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TRANSITIONS IN PHENOLIC POLYMER

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A phenolic polymer has been polymerized under conditions which lead to a crack free solid casting and its compressibility, electrical resistivity and specific heat have been determined. A secondary transition was found by compressibility measurements at about 120°C and its existence confirmed by resistivity and specific heat measurements. Based upon the experimental data we estimate that a glass transition would occur in this polymer at

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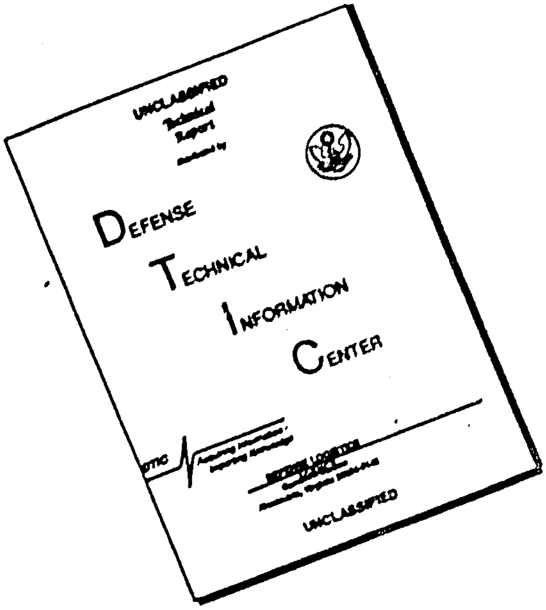

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about 325°C (600°K) if degradation did not occur. The secondary transition is discussed in terms of polymer structure.

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TRANSITIONS IN PHENOLIC POLYMER

The results of the researches reported should aid in our understanding of the polymerization and solid state physics of phenolic polymers and in the use of these polymers in ordnance applications.

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INTRODUCTION

Phenolic polymers are the oldest synthetic polymers known and after sixty-six years of large scale use, are still almost completely uncharacterized physically. Chemically, considerable work has been done[1] but the details of the polymerization process are still obscure. Also, the effect of temperature on the solid polymer is not completely understood. For example, heating at temperatures above 170°C apparently produces some rearrangement of the molecular structure[2].

In addition, there is a major drawback to the use of these polymers and that is their brittleness[3]. This has necessitated the use of various types of reinforcement and/or fillers, however, even when reinforced cracking remains a problem. It has long been known that in order to obtain a polymer in which the maximum possible extent of polymerization is obtained it is necessary to conduct the final stages of polymerization at a temperature somewhat above that of the glass transition of the completely polymerized polymer[4]. When polymerization is conducted in this manner it is frequently (but not always) observed that the polymer has less tendency to crack than the less completely polymerized material. Thus, if one can establish at what temperature the glass transition occurs in the completely polymerized polymer one can then suggest the temperature at which the final stage in the polymerization cycle should be conducted so as to produce a polymer in which the tendency to crack is minimized. To some extent this is also true if the polymerization is conducted at temperatures above that of any secondary transition which may be present.

Presented in this report are the results of a study of the polymerization and solid state properties of cast phenolic polymer. A polymerization cycle has been employed which allowed us to produce crack free castings. Examination of the solid polymer revealed the existence of a small transition in the polymer at about 125°C. The significance of this transition is considered and discussed.

MATERIAL

The polymer used in this investigation was Resinox SC-1008, a product of the Monsanto Polymers and Petrochemicals Co. The manufacturer describes this material as "a phenolic laminating varnish". It is supplied in the form of a 60-64% solution in ethyl alcohol[5].

Specimens used in this study were prepared as follows. Samples for use in the compressibility and specific heat parts of this investigation were cast in small cups while that specimen which was to be used for electrical resistivity measurements was cast in the standard cylindrical electrodes[6]. All the castings were then polymerized thermally under identical conditions. The polymerization cycle employed was as follows:

24 hours at 100°F (38°C)
72 hours at 125°F (52°C)
24 hours at 150°F (66°C)
24 hours at 175°F (79°C)
72 hours at 205°F (96°C)
24 hours at 225°F (107°C)
24 hours at 250°F (121°C)
72 hours at 300°F (149°C)
72 hours at 350°F (177°C)

This very long cycle was employed in order to obtain a fully polymerized polymer. After this cycle a clear amber-brown solid was obtained of density 1.22. No cracks were observed after the above cycle, or after machining, or after any of the experiments herein described.

EXPERIMENTAL

A. Compressibility Measurements

Compressibility measurements to a pressure of 10,000 atmospheres and to temperatures of about 200°C were made in the usual manner. Briefly, this consists of taking a machined polymer specimen, 7.62 cm long and 0.625 cm in diameter, placing it in a modified Matsuoka-Maxwell compressibility tester, and determining the compressibility as a function of temperature and pressure. The source of pressure is a Baldwin-Southwark 30,000 kg capacity Universal Testing Machine. Additional details of the experimental procedure have been given previously[5-7].

B. Electrical Resistivity Measurements

Electrical resistivity measurements were made on the solid phenolic polymer in an effort to determine when polymerization was complete, the effect of high temperature on the polymer and to establish the existence of any transitions within the polymer at high temperatures.

