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TICA STUDY OF ATS-G

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NOTICE

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ATS-G resin was studied using the TICA technique. Effects of air and nitrogen cure environments were accessed and the results were compared with those from a previous study on BADABBA. In general, the findings are consistent with that reported in the previous study, indicating that the environmental effects on curing are inherent to all AT systems. The less thermally stable backbone structure of the sulfone groups led to observation of thermal degradation at high temperature which was not observed with the quinoxaline

resin. Because of the lower glass transition temperature, the air effects in ATS-G are more clearly defined. The importance of air diffusion rate in determining the total air effect is shown in the study.

PREFACE

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aenonautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F.E. Arnold (AFWAL/ML) as the Project Scientist. Co-authors were Dr. C.C. Kuo (Visiting Scientist) and Dr. C. Y-C. Lee, of the Materials Laboratory (AFWAL/MLBP).

This report covers research conducted from January 1981 to October 1981.

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SECTION I

INTRODUCTION

The chemical structures of any ATX systems can be viewed as a combination of two parts, the terminal acetylene groups and the backbone that links the groups together. The backbone structure is always well characterized, but the structure of the acetylene after the cure is an open question currently being pursued under an Air Force-sponsored contract. Resins with different backbones are often cured differently because of the different uncured resin properties. In any attempts to correlate the influence of the backbone structures on the after-cure mechanical properties, it is vital to understand the influence of cure conditions on the properties.

A previous Technical Report (Reference 1) documented the air nitrogen cure effect on TICA behaviors of an Air Force-developed resin--BADABBA. The Discussion Section of Reference 1 notes the importance of studying the air/nitrogen cure effects on the mechanical properties of the AT resins. Unfortunately the quantity of BADABBA on hand was not sufficient for such a study.

ATS-G, also developed by the Materials Laboratory, was used in many recent studies on AT resin properties. The resin, scaled up in pound quantities by Gulf Corp, was being investigated as a potential candidate for further development. We decided to use the ATS-G resins in the study of air/nitrogen cure effects on mechanical properties. To be certain that the air/nitrogen effects observed with BADABBA were applicable to ATS-G as well, we initiated a systematic study of the ATS-G TICA behavior. This report documents the findings of the study.

SECTION II

EXPERTMENTAL

The TICA specimen preparation procedure has been described elsewhere (Reference 2). The ATS-G resin was used "as-is" and Methylene chloride was the solvent used in the impregnation process. The mechanical measurements were made with the Rheometrics Mechanical Spectrometer (RMS) which measured the in-phase and out-of-phase stress responses (a and b component respectively) of the specimen which was subjected to a sinusoidal strain. The instrumental set-up was the same as that reported in Reference 1. All temperature scan experiments were programmed in 2°C/min step changes. The frequency of the strain function was kept constant at 1.6 Hz (10 rad/sec).

All temperature scan experiments were scanned at a 2°C/min rate. A scan-down in temperature of the same rate was immediately followed when the maximum temperature was reached. With the exception of a few experiments at the beginning, which had a maximum temperature of 400°C, all scans had a maximum temperature of 350°C.

All specimen curing were accomplished by using the RMS environmental chamber as the curing oven. Compressed air or vaporized liquid nitrogen was used as the convection medium.

Part of the IR measurements of unreacted acetylene wns done by using a Nicolet instrument (Reference 3). Measurements were also made using a Beckman IR-33. ATS solution in methylene chloride (∿ 1%) was dropped on the KBr windows. The solvent was evaporated very slowly by covering with aluminum foil for one day. Then the windows were subjected to vacuum evaculation for one week. These KBr windows were put in the RMS chamber and were subjected to a temperature increase profile under nitrogen atmosphere similar to the mechanical measurement experiments (2°C/min). The windows were removed one-at-a-time at different temperatures. All IR spectra were taken at room temperature.

SECTION III

RESULTS AND DISCUSSION

TEMPERATURE SCAN IN N_2/AIR

Figure 1 shows the temperature scan of an uncured ATS-G TICA specimen. The scan-up features are very similar to that observed previously with BADABBA (Reference 1). The uncured glass transition temperature based on the b component peak occurred at 30°C. The tan component showed a double peak at this region. The second peak, however, varied both in intensity and position in different runs, and may be due to residual solvent in the specimen.

Just like the BADABBA TICA runs, the resin vitrified at a higher temperature as indicated by the "b" component peak (208°C) and the rise of the "a" component. At the range of 250°C to 300°C, the specimen experienced a temporary softening as shown by the "a" component valley in that region. The ATS-G resin finally went through a glass transition with a "b" component maximum at 366°C.

On the scan down, all three components (a,b and tan δ) had changed. This is contrary to what was observed with BADABBA. With the modified four-stage scheme, the BADABBA scan-up experiment was described as I-II-III-II-III-II in the previous report. Based on Figure 1, the ATS-G scan-up would have to be classified as I-II-III-II-III-II-IV. The scan-down "a" and "b" components indicated that the Tg had been lowered to 342°C, implying stage TV, defined as the region where dTg/dt is negative, has occurred. Degradation is interpreted as the cause of the Tg lowering since it is known from TGA experiments (Reference 4) that sulfone group has a lower thermal stability than the quinoxaline structure in BADABBA.

The valley observed in the region at 250°C to 300°C was previously speculated as an indication of two different reaction effects in the BADABBA report. Further experimentation later showed that the temporary

