	6.5	10.2
	225°C	0.5°C/min	410.3	no yield	6.8	13.5
		30°C/min	411.7	no yield	6.8	13.1
100°C	260°C	0.5°C/min	318.3	8.6	5.5	5.5
		30°C/min	318.9	7.4	4.7	5.2
	225°C	0.5°C/min	358.4	9.3	5.6	5.9
		30°C/min	348.4	8.5	4.3	6.0
160°C	260°C	0.5°C/min	-	-	-	-
		30°C/min	87.3	0.55	0.41	0.46
	225°C	0.5°C/min	-	-	-	-
		30°C/min	147.4	0.81	0.43	0.65

J2-POLYMER



(PACM-n)

Figure 1: The chemical structure of the PACM-n repeat unit. J2-polymer has at least two different values of n for the repeat unit.

FIGURE 2

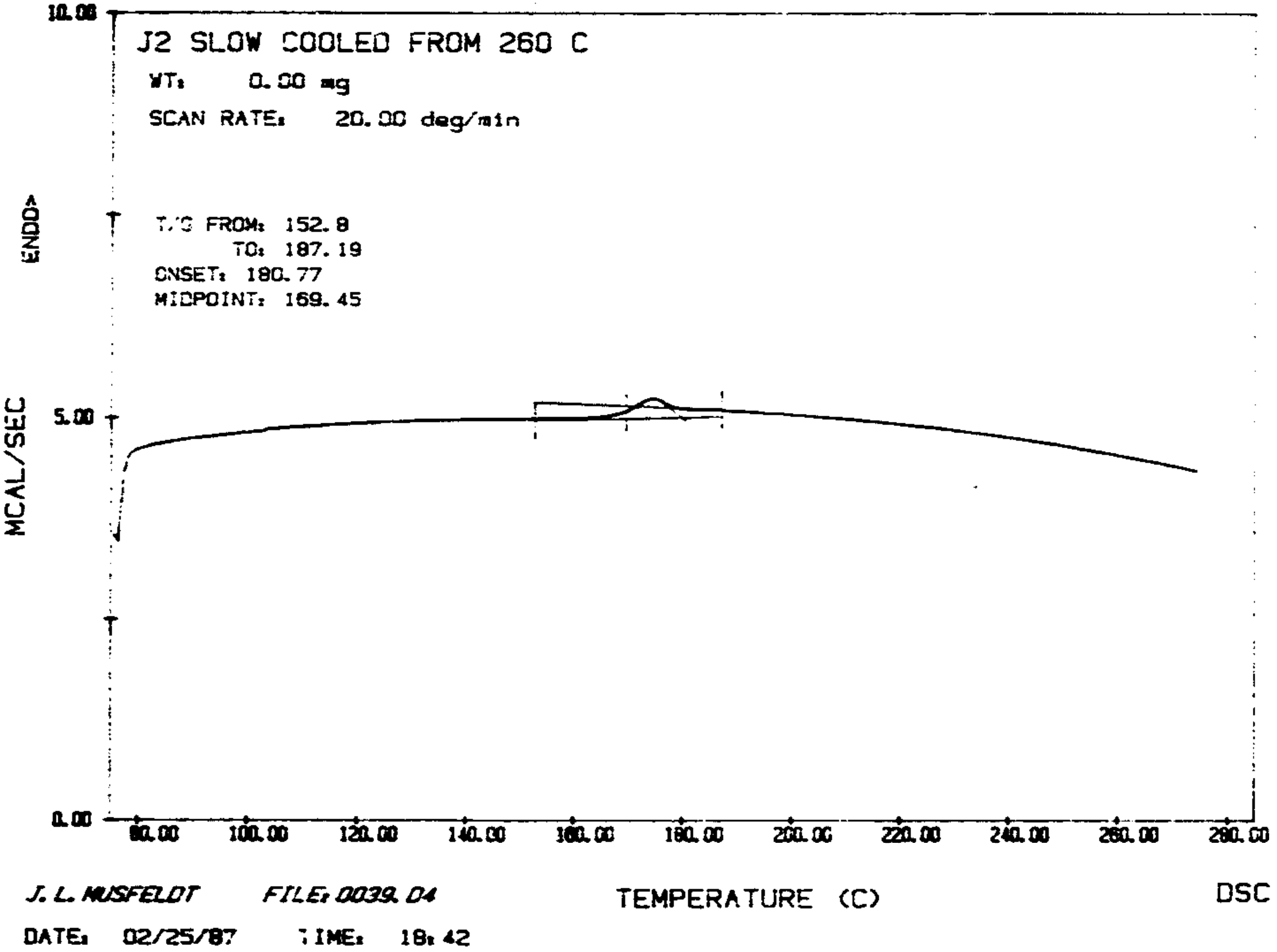

J2 SLOW COOLED FROM 260 C
WT: 0.00 mg
SCAN RATE: 20.00 deg/min
T/G FROM: 152.8
TO: 187.19
ONSET: 180.77
MIDPOINT: 169.45
ENDO>
MCAL/SEC
10.00
5.00
0.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
260.00
280.00
TEMPERATURE (C)
DSC
J. L. MUSFELDT
FILE: 0039.04
DATE: 02/25/87
TIME: 18:42

FIGURE 3

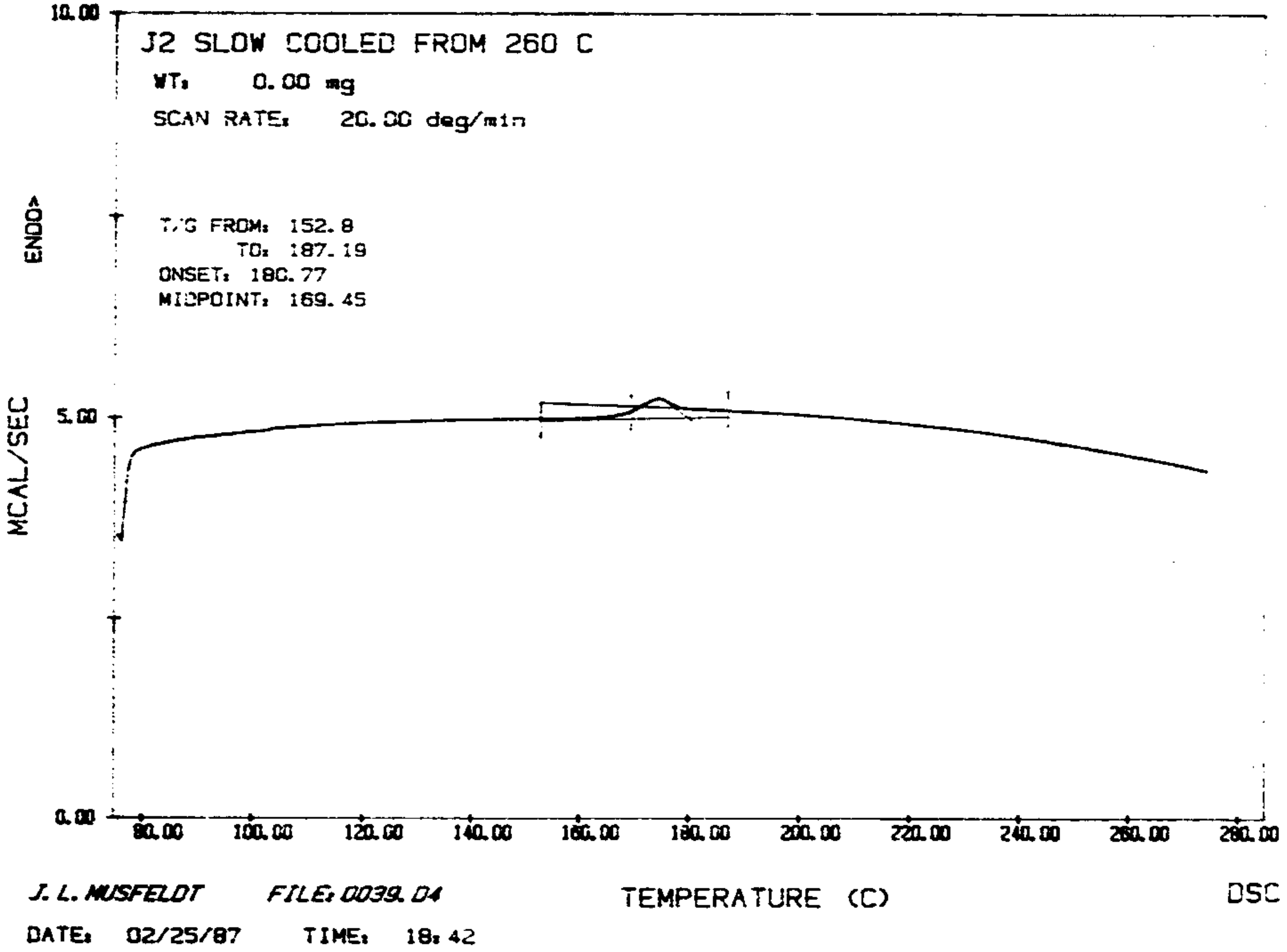

J2 SLOW COOLED FROM 260 C
WT: 0.00 mg
SCAN RATE: 20.00 deg/min
T/G FROM: 152.8
TO: 187.19
ONSET: 180.77
MIDPOINT: 169.45
10.00
5.00
0.00
ENDO>
MCAL/SEC
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
260.00
280.00
TEMPERATURE (C)
J. L. MUSFELDT
FILE: 0039.04
DSC
DATE: 02/25/87
TIME: 18:42