This was done as follows. Once polymerization was thought to be complete, the standard cylindrical electrode, which contains a thermocouple embedded within the polymer, was heated in an oven to a predetermined elevated temperature and maintained at this temperature for about one hour. During this interval the electrodes are connected to a continuous current monitoring device (CCMD)[6]. The oven is then shut off and the polymer is allowed to slowly cool down while the change in the electrical resistivity is continuously measured. This is done several times at increasing temperatures and when, after repeated temperature cycling the resistivity vs. temperature is reproducible, complete polymerization has been obtained[6].

Whenever abrupt changes occur in the resistivity plot over a short temperature interval these changes are indicative of a transition occurring within the polymer. Additional details of electrical resistivity methods have been previously given[6].

C. Specific Heat Measurements

The specific heat as a function of temperature was determined in a Differential Scanning Calorimeter. The operation of this instrument has been described in detail elsewhere[8,9]. The results obtained for the phenolic polymer are typical of amorphous crosslinked polymers.

RESULTS

The results of this investigation are shown on Figures 1 to 6. Figure 1 is a plot of the change in volume, $\Delta V/V_0$, of the phenolic polymer when compressed to a pressure of 7×10^9 dynes/cm^2 (~7,000 atmospheres) at 160°C. It will be noted that there is a progressive change in volume with increasing pressure. Volume changes of this type are the general case with amorphous polymers. A similar plot was obtained for the isotherm at 25°C.

Figure 2 is a typical stress-strain plot, obtained directly from the recorder of the Baldwin-Southwark Universal Test Machine. This plot is of interest in that close examination reveals a small inflection about midway along the plot. This inflection suggests that a transition is occurring. On the assumption that a transition exists in this temperature (~160°C) and pressure (~4,000 atm) region we ran a series of isotherms between 144° and 175°C and examined the stress-strain plots for inflection points. These were found and the temperature and pressure of these points are plotted on Figure 3. On the basis of these points and their pressure dependence we concluded that there is a transition at about 120°C.

On Figure 4 we show the electrical resistivity of the fully polymerized polymer after extensive (72 hours) at 400°F (204°C) post-cure plotted against the reciprocal of the absolute temperature. The change in slope at a resistivity of about 4×10^{12} ohm-cm indicates that a transition is occurring in this region.

Figure 5 is a plot of the specific heat vs. temperature. As can be seen the specific heat increases in a linear fashion until at temperature of about 120 - 125°C where a small transition occurs. Generally, the magnitude and temperature dependence of the specific heat is typical of polymers.

Figure 6 is a drawning of the idealized structure of solid phenolic polymer.

DISCUSSION

When this investigation was started we were unable to find any significant amount of experimental data on the physical properties of phenolic polymers. Many scattered references exist, of course, to various mechanical, electrical and thermal properties of various phenolic polymers but most of this data is not suitable to be applied even generally to the phenolic considered here. Little of this data could be considered as scientific information. Furthermore, the phenolic considered here is in use throughout the Defense Department so that a need exists for the information developed in this investigation.

A. Compressibility of Phenolic Polymer

We determined the bulk compressibility of this polymer as a function of temperature and pressure over the range 25°C to 175°C and at pressures up to 9,000 atmospheres. At temperatures above 140°C a small inflection point (or short region) was noted in the stress-strain plot. At higher temperatures this inflection point was observed at still higher pressures. Plotting the pressure where this inflection is observed and the temperature at which the compressibility was measured yields the plot shown on Figure 3. The scatter of points is greater than is usually obtained in measurements of this type but the points fall on an approximate straight line. The scatter may well be caused by errors in accurately picking up the exact point of transition from the stress-strain plot. This often happens when the transition is small. Drawing a straight line through the data points and extending it to the temperature axis indicates that a transition of some type is occurring at about 120°C. The procedure described above has been used many times for locating both glass transitions, T_g[7], and melting points, T_m[10].

The slope of the pressure vs. temperature plot is 0.010°/atm. This is small, usually the pressure dependence of both the glass transition and the melting point are higher i.e. about 0.025 - 0.030°/atm. Previous work on crosslinked polyepoxide polymers[11] has indicated that small slopes of this type are caused by small secondary transitions within the polymer. The one considered here is most likely of this type. This fact could also contribute toward explaining the scatter of the data points. Small transitions are frequently slow to transform from one form to another because of extremely high bulk viscosity which is characteristic of the glassy state. The change in volume, which is the driving force behind high pressure transitions of this type is also small, i.e. of the order of a percent or two, hence locating the exact pressure at which it occurs becomes difficult.

One may contrast the diffuse nature of this transition with the sharp highly pressure and temperature dependent nature of the melting point of crystalline polymers. In crystalline polymers the change in volume upon melting is large i.e. about 20%, while in conventional amorphous polymers the change in volume at the glass transition is of the order of 5 to 10%. On the basis of these considerations we may conclude that the transition in the phenolic polymer is a secondary transition and that $dP_{sec}/dP = 0.010°/atm$.