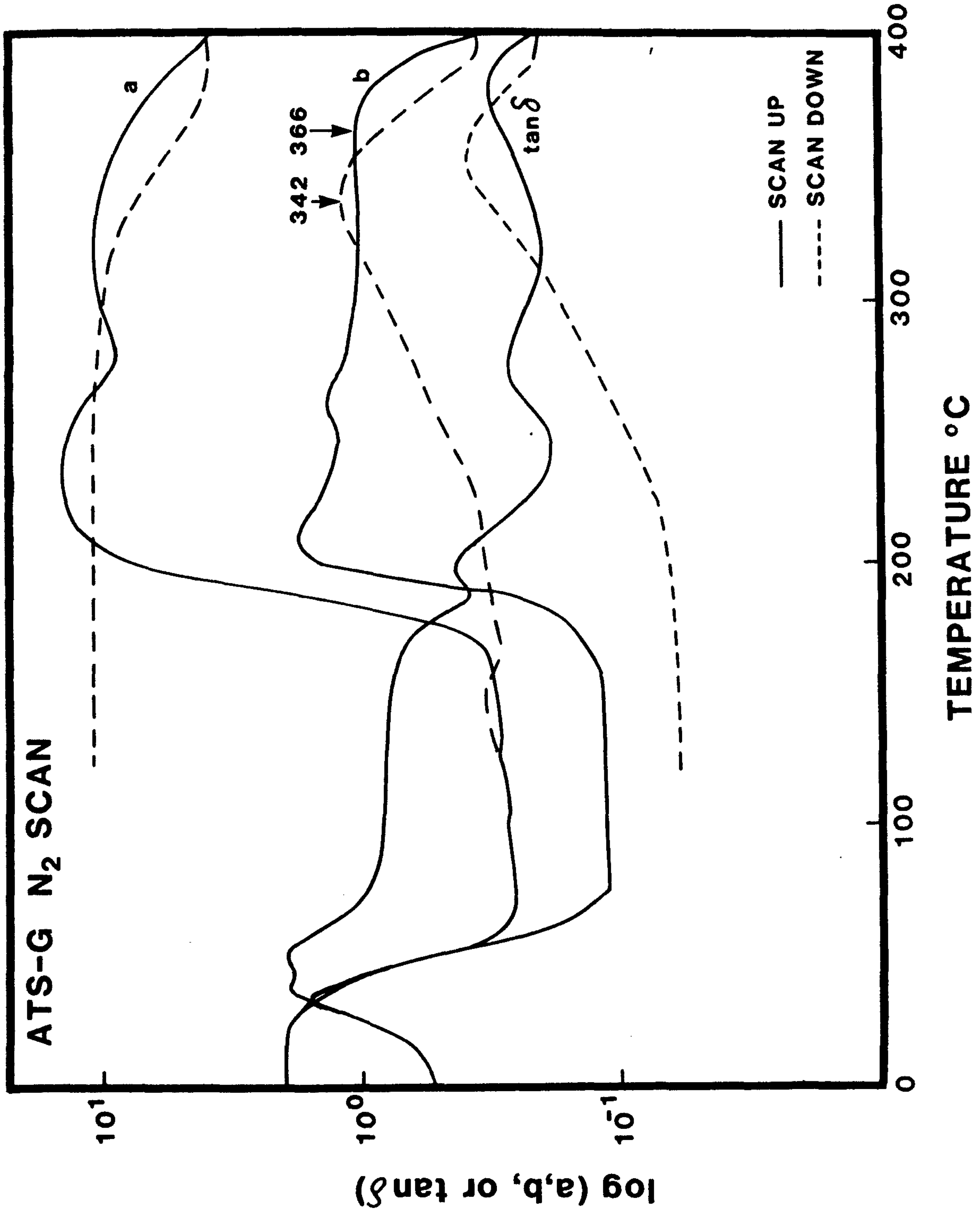

Figure 1. Nitrogen Scan of Uncured ATS-G (to 400°C)

softening was actually due to volatile coming off the cloth used (Reference 5). The valley at that region will not appear if another roll of cloth was used. The interpretation of the valley region as another II-III stage is still correct, but it should not be used as supportive evidence of the presence of a higher temperature reaction.

The experiment was repeated, but the maximum scan temperature was 350°C instead of 400°C. The high-temperature-region features, as shown in Figure 2, did not show sign of degradation. It is not to say that degradation will not occur at this temperature; but within the time scale of this experiment, it is negligible. This interpretation is supported by data presented in a later section. The result indicated that the specimen had a final Tg above 350°C. The stage IV effect was eliminated from the experiment, thus making it more convenient to compare with air-cured specimens.

Figure 3 shows the IR result and a DSC scan of the ATS-G. The disappearance of the acetylene band at 3300 cm^{-1}, as a function of temperature, was measured during a 2°C/min scan in nitrogen. The acetylene bands were ratioed to the peaks 3030 cm^{-1} and 1100 cm^{-1} (assigned to aromatic and sulfone structures, respectively) as internal standard, and were normalized to show the percent of acetylene reaction. The IR data are plotted in Figure 3(a) as circles. They indicated that no appreciable reaction occurs until about 150°C. Then the reaction consumed the acetylene at a fast rate until, at about 220°C, the acetylene concentration started to level off. The rapid decrease of the acetylene concentration matched well with the rapid rise of the "a" component in Figure 1.

Figure 3(b) shows the DSC trace in a 2°C/min program rate. Because of better sensitivity, the reaction was shown to start at a lower temperature ($\sim$ 110°C). The reaction rate maximum was at 190°C, which incidentally was the tan δ vitrification peak temperature in Figure 1.

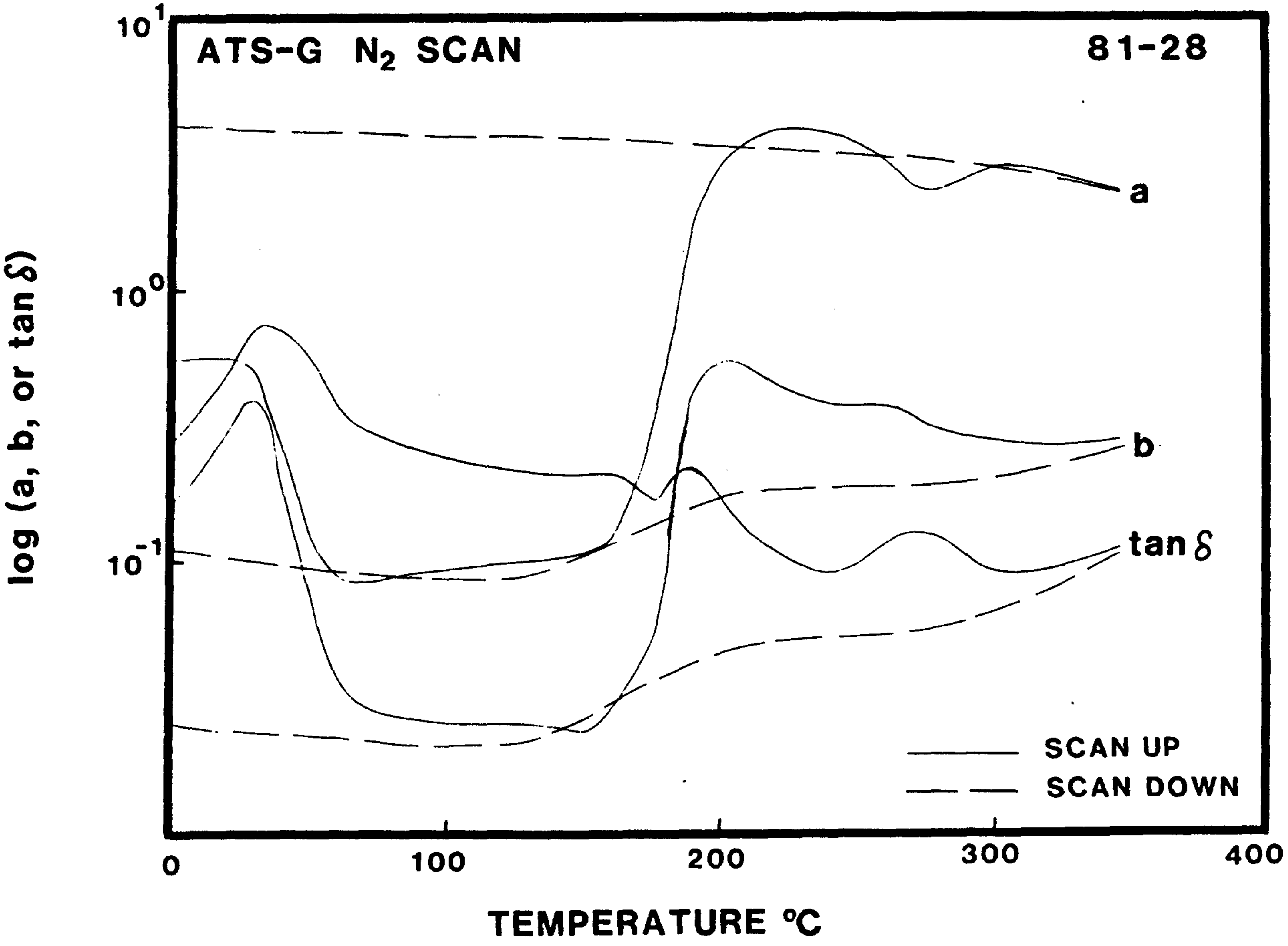

Figure 2. Nitrogen Scan of Uncured ATS-G (to 350°C)