FIGURE 4

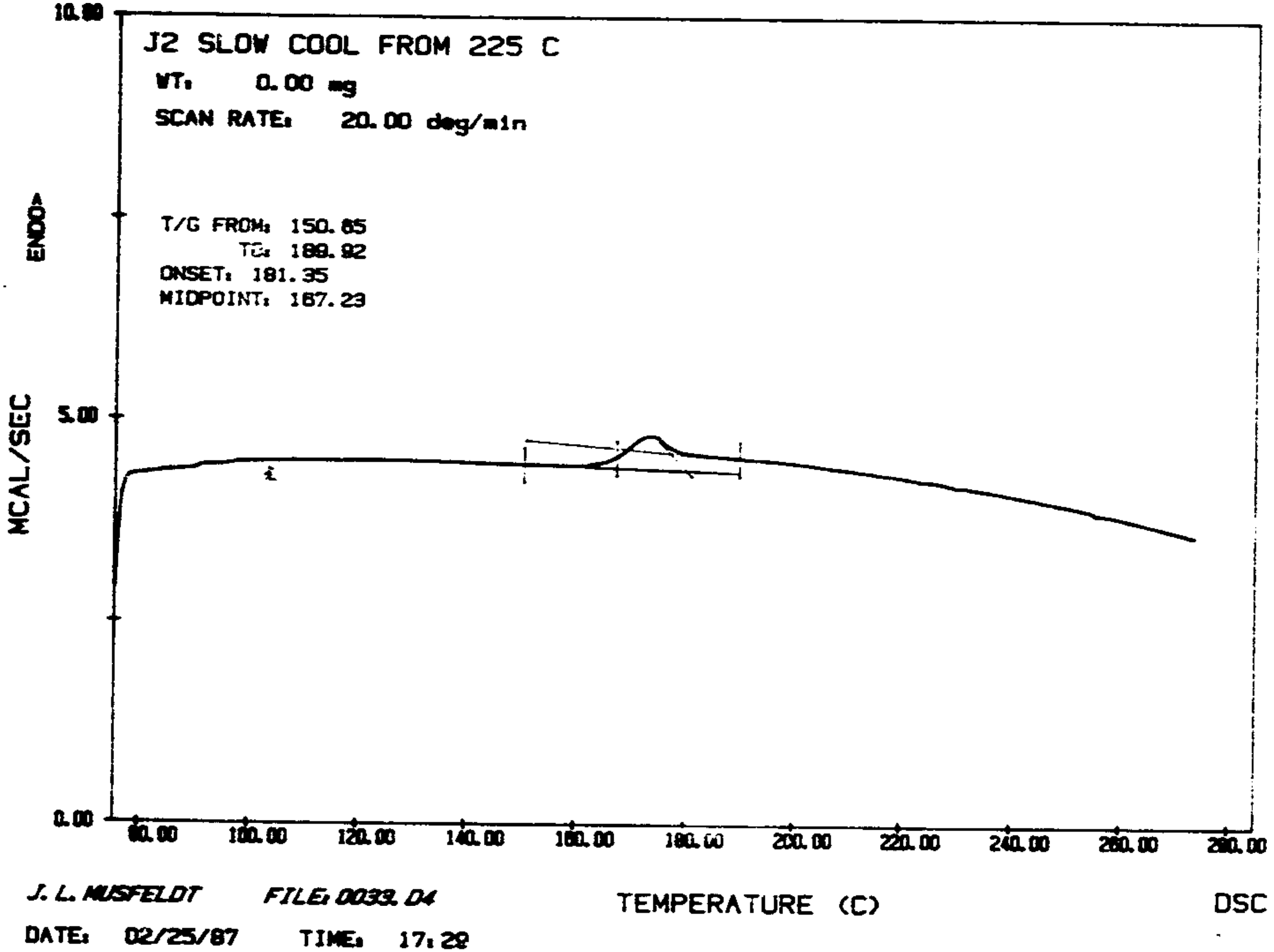
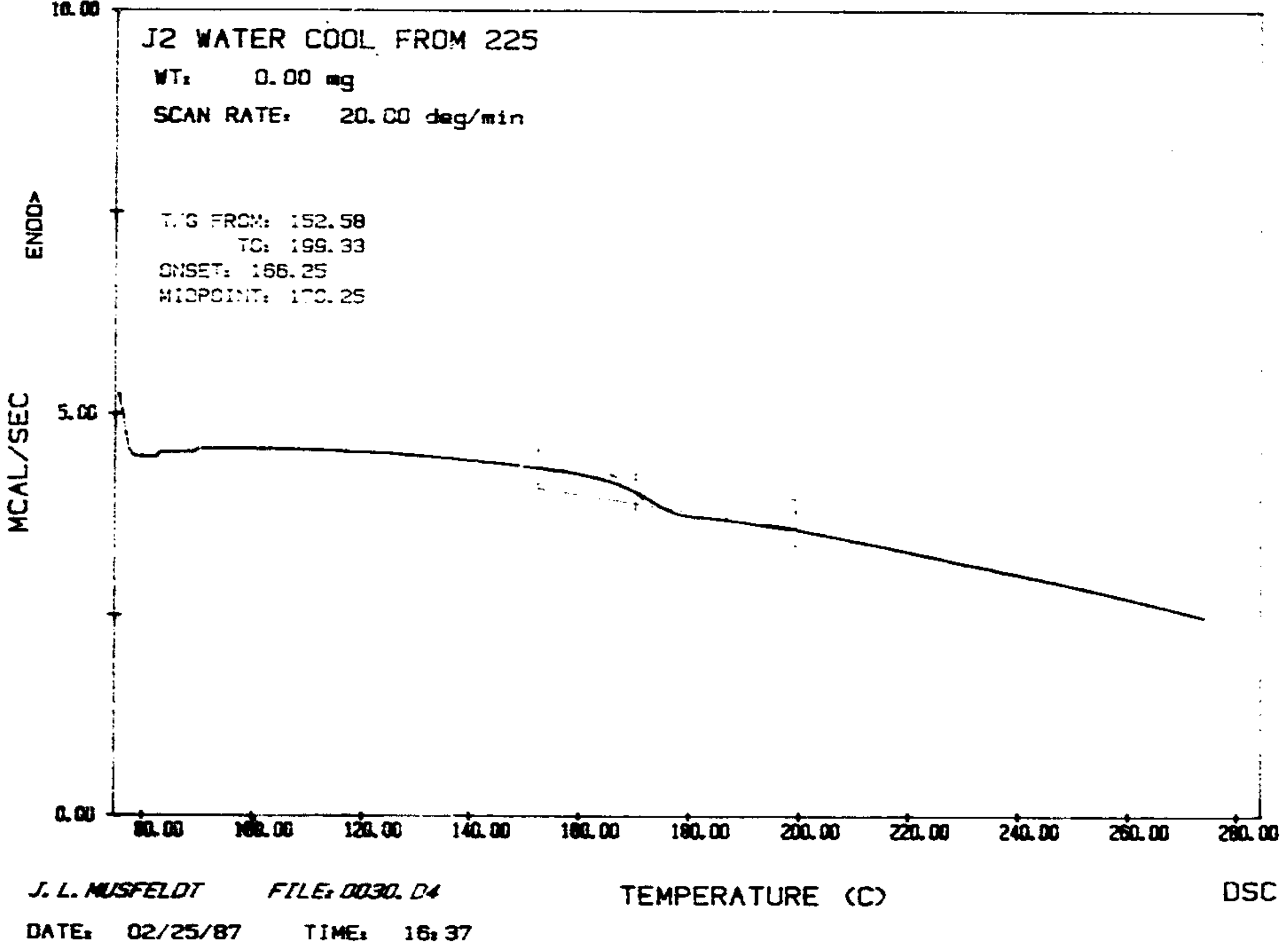

J2 SLOW COOL FROM 225 C
WT: 0.00 mg
SCAN RATE: 20.00 deg/min
T/G FROM: 150.65
TG: 188.92
ONSET: 181.35
MIDPOINT: 187.23
10.00
5.00
0.00
ENDO>
MCAL/SEC
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
260.00
280.00
TEMPERATURE (C)
DSC
J. L. MUSFELDT
FILE: 0039.D4
DATE: 02/25/87
TIME: 17:28

FIGURE 5


J2 WATER COOL FROM 225
WT: 0.00 mg
SCAN RATE: 20.00 deg/min
T/G FROM: 152.58
TO: 199.33
ONSET: 166.25
MIDPOINT: 170.25
10.00
5.00
0.00
ENDO>
MCAL/SEC
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
260.00
280.00
TEMPERATURE (C)
J. L. MUSFELDT
FILE: 0030.D4
DSC
DATE: 02/25/87
TIME: 16:37