Shown in Figure 1 is a plot of the change in volume, $\Delta V/Vo$ vs. pressure at 160°C. This plot is typical of those of crosslinked polymers in the glassy state. A very similar plot was obtained at 25°C which indicates that the compressibility of this polymer is not highly temperature dependent.

While the above evidence is normally sufficient to identify a transition in a polymer it would appear that the existence of this transition should be confirmed by additional experimental techniques. These will be considered below.

B. Electrical Resistivity Measurements

At the start of this investigation only the most general concept was available as to how the samples of phenolic polymer were to be polymerized. Indeed, there was considerable evidence to support the idea that the bulk polymer could not be prepared because of the extreme tendency of the polymer to crack in the final stages of polymerization. The polymerization cycle was such as to cause crosslinking to proceed at a slow rate and thus avoid the locking in of such stresses which could produce cracking. We were also faced with the problem of not having any real control (or index) of the extent of polymerization.

We have previously shown that electrical resistivity measurements made as a function of temperature are an excellent tool for measuring the rate and extent of polymerization[6]. Many years ago, we attempted to determine the electrical resistivity of a phenolic polymer during polymerization but were unable to obtain a steady state because of the splitting out of water due to the condensation nature of the polymerization process. However, using the phenolic considered herein water is not split out during the crosslinking process, and resistivity measurements can thus be made during polymerization.

We measured the resistivity during and after the polymerization cycle. Measurements were made after heating at 250°F (121°C), 300°F (139°C), 350°F (177°C), and 400°F (204°C). These measurements were to check on the completeness of polymerization. Previous studies have shown[6] that a test for completeness of polymerization is the ability to exactly reproduce the temperature dependence of the resistivity over a broad temperature range after repeated postpolymerization. If polymerization is not complete the temperature dependence of the resistivity will be displaced toward the left in Figure 4 while degradation will displace the plot toward the right. In the present case the polymerization cycle conducted at 400°F (204°C) yielded resistivity data which superimposed on the data obtained after cycling at 350°F (177°C). We conclude that the polymerization cycle described earlier in this report yielded a completely polymerized polymer after the final cycle at 350°F (177°C).

Examination of Figure 4, which is a semi-logarithmic plot of resistivity vs. 1,000 times the reciprocal of the absolute temperature, yields additional information. For example, at a resistivity of 4.5×10^{12} ohm-cm and at a temperature of about 125°C there is a change in the slope of the plot. We have previously shown that changes in slope on plots of this type occur as the result of a transition within the polymer[6]. This change in slope occurs at the same temperature as does the indicated transition as determined by compressibility measurements. Resistivity measurements do not indicate just what type of transition is occurring but by the magnitude of the change in slope one can conclude that the transition is small and is occurring in the glassy state.

The magnitude of the resistivity is also of interest here. The maximum measured value is 1×10^{15} ohm-cm at a temperature of 80°C. This implies that at 25°C the magnitude of the resistivity of the polyme will be very high $\sim 10^{26}$ ohm-cm. This is higher than the usual estimates for phenolic polymers of this type[5] but is not unreasonable. From the slope of the plot we calculated a value of 69 Kcal/mole for the activation energy of the electrical conduction process, E_c. Some years ago we proposed a classification of the properties of solid polymers by the magnitude of E_c[12] and this system has been adopted by others[13]. This value is very high and suggests a very highly crosslinked brittle, glassy polymer. At higher temperatures, that is above the transition, $E_c = 26$ Kcal/mole which is a more typical value for a polymer.

On the basis of resistivity measurements we conclude that a transition exists in this polymer in the glassy state at about 125°C and that it is small.

C. Specific Heat Measurements

As a final check on the validity of the transition we determined the specific heat, C_p, over the temperature range 40°C to 200°C and the results are shown in Figure 5. It will be noted that the specific heat rises in a linear manner up to about 125°C followed by a change in slope with another linear increase till about 200°C. The change in slope which starts at about 125°C is indicative of a transition within the polymer. However, the slope of the plot is of interest. When a glass transition occurs the C_p shows an increase over a narrow temperature region while a secondary transition is usually shown by a change in the slope of the C_p vs. T plot[14]. Thus, from the change in slope of the plot we conclude that the previously noted transition is real, occurs at about 125°C and is a secondary transition within the glassy state.

Having measured the C_p of this polymer at 30°C $C_p = 0.337$ cal/°gm it is of interest to make a few calculations. The thermodynamic relationship

$$C_v = C_p - \frac{VT\alpha^2 K}{\beta} \qquad (2)$$

where V the specific volume is 0.826 cm^3/gm, β is the compressibility 1.35×10^{-5} atm^{-1}, $\alpha$is the cubic coefficient of expansion, 3.1×10^{-4}/o, T is the absolute temperature, 303°K, Cp and Cv are the specific heats at constant pressure and constant volume and K is a constant 0.0242 cal/cm^3.

Using these data, all of which were measured at this Laboratory, we calculate C_v to be 0.333 cal/gm° and C_p/C_v to be 1.01. Again this is a value for a hard polymer if in the glassy state.