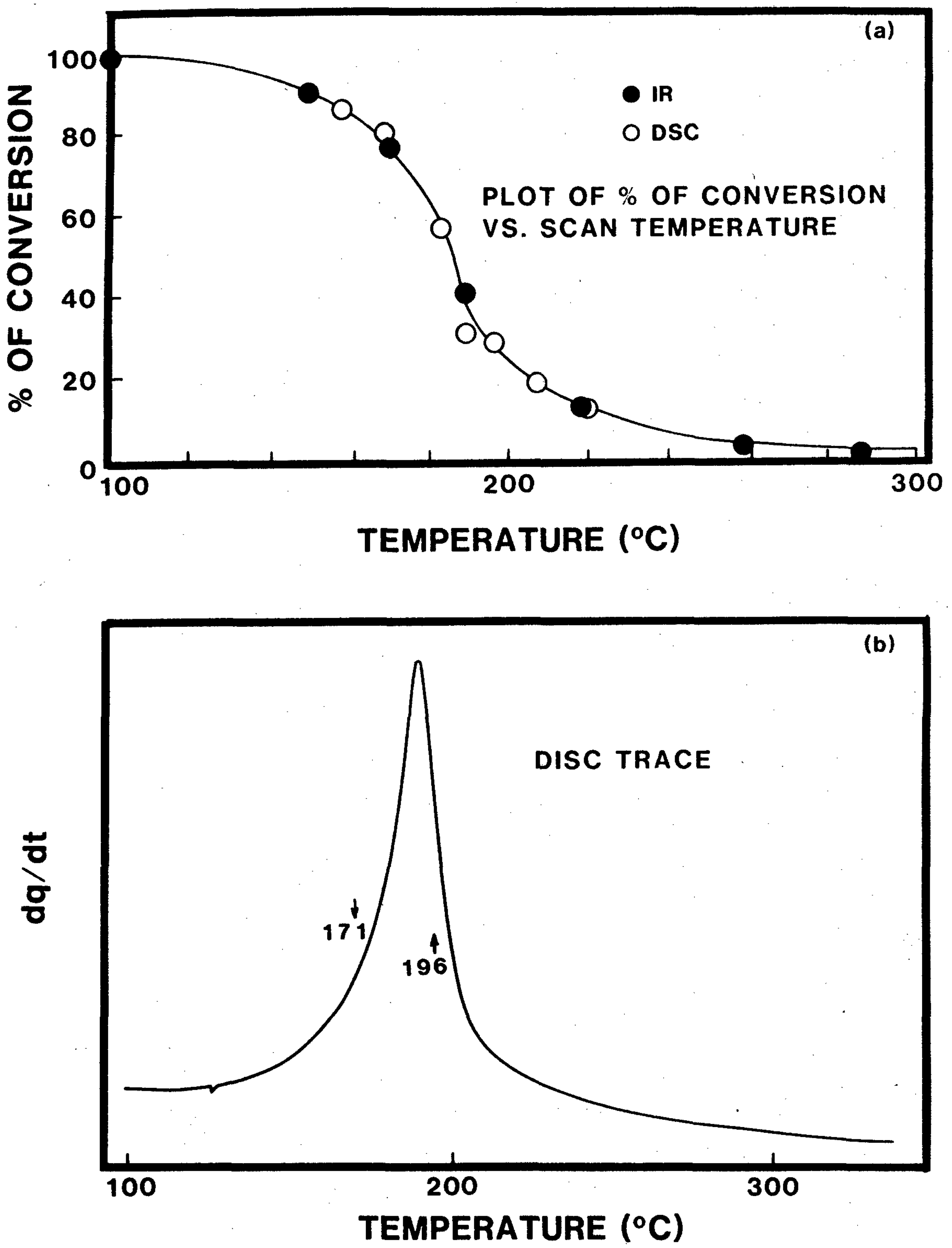

Figure 3. Percent of Acetylene Disappearance Compared with Percent of Exotherm under a 2°C/min scan

Ignoring the change in heat capacities between the "before-reaction" resin and the reacted material, a straight line was drawn as the baseline for the reaction exotherm. The areas under the exotherm at various temperatures were measured using the paper cut-and-weight method. After normalization with the total area of the exotherm, the extent of reaction as determined by DSC are plotted in Figure 3(a) as triangles. They agreed well with the results obtained via the IR peak determination. At the peak of the exotherm, the DSC data indicated a 57% reaction, while the IR data at 190°C gave 58%. The good correlation between the disappearance of the acetylene and the DSC data is in agreement with an earlier finding by J.M. Pickard et al. (Reference 6) using (3-phenoxylphenyl) acetylene.

Combining both sets of data, a curve can be drawn to represent the extent of acetylene group disappearance in a 2°C/min scan rate under nitrogen environment. This information can be used in conjunction with other experiments under a similar scan rate, but care should be taken if it is used with experiments with other cure history. Findings by McDonnel Douglas under an Air Force-sponsored contract (Reference 7) indicate there may be structural differences in the reacted products cured at different temperatures. Thus the products obtained from 50% reaction under a 2°C/min scan may be different from a 50% reaction product from an isothermal cure.

Figure 4 shows the scan under air environment. Like the BADABBA results, the air scan data suggested a I-II-III-II-R-II-III type of behavior. The valley between 250 to 300°C has been reduced to a plateau. The scan down curves indicate that the final Tg has been advanced to above 400°C. However, there is one aspect of this scan that is different from BADABBA. For the rise of the "a" component around the vitrification region, there was no observable difference between the air scan and the nitrogen scan data for BADABBA. Comparing Figure 1 with Figure 4 shows that the air scan rise was slower than the nitrogen scan data. The nitrogen scan data indicates that the "a" component was very close to the peak value of the rise at 200°C, but Figure 4 shows that the a component was only half-way in the rise. The