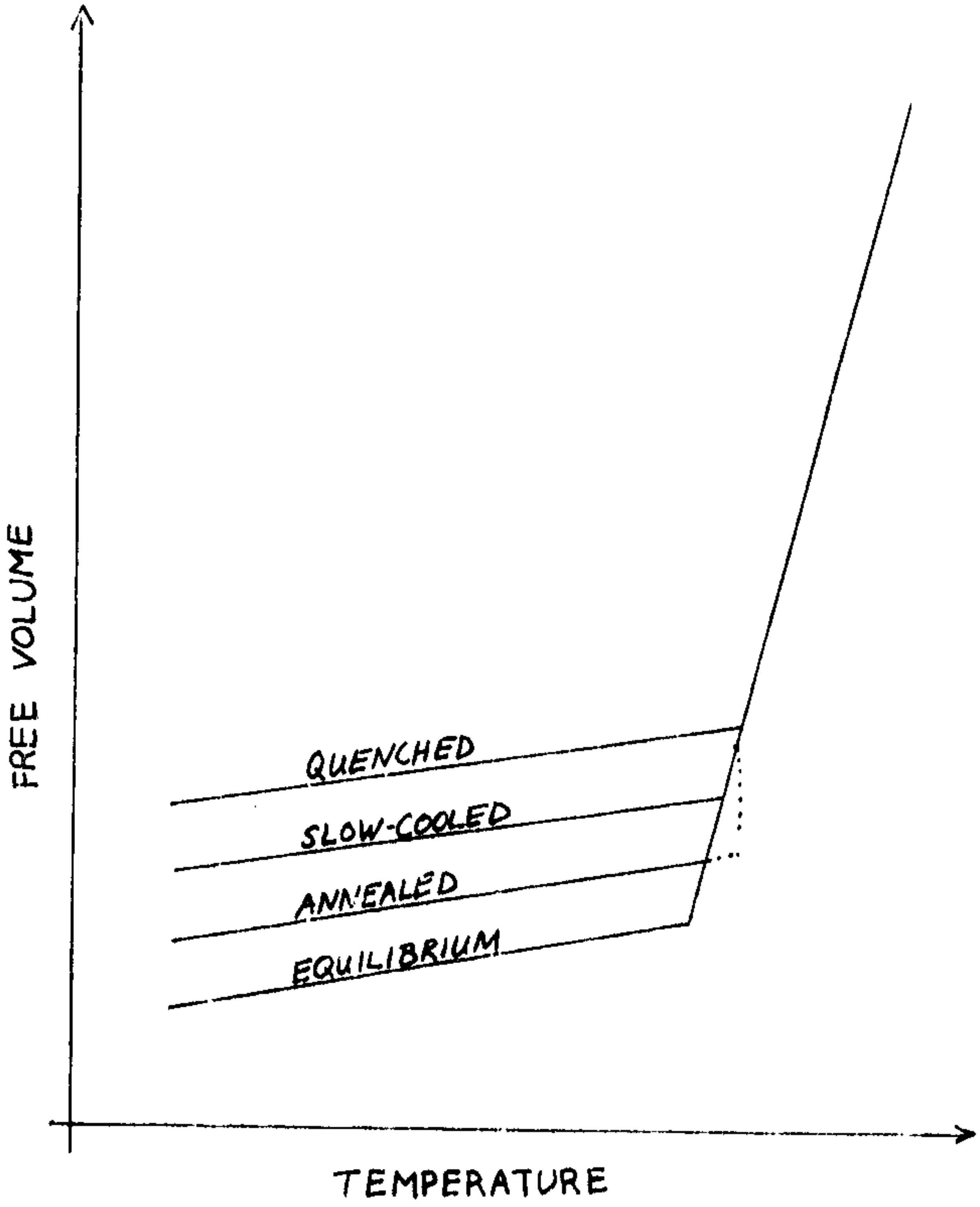


FIGURE 6

FREE VOLUME VS. TEMPERATURE

EFFECTS OF THERMAL HISTORY
AND ANNEALING

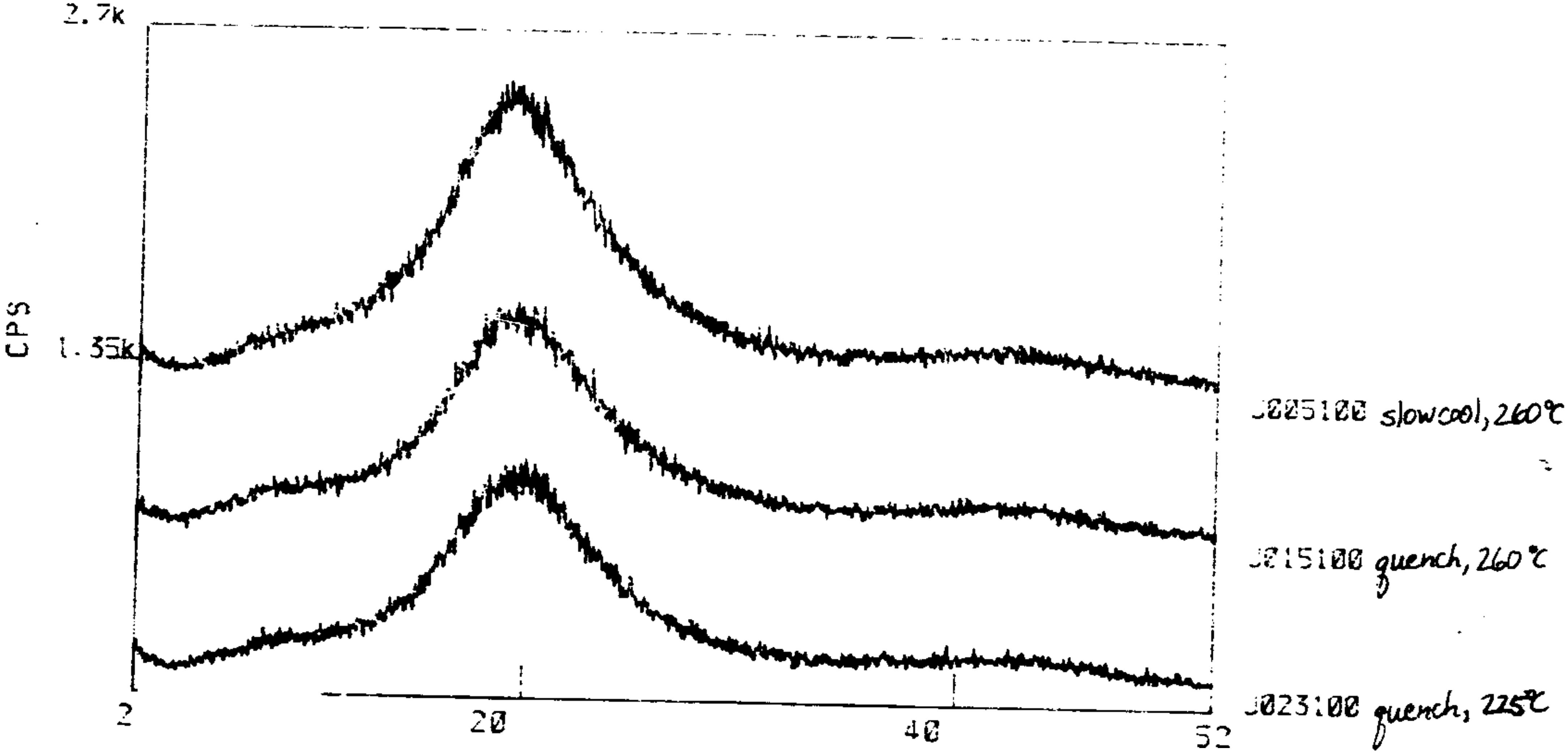


FIGURE 7: X-RAY SCANS
REFLECTION MODE

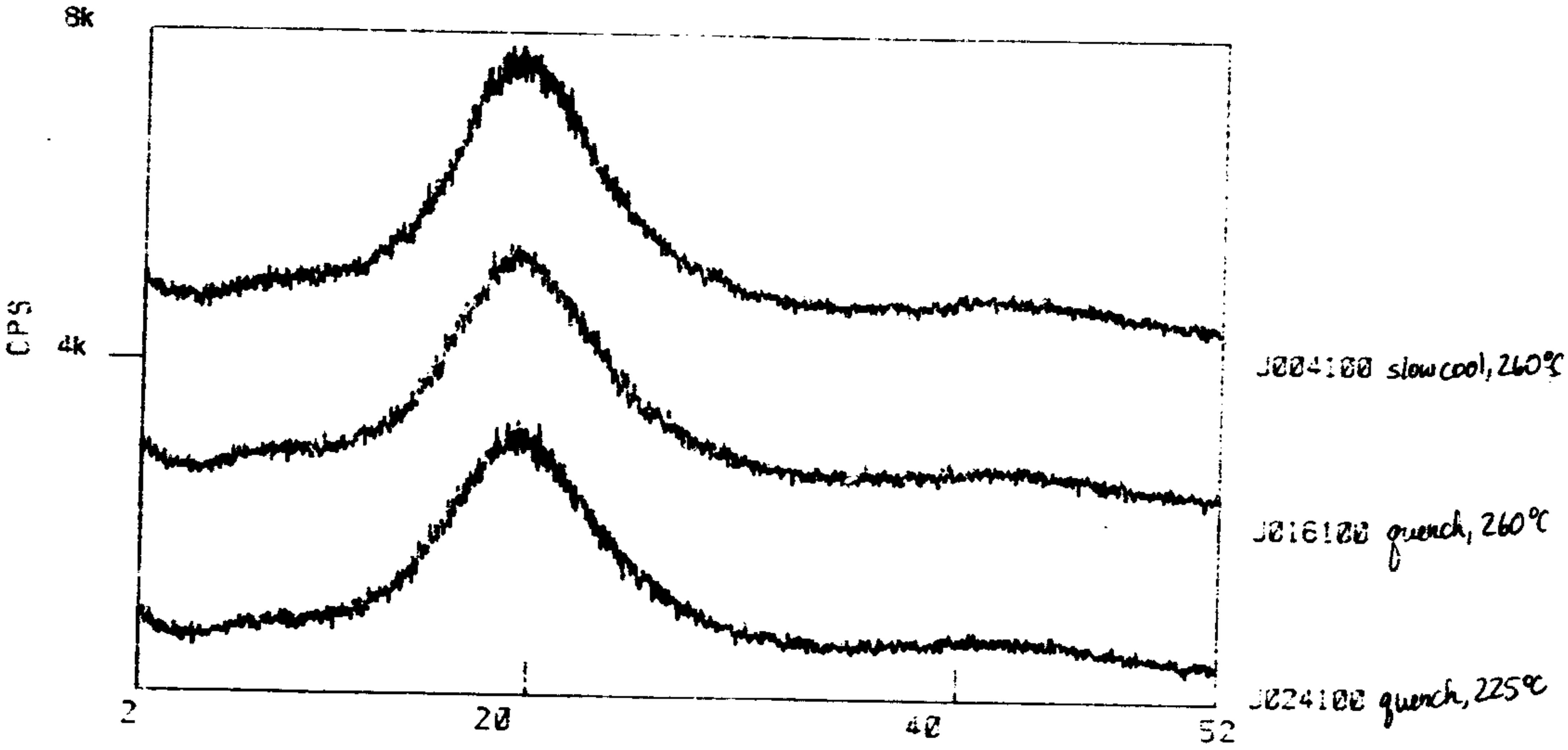


FIGURE 8: X-RAY SCANS
TRANSMISSION MODE

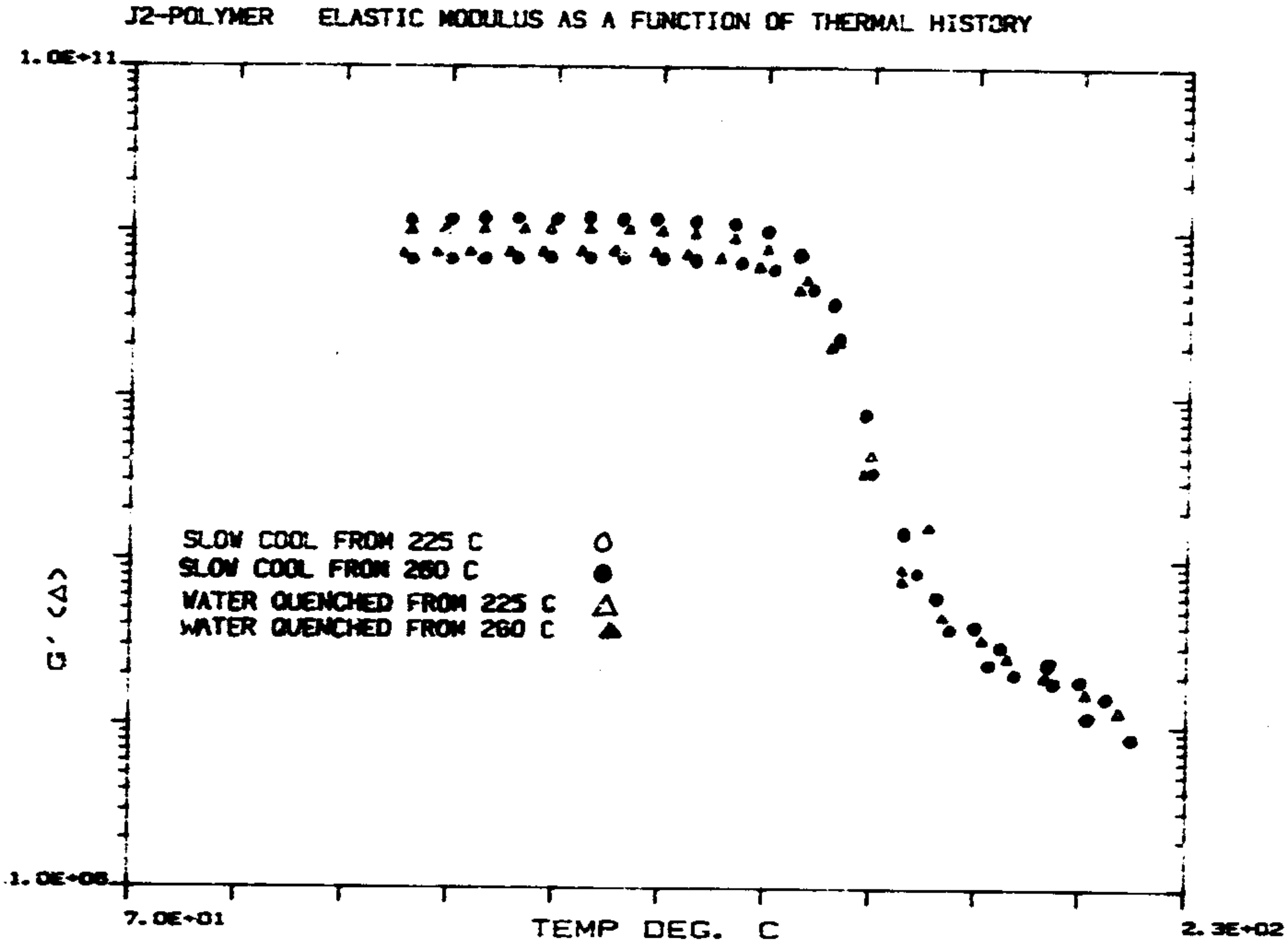

J2-POLYMER ELASTIC MODULUS AS A FUNCTION OF THERMAL HISTORY
1.0E+11
1.0E+08
7.0E+01
2.3E+02
TEMP DEG. C
G' <Δ>
SLOW COOL FROM 225 C ○
SLOW COOL FROM 260 C ●
WATER QUENCHED FROM 225 C △
WATER QUENCHED FROM 260 C ▲