Some years ago we developed a corresponding states method for obtaining C_p/C_v from the value of the glass transition temperature or vice versa. Using this procedure[15] and the C_p/C_v value of 1.01 we estimate that Tg for this phenolic polymer should occur at about 600°K. Previously we have shown[16] that generally

$$T_{sec} \simeq 2/3\ T_g \qquad (3)$$

where T_{sec} is the temperature of the secondary transition and Tg is the temperature of the glass transition. Taking T_{sec} to be about 125°C or 398°K yields Tg of about 597°K which is, of course, excellent agreement with the value obtained from the corresponding states relationship. The problem here is that this polymer degrades of temperatures at about 500°K so that direct measurement of T_g would be very difficult or perhaps impossible. However, the ability to predict Tg is of considerable interest.

D. Structural Factors.

While the ability to locate, confirm, and predict the transitions of polymers is of much interest it is of still greater interest to explain why transitions occur. Much effort has been expended in this area but progress has been slow[17]. In the case of a highly cross-linked phenolic polymer many of the more obvious thermal motions commonly associated with transitions in polymers are not present. However, to a first approximation it would appear that the most likely molecular area where increased molecular motion could occur would be either in the methylene bridges between the benzene rings or the ether linkages between the same rings.

In Figure 6 we show a simplified, idealized outline of the structure of the phenolic polymer used in this investigation. Both the methylene $-CH_2-$ and ether $-CH_2-O-CH_2-$ linkages are shown. Depending upon how the polymerization is conducted the ratio of these two linkages in the fully cured polymer in generally 2-3 methylene to each ether linkage.

Considerations of the structure of these two types of linkages suggests that the ether linkage is the more likely of the two to exhibit in-chain motion at elevated temperatures which would give rise to a transition. Furthermore, it is well established that any oxygen atom along a polymer chain serves as a swivel. This limited (or sterically restricted) type of motion is consistant with a small transition at elevated temperatures.

As previously noted dPsec/$_{dp}$ is 0.010 °/atm, this is a smaller value than is usually associated with a glass transition, Tg, or melting, Tm, but is close to the value previously found for secondary transitions in cross-linked polymers. One can generalize that a glass transition involves the molecular motion of about twenty repeat units[17] with the associated change in volume whereas a secondary transition involves the molecular motion of many fewer repeat units. Thus, the pressure dependence of the secondary transition would be expected to be much smaller, which is the case of the two secondary transitions studied to date.

We conclude that the small secondary transition in this phenolic polymer is likely associated with in-chain motion of the $—CH_2—O—CH_2—$ linkage.

Regardless of the nature of this transition an important point should be noted in regard to the polymerization of this polymer. While it is now well established that, in order to obtain optimum polymerization, the final stage of the polymerization cycle must be conducted at temperatures well above 125°C it is not so well established that at lower degrees of polymerization one must always be at temperatures above Tsec. Until the exact relationship between Tsec and extent of polymerization is known this is difficult to do. It does, however, appear that once the solvent has been removed from the polymer one should slowly go to high temperatures.

CONCLUSIONS

By means of long polymerization cycle we have prepared specimens of cast phenolic polymer free of cracks.

Employing standard compressibility measurements we have found that a secondary transition exists in phenolic polymer at about 125°C.

The existence of this transition is confirmed by electrical resistivity and specific heat measurements.

Based upon the existence of a secondary transition of about 125°C (398°K) we predict that a glass transition occurs in this phenolic polymer at about 600°K.

RECOMMENDATIONS

It is recommended that additional studies be conducted on the polymerization of this polymer. In particular, the effect of conducting the polymerization above and below the secondary and glass transition should be studied. It is also recommended that an attempt be made to determine the glass transition temperature of the solid phenolic polymer.