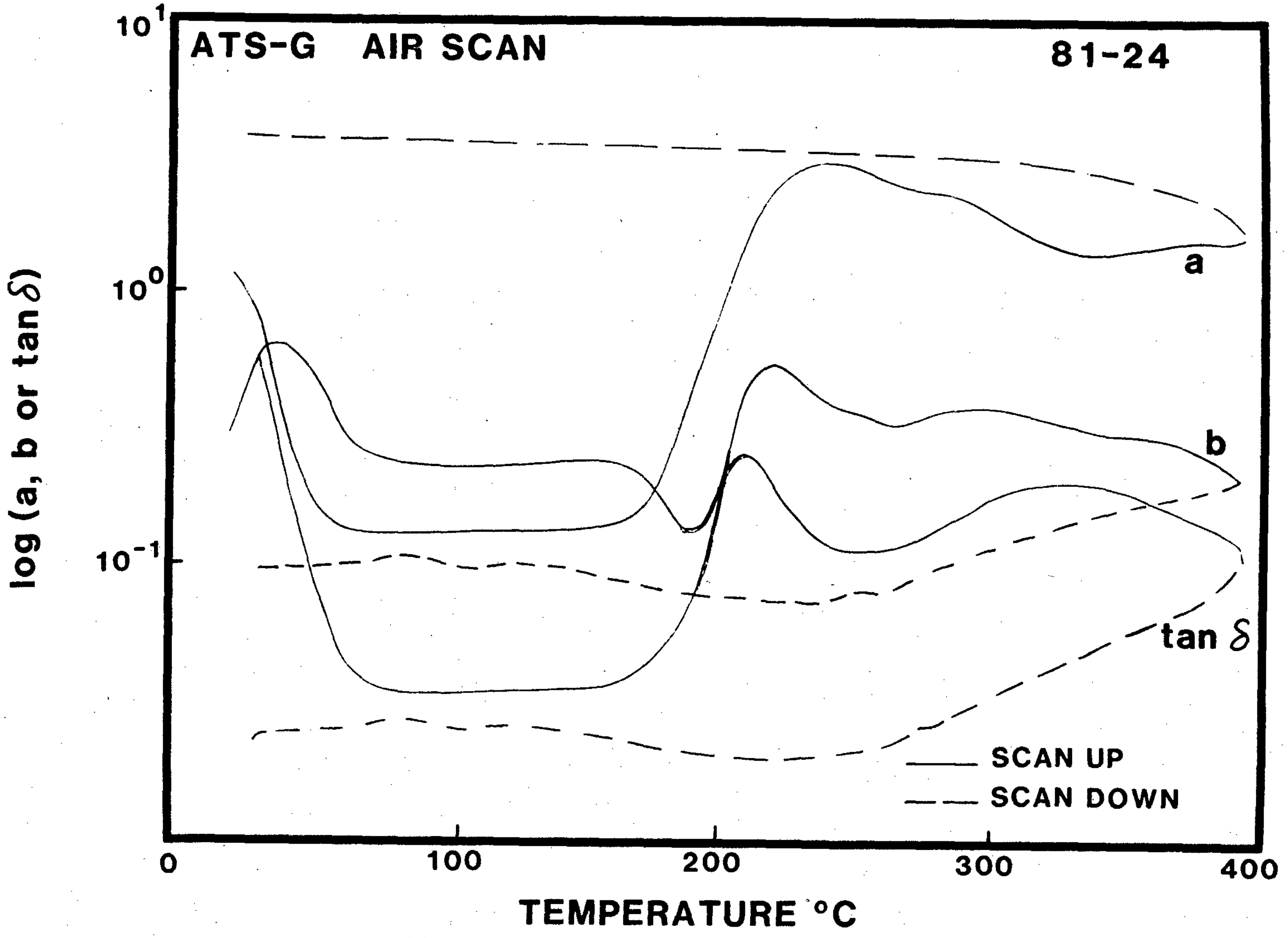

Figure 4. Air Scan of Uncured ATS-G (to 400°C)

nitrogen scan shows a vitrification peak of 208°C; and the corresponding air scan peak was 222°C.

This observation implies that the cure kinetic rate in the presence of air is slower than that in the absence of air. This was supported by the isothermal curing data to be reported in a later section. The reason BADABBA did not show similar differences in the temperature scans may be because of the high uncured Tg of BADABBA. The range of temperature where the resin was in the liquid state was shorter, and the viscosity level was higher than that of ATS-G. This will be explored further in a later section.

The final stage in the scan is Stage III. Just like BADABBA, the cause of the Tg increase could be due to high temperature oxidative crosslinking. The fact that the results show the Stage III instead of Stage IV does not mean degradation did not occur in the presence of air. It merely means that the oxidative crosslinking predominated over the degradation effects at this temperature range.

To make direct comparison with Figure 2, where the thermal degradation was minimized by stopping the temperature scan at 350°C, a similar scan in air was shown in Figure 5. Similar to the scan-up results of Figure 4. The "b" component showed a peak at 300°C. The scan down results indicate that the Tg had been moved up to 337°C.

ISOTHERMAL CURE IN N_2/AIR

The TICA specimens were isothermally cured at different temperatures under air/nitrogen environment. A typical cure diagram is shown in Figure 6. In general, three reference points can be identified: the first and second tan peak and the b maximum. The times required to reach these points are denoted as Tgel, T_δ and T_b, respectively (Reference 2). As noted in previous publications, these times did not take into account the time required to heat up the sample chamber. Therefore the times measured are associated with the