FIGURE 9

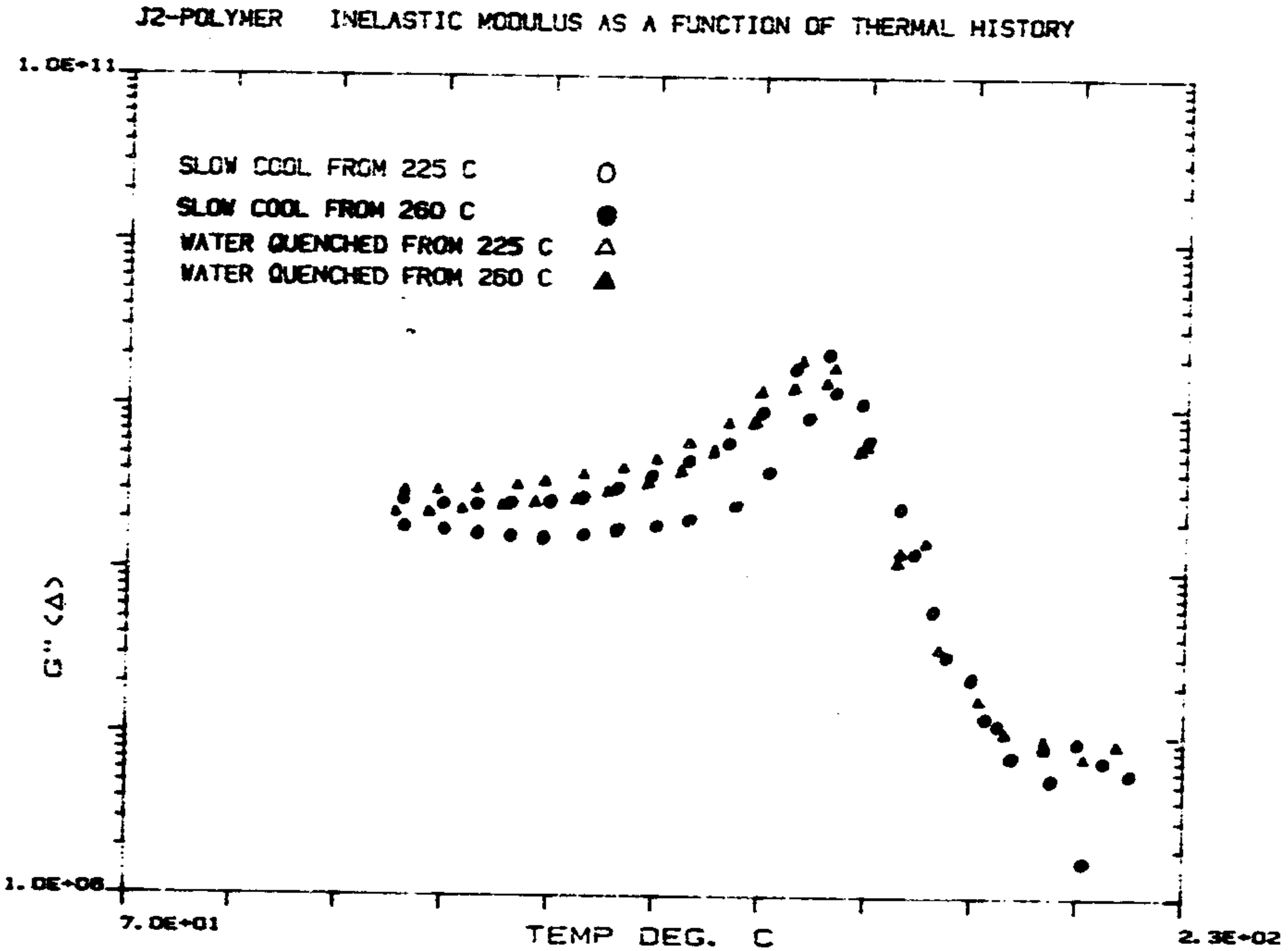

J2-POLYMER INELASTIC MODULUS AS A FUNCTION OF THERMAL HISTORY
SLOW COOL FROM 225 C ○
SLOW COOL FROM 260 C ●
WATER QUENCHED FROM 225 C △
WATER QUENCHED FROM 260 C ▲
1.0E+11
1.0E+08
G'' (Δ)
7.0E+01
TEMP DEG. C
2.3E+02

FIGURE 10

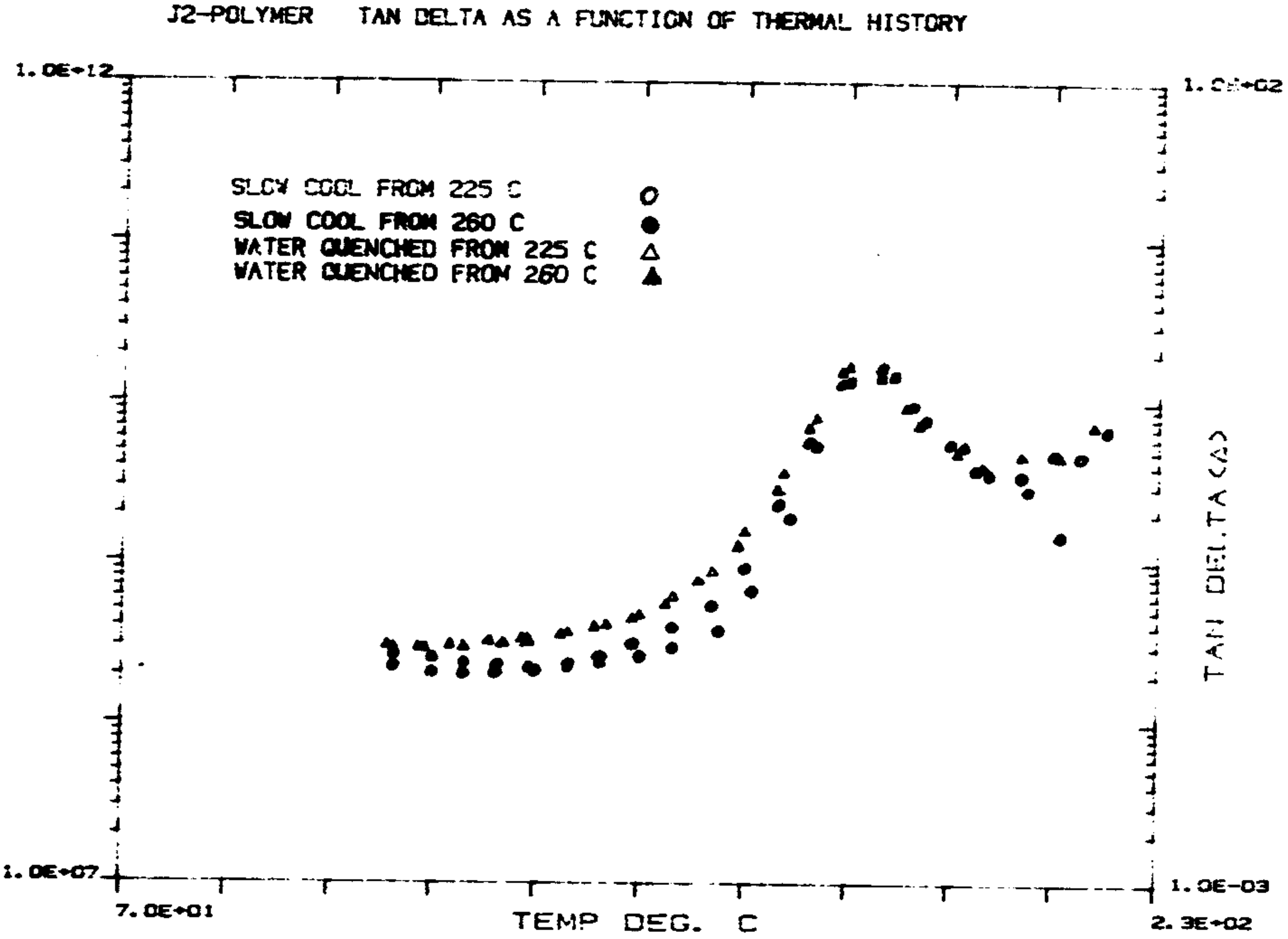

J2-POLYMER TAN DELTA AS A FUNCTION OF THERMAL HISTORY
1.0E+12
1.0E+07
1.0E+02
1.0E-03
SLOW COOL FROM 225 C ○
SLOW COOL FROM 260 C ●
WATER QUENCHED FROM 225 C △
WATER QUENCHED FROM 260 C ▲
7.0E+01
TEMP DEG. C
2.3E+02
TAN DELTA (A)