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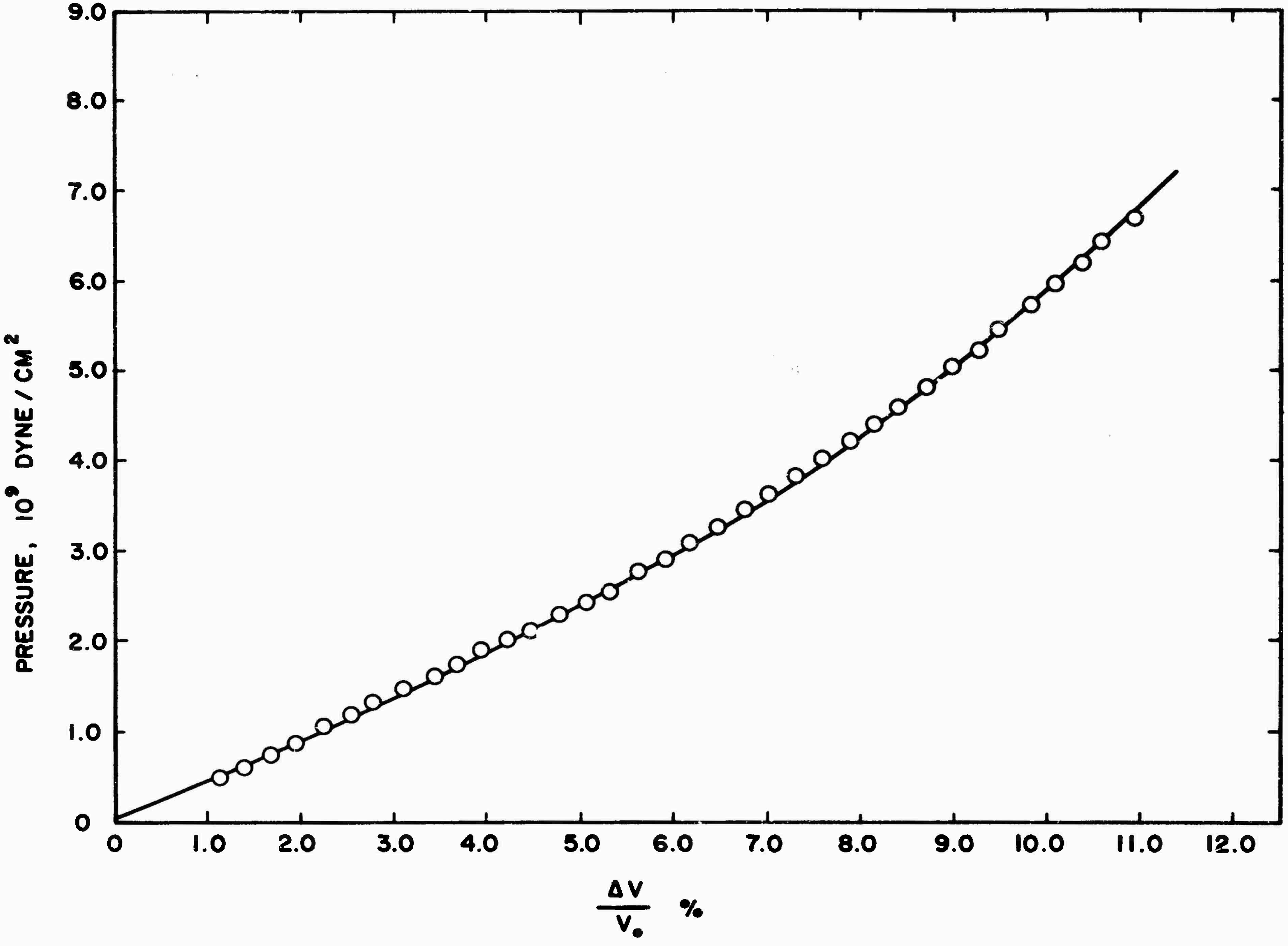