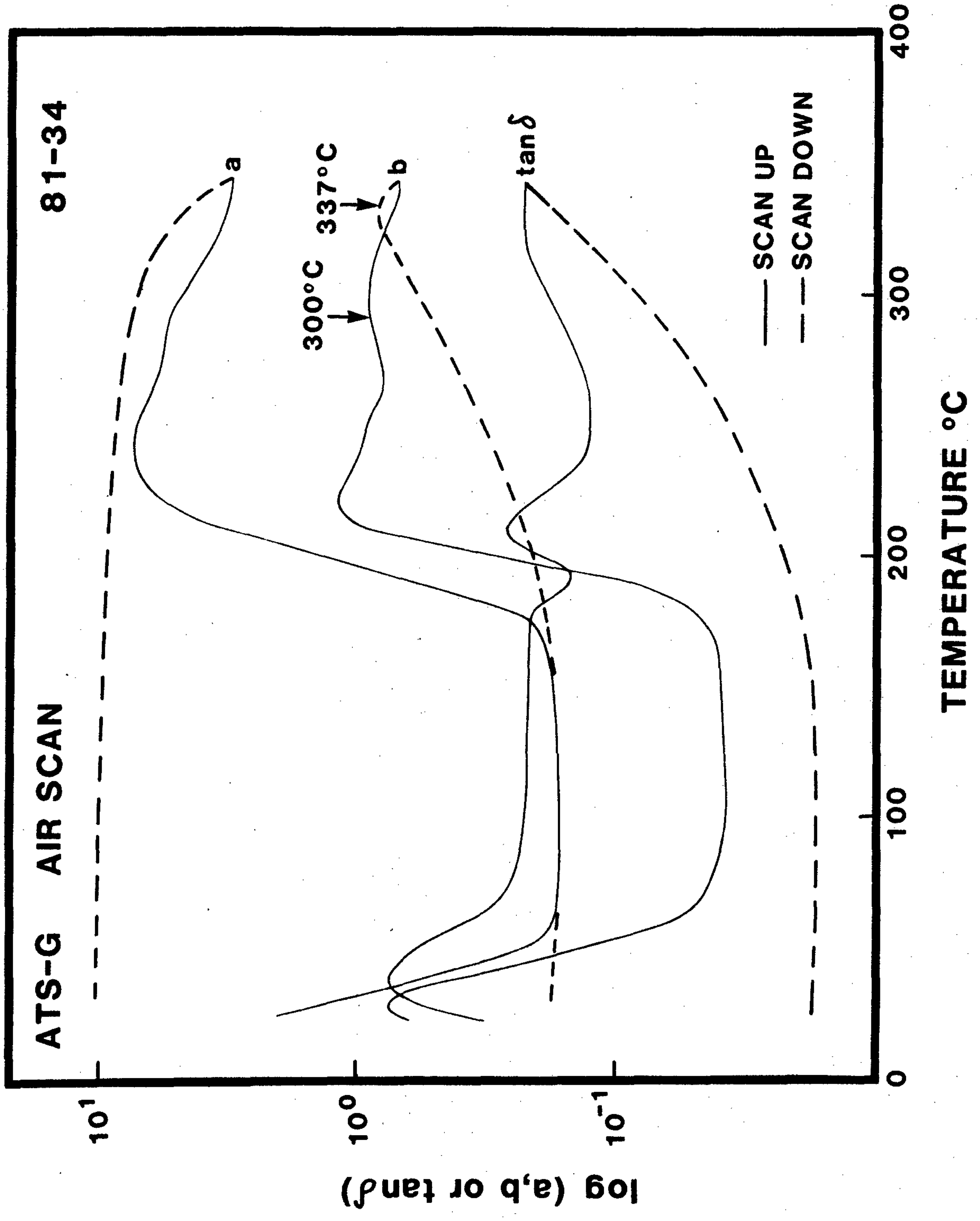

Figure 5. Air Scan of Uncured ATS-G (to 350°C)

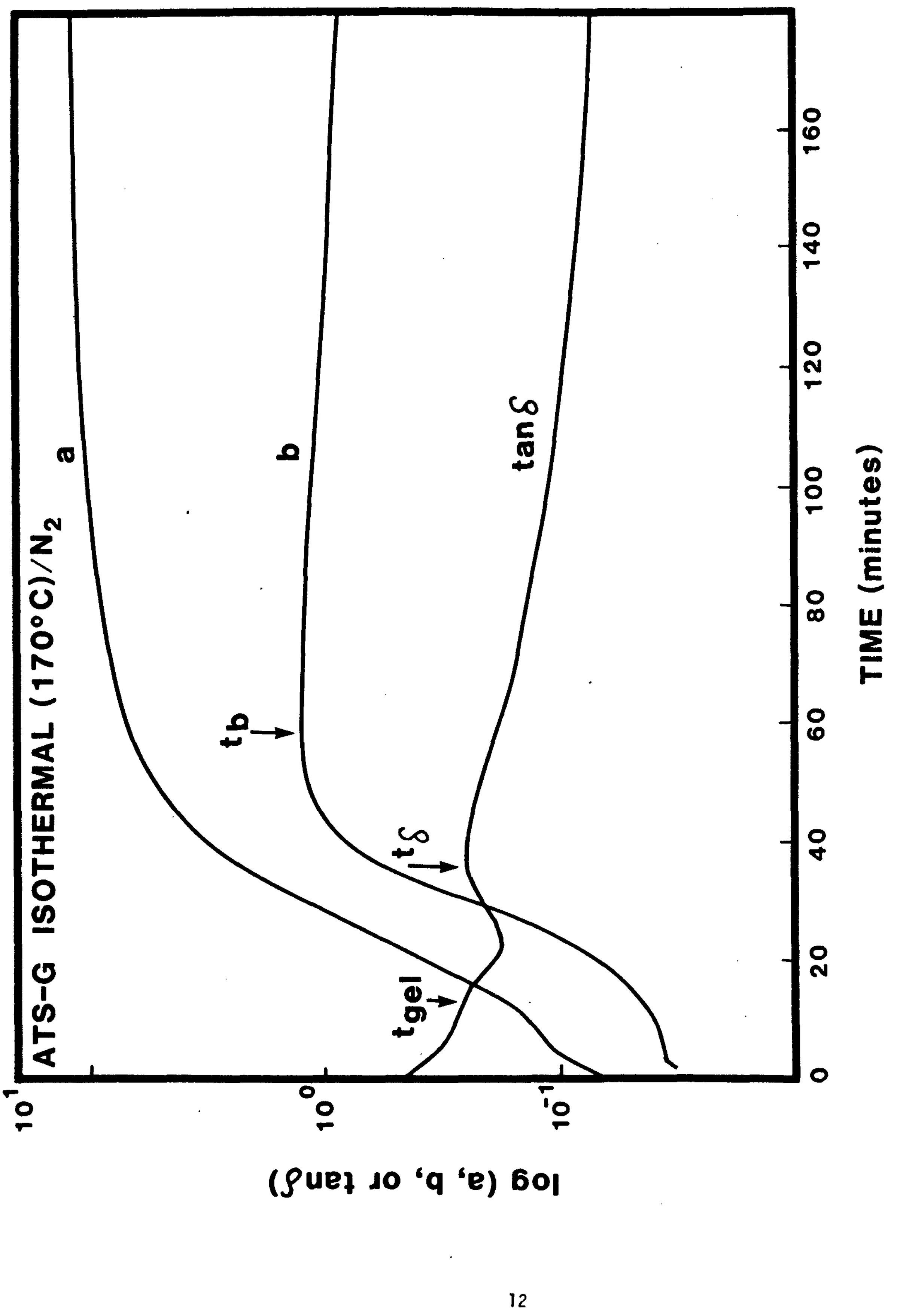

Figure 6. Isothermal TICA Results of ATS-G at 170°C

experimental procedure used. For short time values, they do not represent the true kinetic data.

The values under air and nitrogen environments are listed in Table 1. The log values of Tgel and T_b are plotted vs temperature in Figure 7. In all cases, the times recorded in the air cure experiments are longer than those for the corresponding nitrogen cure experiments. This wns different from that observed in the BADABBA experiment. With the BADABBA data, the times were all comparatively short. The air-cure times were shorter than the nitrogen-cure times and the difference was because of experimental artifacts owing to different temperature-increase profiles. The lower uncure glass transition temperature of the ATS-G made lower temperature measurements possible. The long time of cure required at the low temperatures dwarfed the temperature-increase-profile effects. Obviously, the presence of air decreases the kinetic rate of curing. The differences progressively decrease with higher cure temperature or shorter reaction time, indicating the role of air diffusion in influencing the Air/Nitrogen cure effects.

Although the first tan δ peak has been labelled as a gel peak, it is not the gelation in the classical sense (Reference 2). However, if these peaks occurred at the same extent of conversion over a temperature range, the Tgel data can be used to calculate the activation energy. Two samples were isothermally cured at 131°C and 183°C under nitrogen to the gel peak maxima and were thermally quenched to stop the reaction. Subsequent scans revealed these samples to have Tg's of 68°C (131°C cure) and 69°C (183°C cure). The difference is well within experimental uncertainties. Similar experiments were repeated under the air-cure environment, and the Tg's were 72°C (131°C) and 69°C (183°C cure). The good agreements of the Tg values implies that the extents of conversion of all points within that temperature range are very close and that the tgel values can be used to approximate the cure activation energy. Linear fitting of these data yields $\Delta E = 16$ kcal/mole for nitrogen cure and $\Delta E = 22$ kcal/mole for air cure.

Cure activation energy had been evaluated with different methods. Variable rate DSC scanning experiments (Reference 8) developed by W. Adams and I.J. Goldfarb yielded $\Delta E = 20$ kcal/mole. A different variable rate DSC experiment which uses the peak exotherm for calculation reported E = 23.7 kcal/mole (Reference 9).