FIGURE 11

Figure 12: VISCOSITY OF J2 vs. TIME AT 260 C

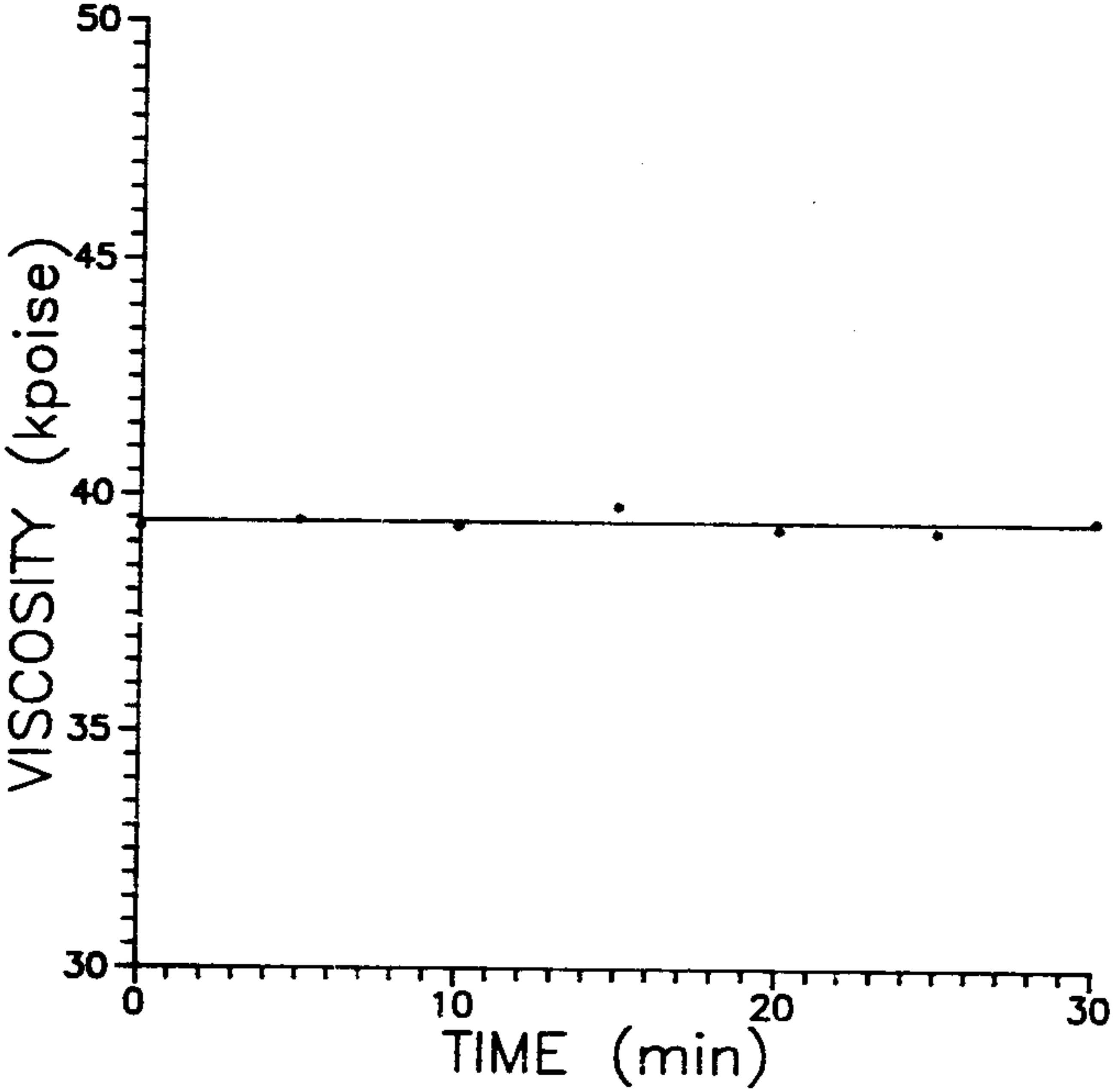


Figure 13: VISCOSITY OF J2 vs. TIME AT 225 C

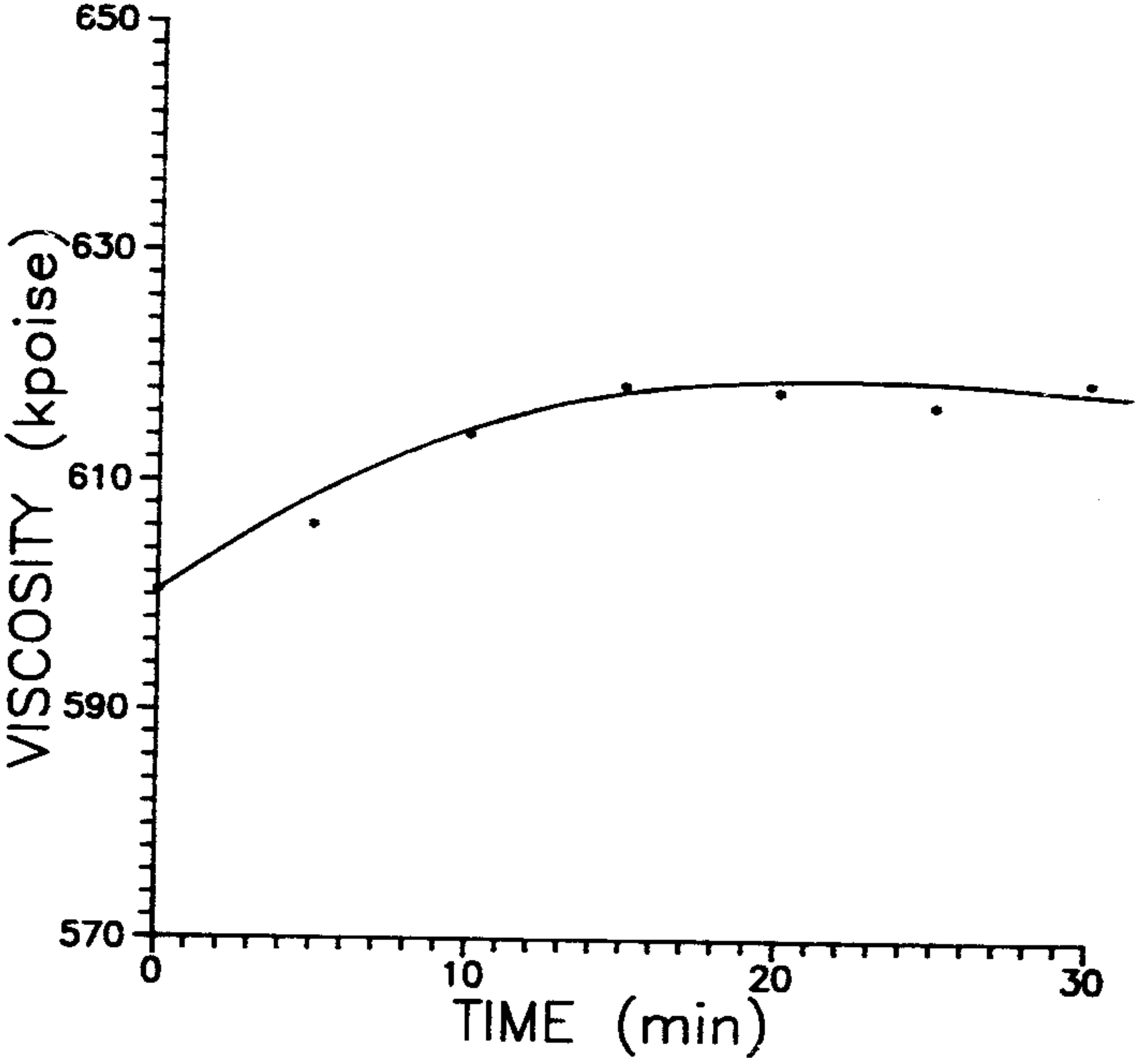
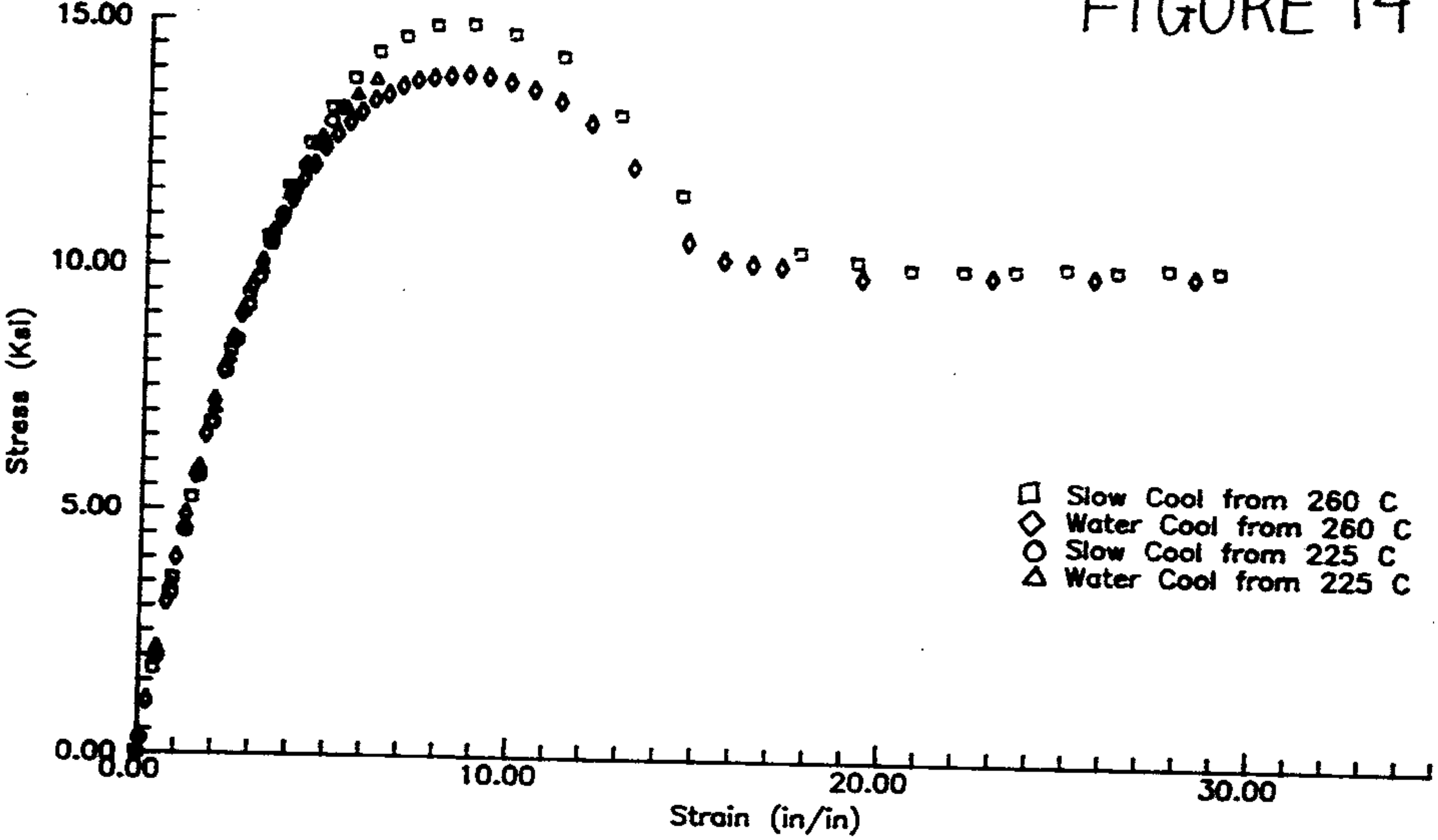
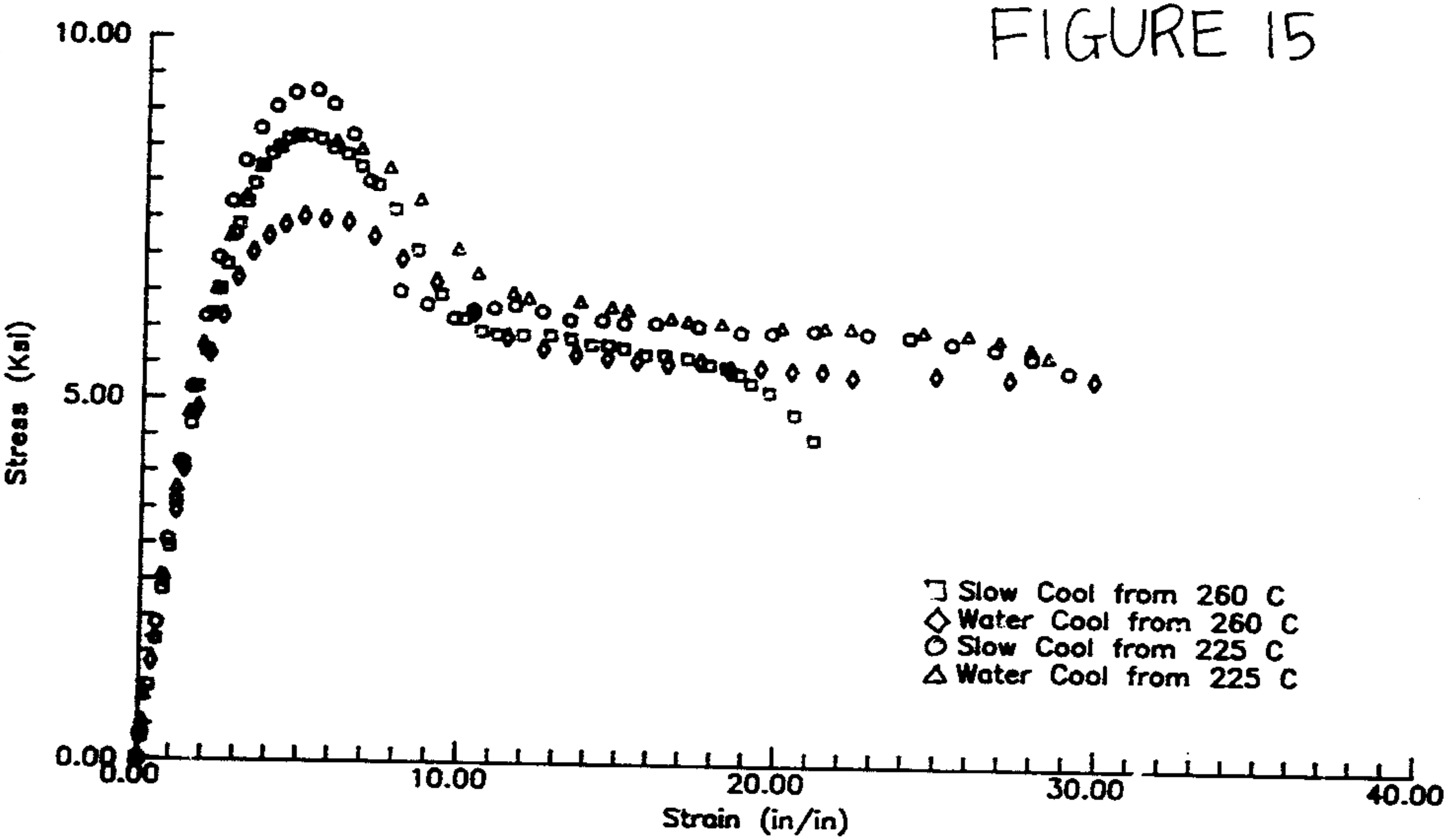