FIG. 1 COMPRESSIBILITY OF PHENOLIC POLYMER AT 160 °C

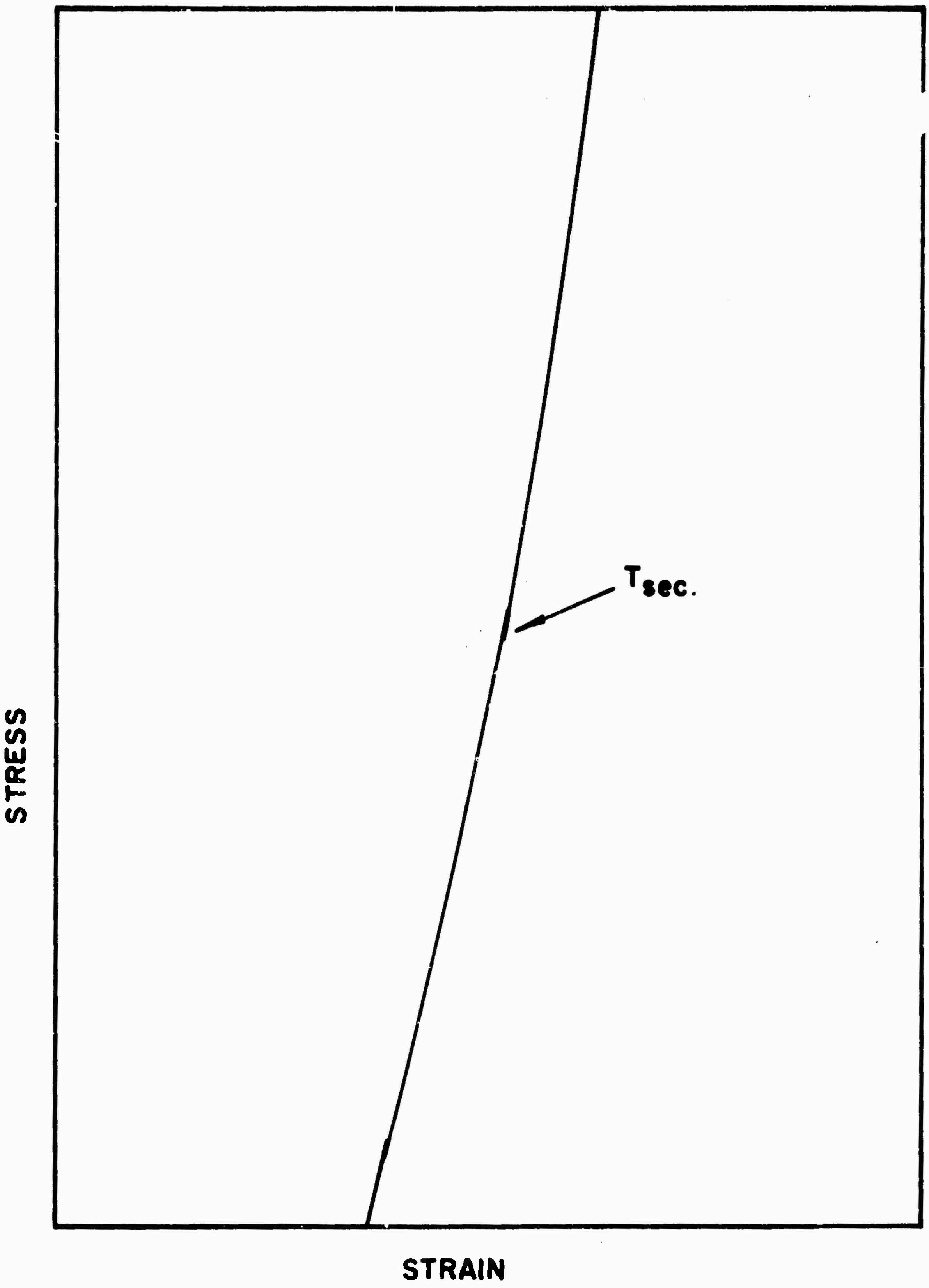

FIG. 2

STRESS - STRAIN PLOT FOR PHENOLIC POLYMER
AT 160° C

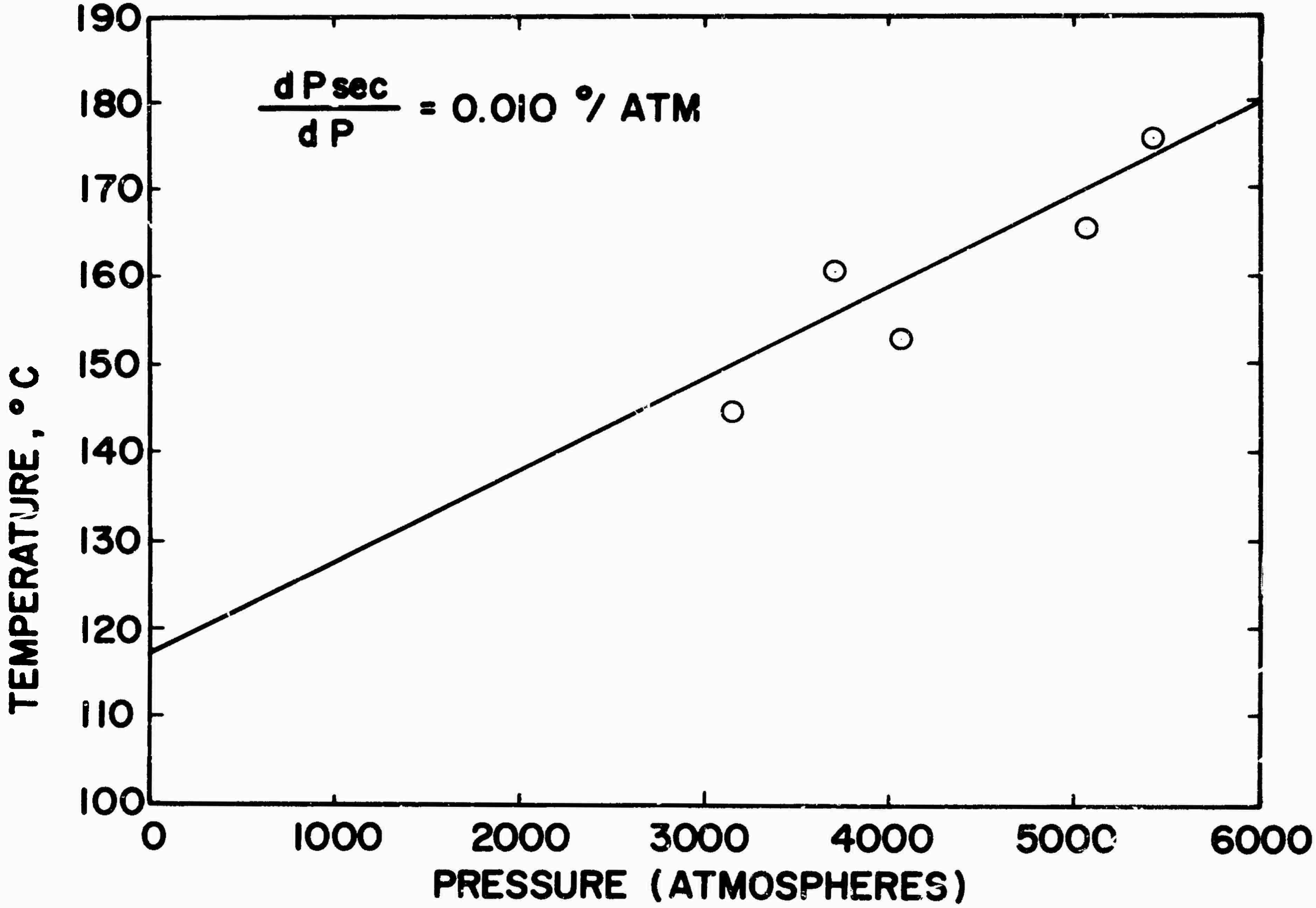

FIG. 3 PRESSURE DEPENDENCE OF THE SECONDARY TRANSITION IN PHENOLIC POLYMER (SC-1008)