TABLE 1

RESULTS FROM TICA ISOTHERMAL CURE EKPERIMENTS OF ATS-G

Temperature °C	t_{gel} min.	t_δ min.	t_b min.
N_2Cure			
131	56	170	340
150	21	68	123
171	11	33	58
190	6.7	17	28
211	3.4	8.1	13
233	-	4.2	9.3
250	-	-	8.3
258	-	-	8.3
Air Cure			
130	120	455	680
150	36	160	235
170	11	56	82
190	6.0	24	35
210	3.3	10.2	18
229	2.8	6.6	12

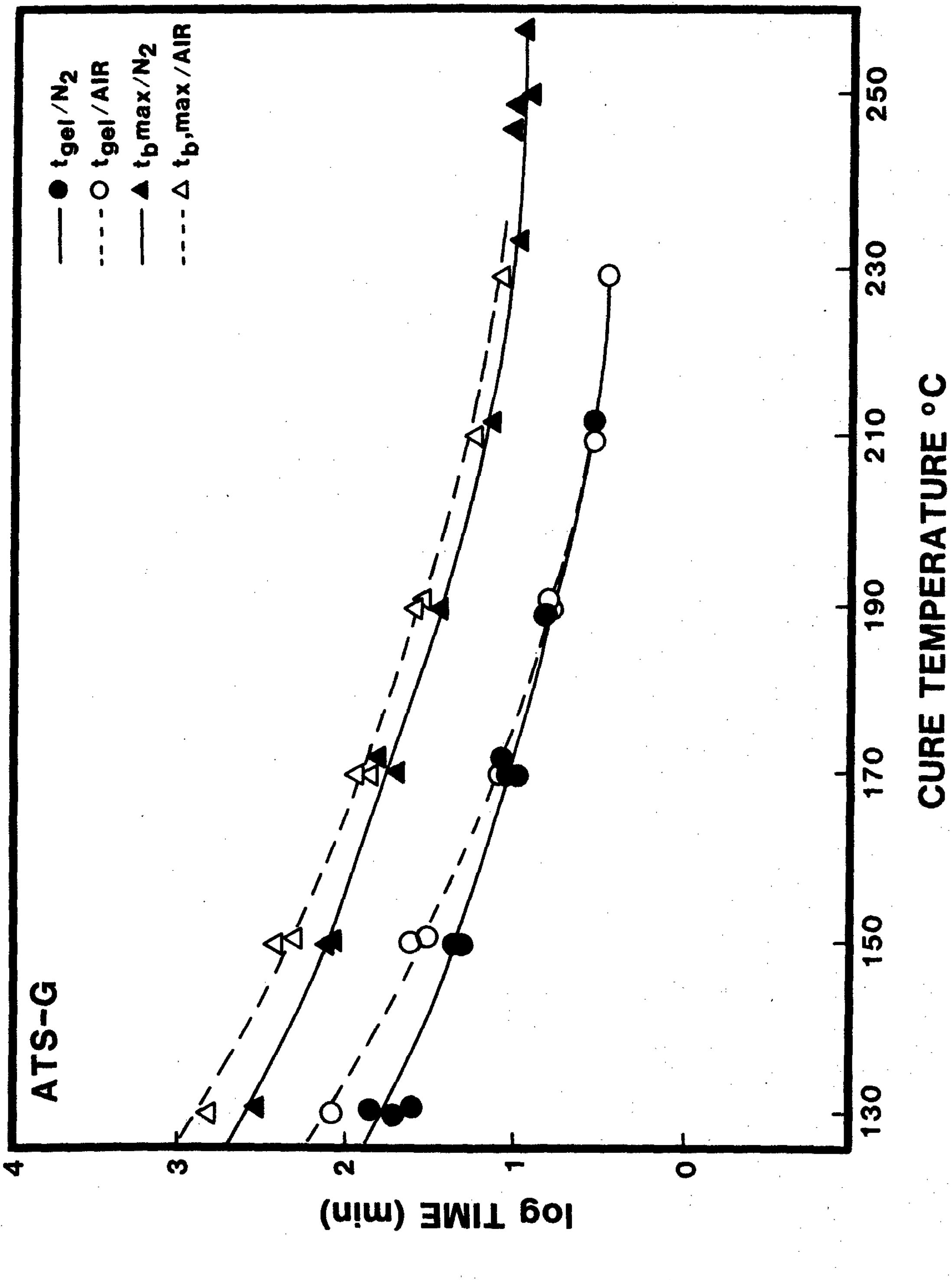

Figure 7. TTT Diagram of ATS-G

Results from University of Dayton Research Institute showed a value of 21 kcal/mole (Reference 10). Using the definition of gelation proposed by Tung and Dynes (Reference 11) for dynamic viscosity measurements, we have taken data at the points where tan δ = 1 to calculate the activation energy. A value of 22 kcal/mole (Reference 12) was obtained. The value obtained for the air cure in this work appears to agree with all the others, but the nitrogen cure value is too low. This discrepancy is interesting because all the other works are supposedly done under inert atmosphere.

On the other hand, if the assumption that the cure states at the tan peak being an iso-cure-state was incorrect, then at higher temperature the peak will occur at a higher extent of cure. Thus even though a straight line can be obtained from the log t vs 1/T plot, a systematic error would have been introduced to lower the slope of the line, which would, in turn, give a lower activation energy value.

TEMPERATURE SCANS OF PARTIALLY CURED SPECIMENS

Figure 8 shows the temperature scan under nitrogen environment of a specimen that had been cured for 4½ hours under nitrogen. A glass transition was observed at 119°C. Based on the curing kinetics data of AT, the additional cure effect at this temperature should be insignificant, so the value is the partially cured specimen's Tg. The first rate conversion occurred at 160°C followed by a vitrification peak at 192°C. Similar to BADABBA data, the precuring in N_2 did not affect the temporary softening at 275°C. The maximum temperature of the scan was at 350°C to avoid the complication of thermal degradation. The data indicate that such a scan history had cured the specimen to a Tg of above 350°C.

A similar scan was performed on a specimen that hnd been cured in air for 4½ hours. The results are shown in Figure 9. By comparison with the nitrogen cure results, one can observe that the partially cured Tg has been lowered to 96°C. Similarly, the first rate conversion point wns lowered to 141°C. The vitrification peak was unaffected at 192°C. The changes in the volatile effect under air cure are consistent with