FIGURE 14



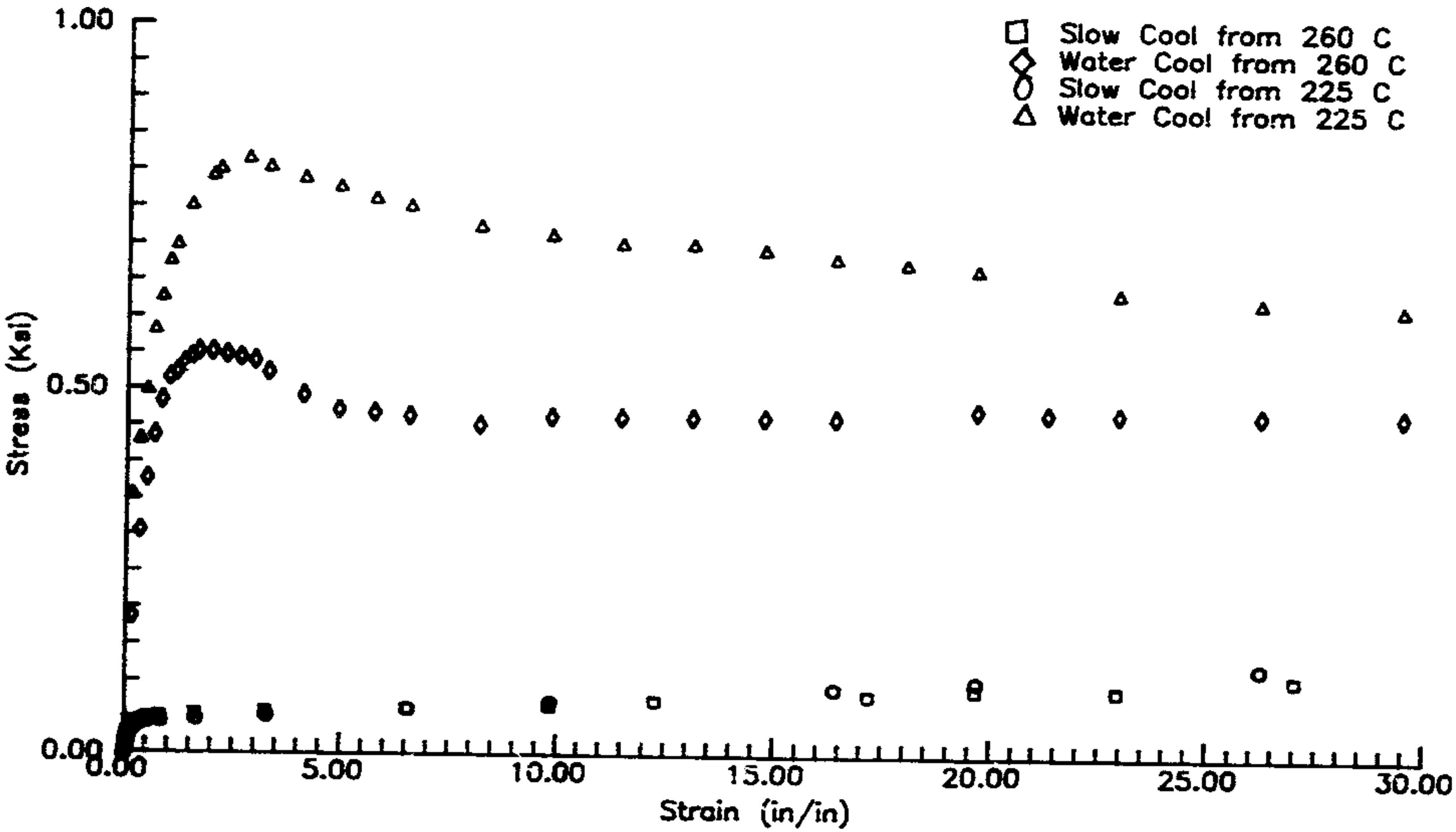
Stress Strain Curve of J2 polymer at Room Temperature
Cooling rate and Processing Temperature Effects.

FIGURE 15



Stress Strain Curve of J2 polymer at 100 C
Cooling rate and Processing Temperature Effects

FIGURE 16



Stress Strain Curve of J2 polymer at 160 C
Cooling Rate and Processing Temperature Effects.