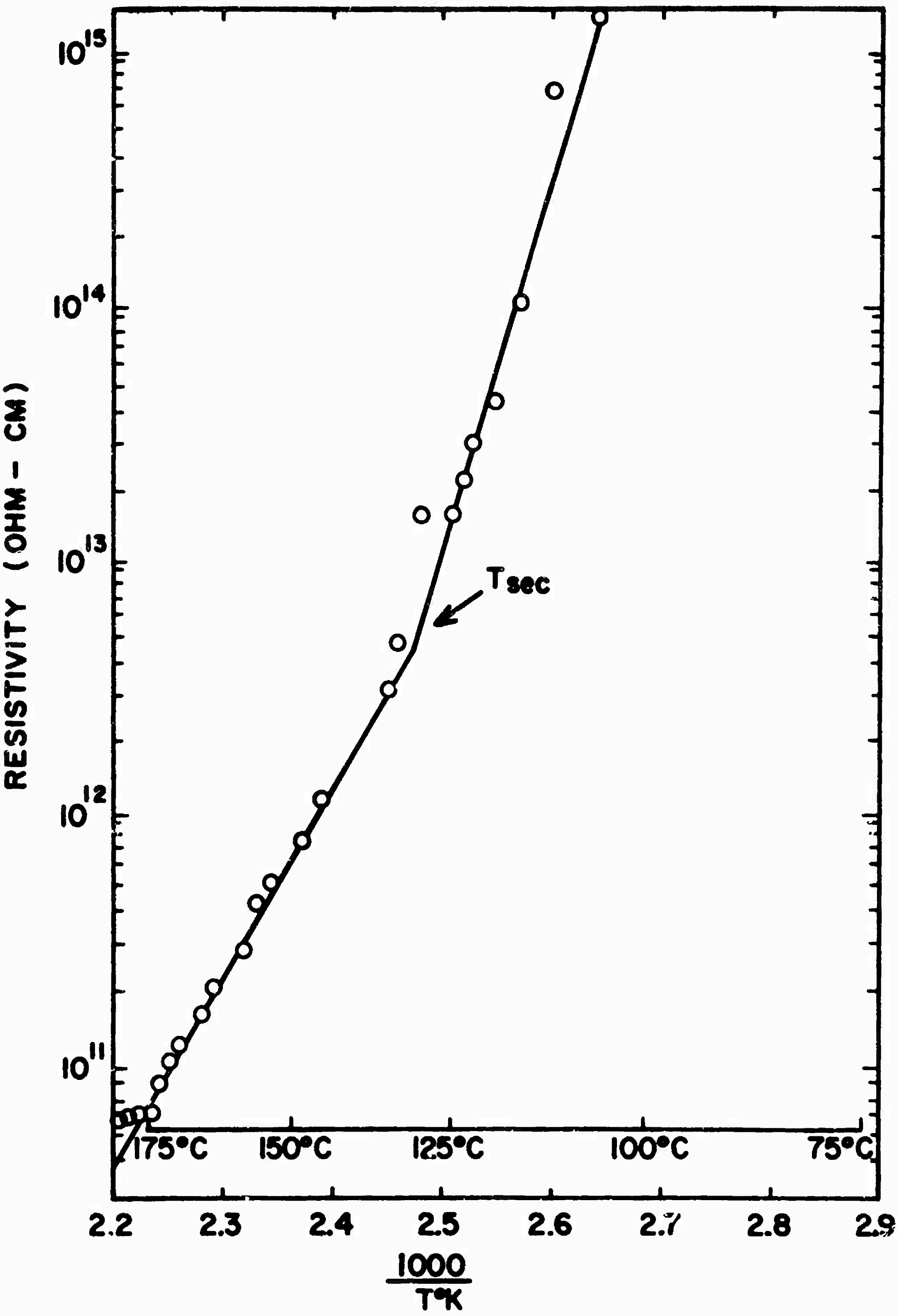

FIG. 4

RESISTIVITY OF A PHENOLIC POLYMER AS A FUNCTION OF TEMPERATURE

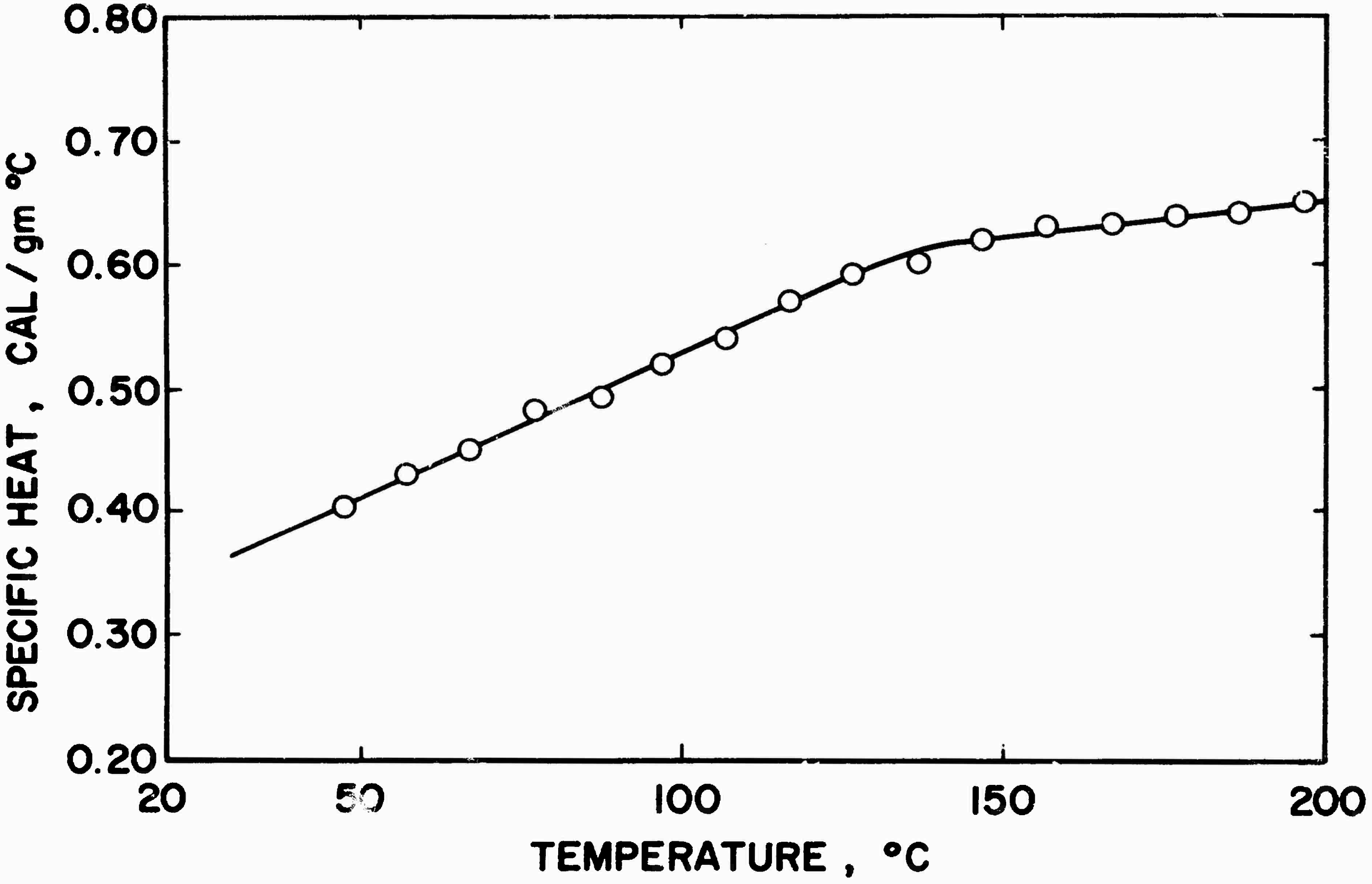