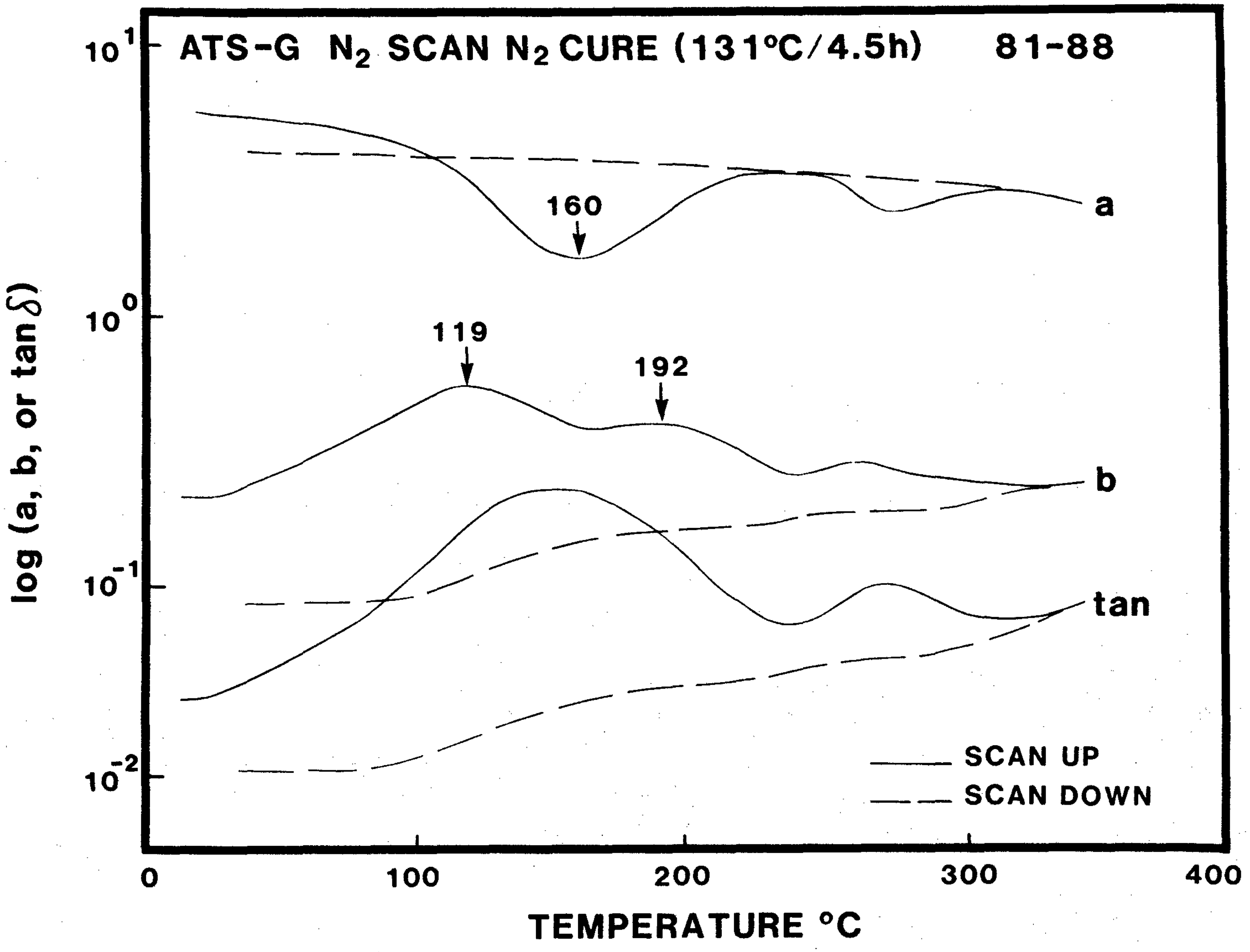

Figure 8. Nitrogen Scan of ATS-G Pre-cured in Nitrogen at 131°C (4-1/2 h)

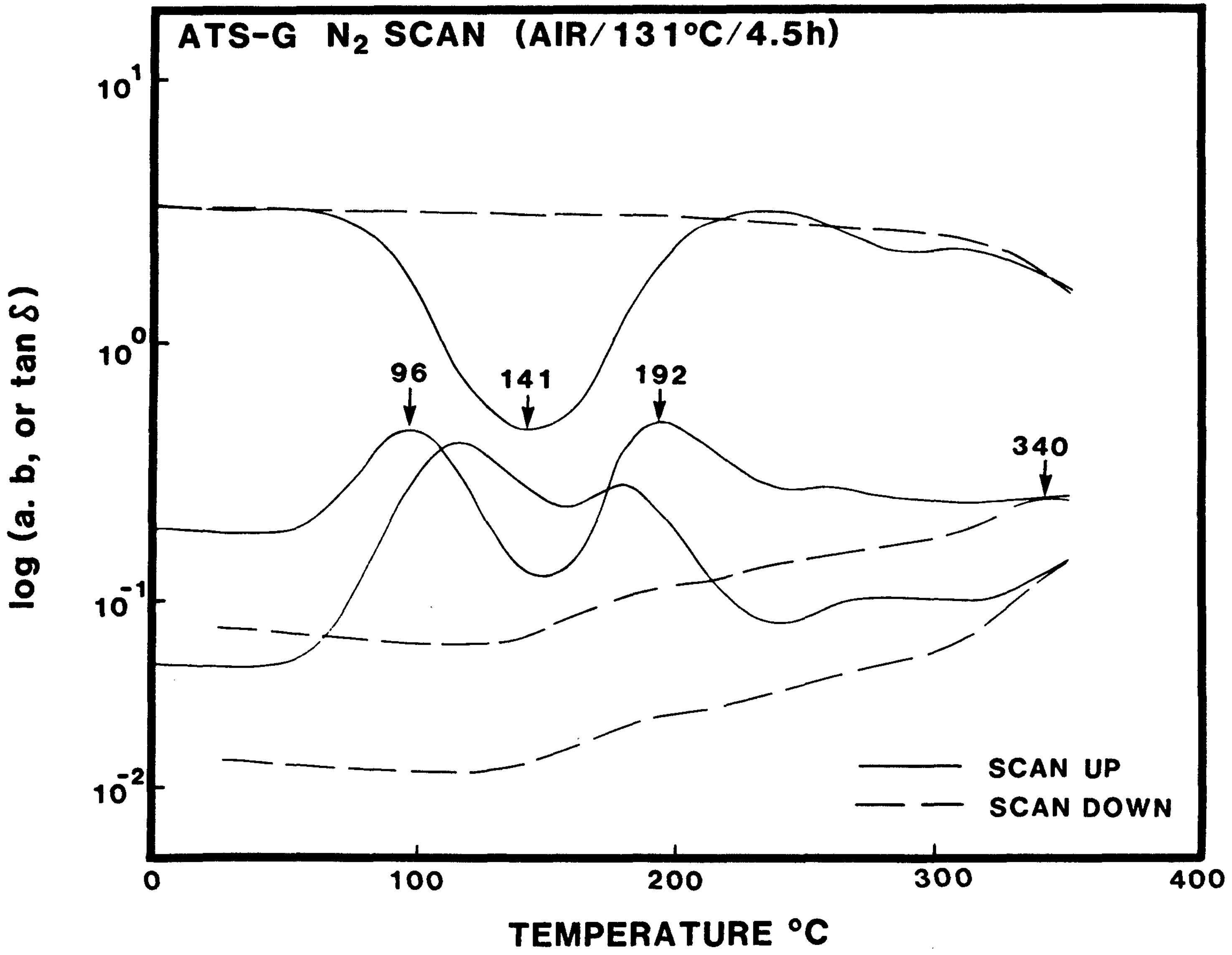

Figure 9. Nitrogen Scan of ATS-G Pre-cured in Air at 131°C (4-1/2 h)

that reported with the quinoxaline system. The specimen had a Tg of 340°C after the scan.