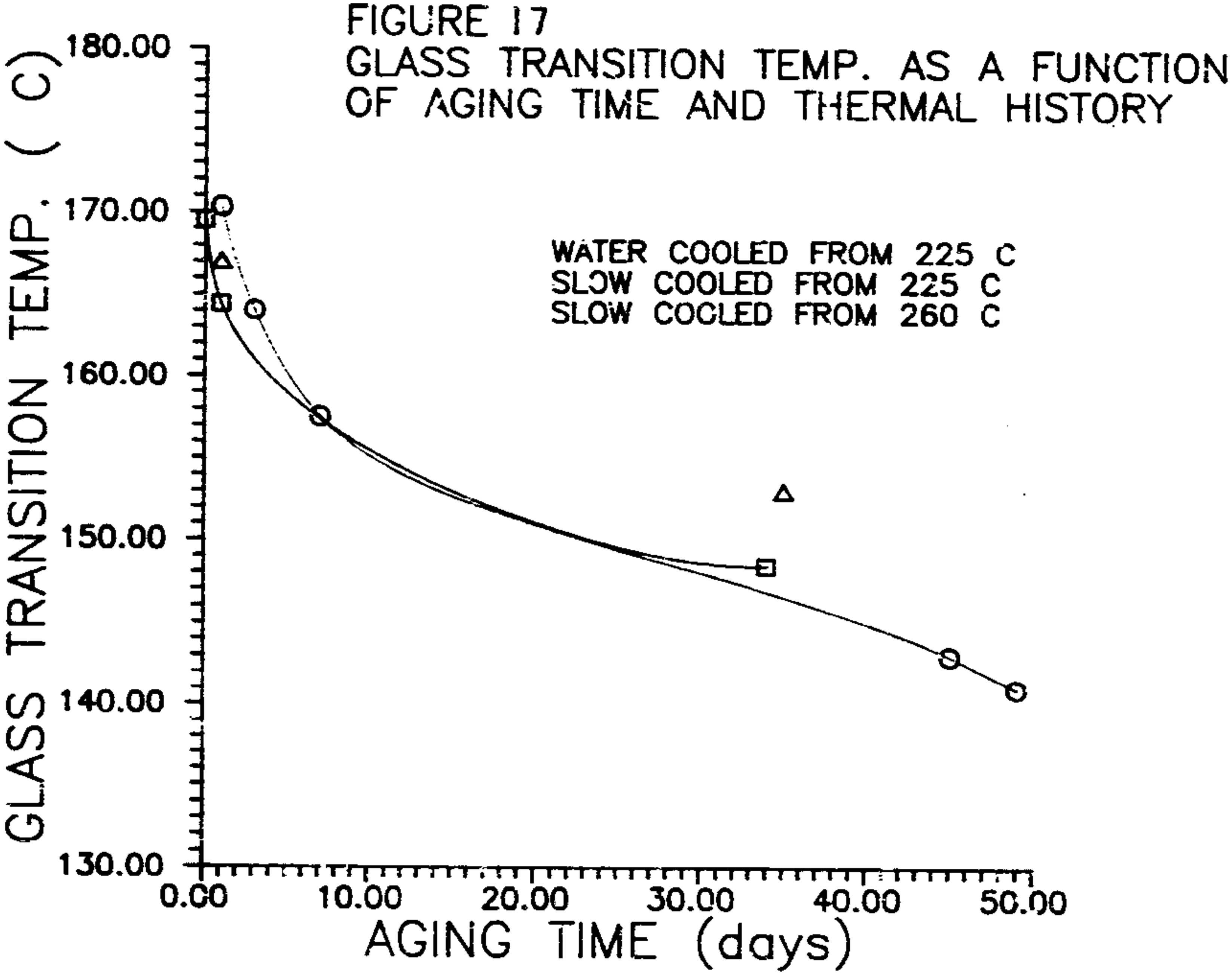
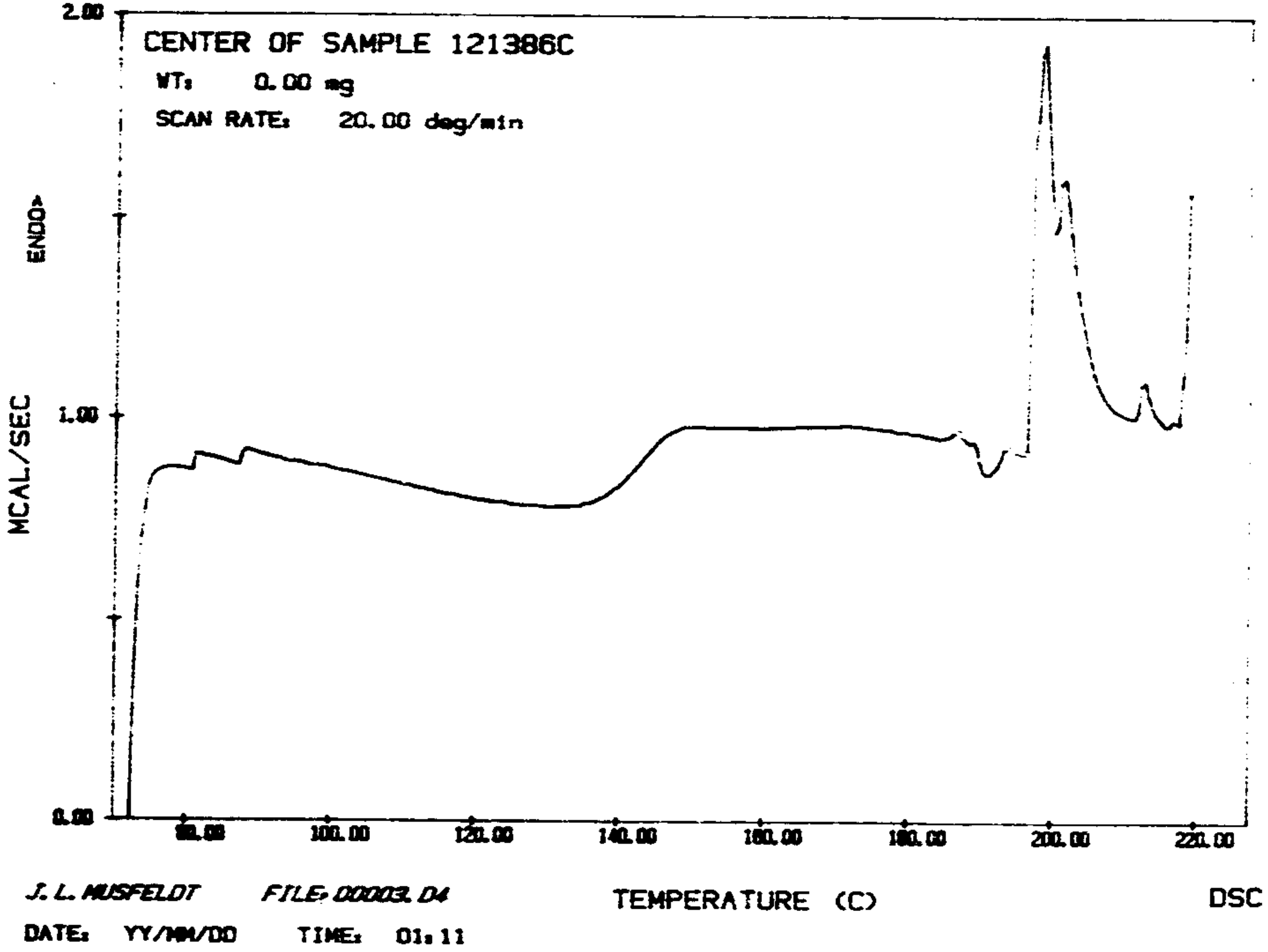


FIGURE 17
GLASS TRANSITION TEMP. AS A FUNCTION OF AGING TIME AND THERMAL HISTORY

FIGURE 18


CENTER OF SAMPLE 121386C
WT: 0.00 mg
SCAN RATE: 20.00 deg/min
2.00
1.00
0.00
ENDO>
MCAL/SEC
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
TEMPERATURE (C)
DSC
J. L. MUSFELDT
FILE: 00003.D4
DATE: YY/MM/DD
TIME: 01:11

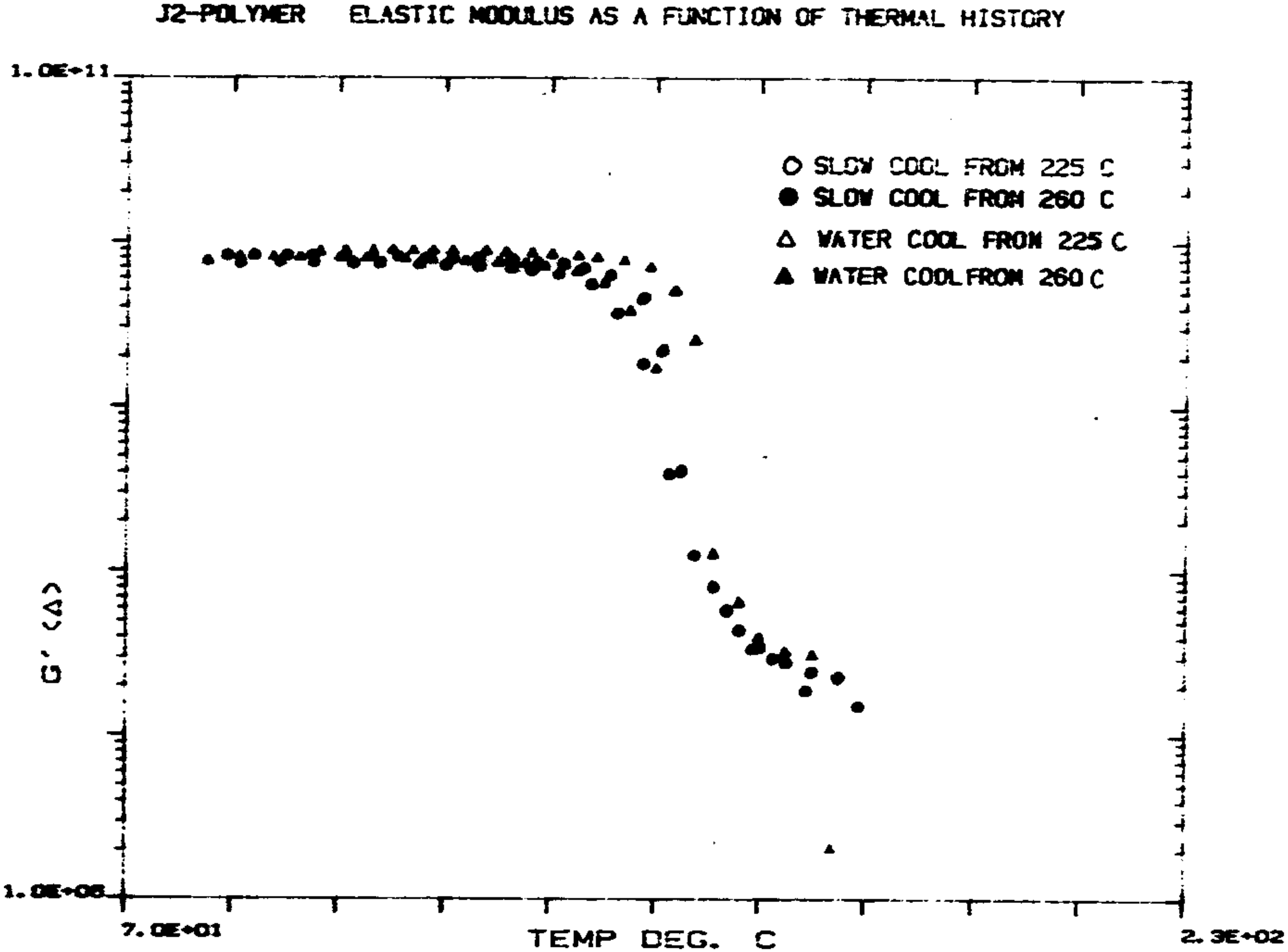

J2-POLYMER ELASTIC MODULUS AS A FUNCTION OF THERMAL HISTORY
○ SLOW COOL FROM 225 C
● SLOW COOL FROM 260 C
△ WATER COOL FROM 225 C
▲ WATER COOL FROM 260 C
1.0E+11
1.0E+06
G' (Δ)
7.0E+01
2.3E+02
TEMP DEG. C