FIG. 5 SPECIFIC HEAT OF PHENOLIC POLYMER (SC-1008) AS FUNCTION OF TEMPERATURE

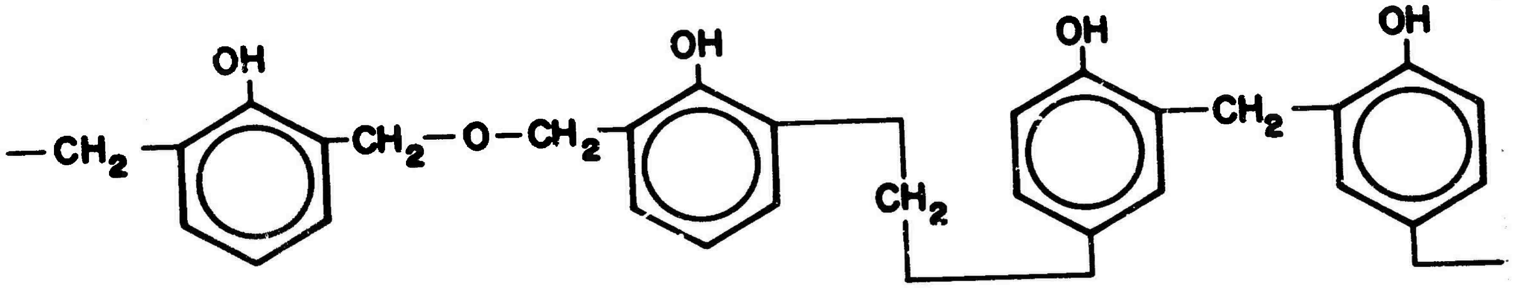

FIG. 6 STRUCTURE OF RESOLE TYPE PHENOLIC