FIGURE 19

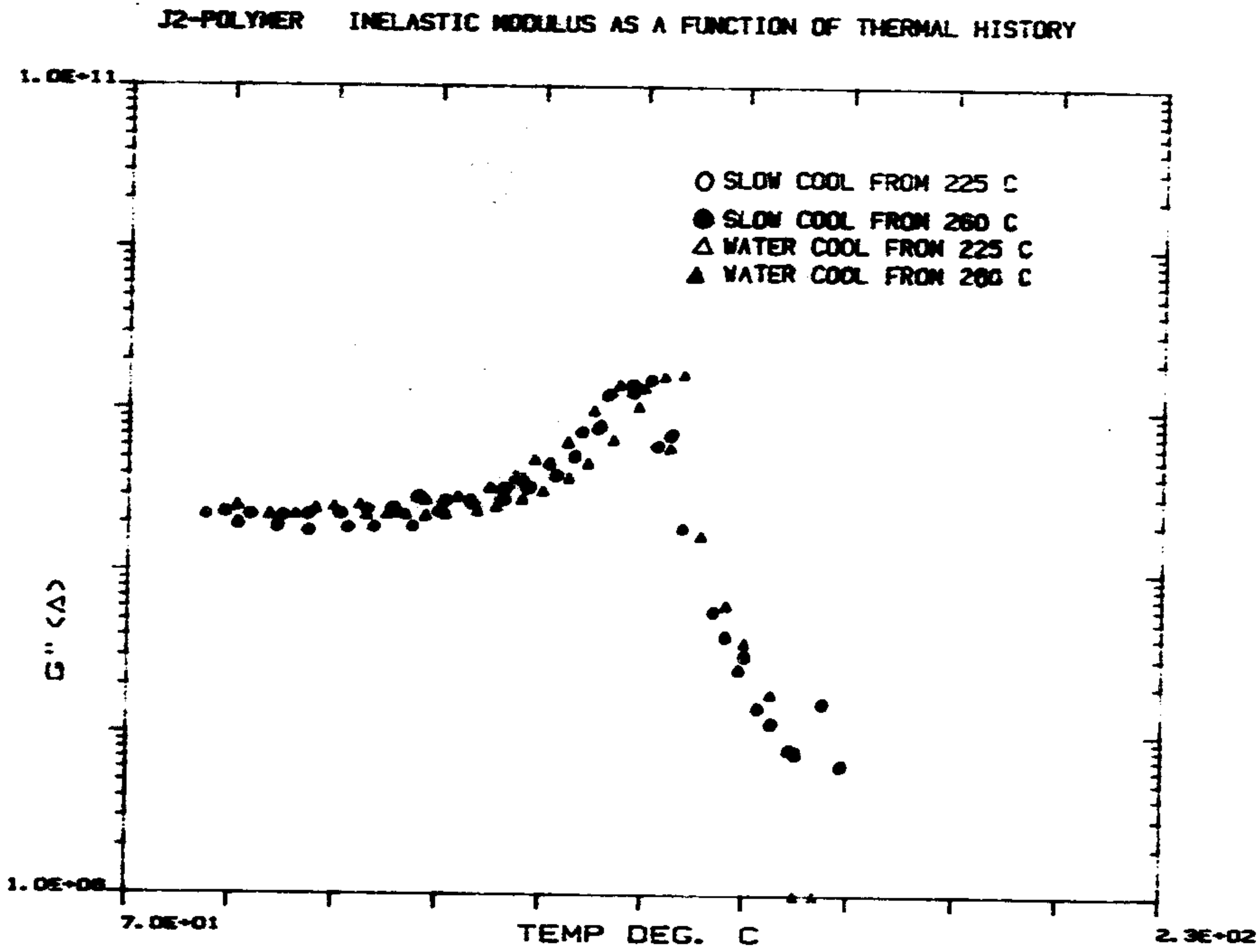

J2-POLYMER INELASTIC MODULUS AS A FUNCTION OF THERMAL HISTORY
1.0E+11
1.0E+08
G'' (Δ)
7.0E+01
2.3E+02
TEMP DEG. C
○ SLOW COOL FROM 225 C
● SLOW COOL FROM 260 C
△ WATER COOL FROM 225 C
▲ WATER COOL FROM 260 C

FIGURE 20

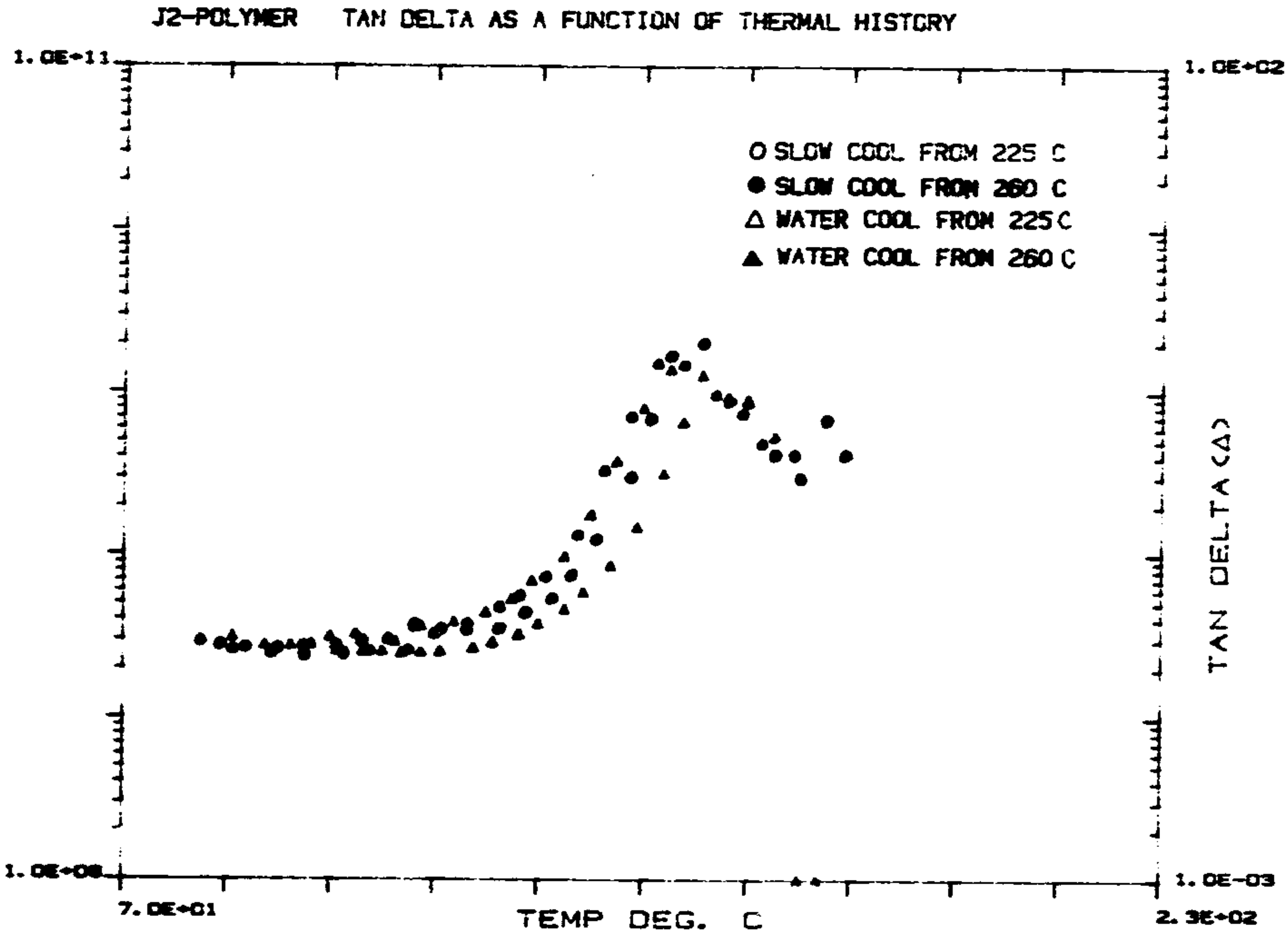

J2-POLYMER TAN DELTA AS A FUNCTION OF THERMAL HISTORY
1.0E+11
1.0E+08
1.0E+02
1.0E-03
○ SLOW COOL FROM 225 C
● SLOW COOL FROM 260 C
△ WATER COOL FROM 225 C
▲ WATER COOL FROM 260 C
TAN DELTA (△)
7.0E+01
2.3E+02
TEMP DEG. C

FIGURE 21

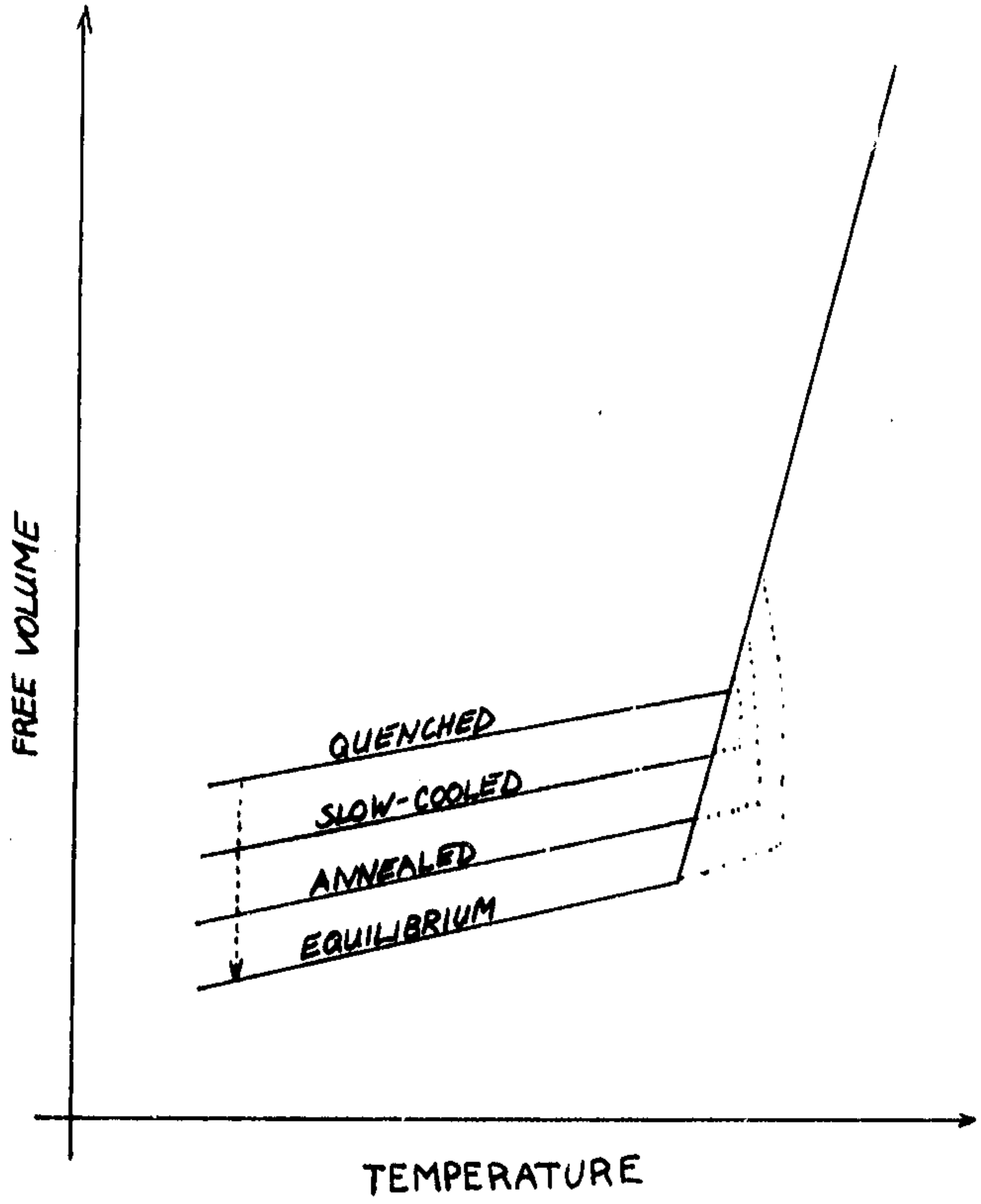


FIGURE 22

FREE VOLUME VS. TEMPERATURE
AFFECT OF PHYSICAL AGING ON T_g