For the quinoxaline results, the partially cured Tg peak was not observed, and the first b component peak was associated with the rate conversion point. The shape of the peaks had suggested that the air-cured specimen had a lower partially cured Tg, but the rate conversion temperatures are the same. Because of the lower uncured Tg of the ATS-G, low-temperature partially cured Tg can be observed from the scans, and the results showed clearly that the air-cured specimens had lower Tg's than the corresponding nitrogen-cured specimens.

The lower partially cured Tg under air is consistent with the isothermal curing results which show that cure kinetic rate is slower in air. During the nitrogen scan, the additional cure kinetics should be the same and, similarly, the rate conversion point should be the same temperature. The difference in rate conversion points observed in Figures 8 and 9 may imply different reactions occuring during the scan due to different pre-cure conditions. Another feasible explanation is that the higher partially cured Tg also caused a higher viscosity level at each temperature, which retards the overall reaction rate differently even though the activation energies are the same in both cases. In light of the agreement in the vitrification temperature, it is likely that the latter case is true.

Figure 10 shows the temperature scans of two specimens that had been cured in N_2 at 250°C for 4½ hours. One scan was done under air atmosphere. Both scans indicated that the final Tg's were above 350°C. Judging from the shape of the high temperature response, one may conclude that at 350°C the air scan specimen was closer to the glass transition peak than the nitrogen scan specimen. Although it is not clear whether that is a result of slower cure kinetic rate of a lower final Tg, the results indicate that different post-cure conditions can also change the resin properties even though the major portion of the reactions was identical in the precuring.

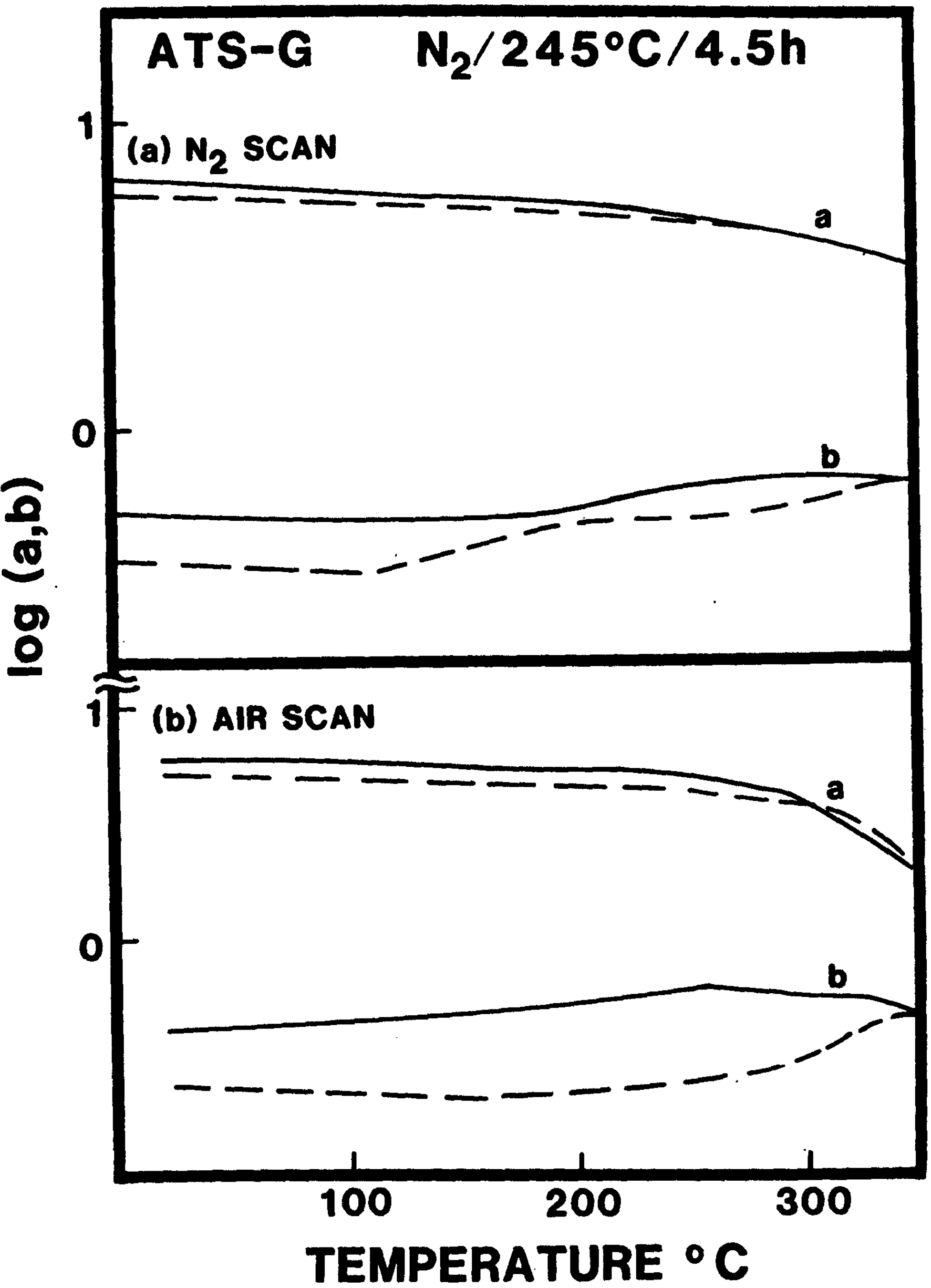

Figure 10. Nitrogen Scan and Air Scan Results of ATS-G Pre-cured at 245°C (4-1/2 h)

EFFECTS OF TDME AND TEMPERATURE OF CURE

TICA specimens with different isothermal curing conditions were scanned in temperature under nitrogen environment. The first "b" component peak (or shoulder) which was associated with the partially cured state was labelled at Tc as in the previous report. Similarly, the last "b" component peak was labelled as TgB(∞). For the quinoxaline systems, the scan-up TgB(∞) values were the same as the scan-down values with the exception of one run. With the ATS-G, they are usually different. The peaks at about 260°C were unchanged regardless of pre-cure history. The Tc's and the TgB(∞) are listed in Table 2.

At low temperature, Tc values are indeed the partially cured Tg of the specimen. For those higher temperature values, the additional cure effect was more significant, and the peak temperature may not be the partially cured Tg. Nevertheless these values can be used as a parameter describing the cure state before the scan. Those data are plotted in Figures 11, 12 and 13. Figure 11 shows the Tc as a function of cure temperature with 4½ hours of cure time. Figure 12 shows the Tc as a function of cure thme at the cure temperature of 131°C. Figure 13 shows the Tc as a function of cure time at 183°C. Figure 11 shows that the difference between the air and nitrogen cure decreases with increasing cure temperature; Figure 12 shows that the difference increases with increasing time; and Figure 13 shows only a slight increase in the difference between the air and nitrogen cure Tc at the short-time region. These data can be rationalized through the consideration of three factors: (1) amount of additional cure at Tc, (2) quenching of reaction rate after vitrification and (3) air diffusion through the specimens. We will consider each factor individually and describe how each influences the difference in Tc between air-cured and nitrogen-cured specimens.

No discernible difference in Tc was observed between air-cured and nitrogen-cured BADABBA specimens. As explained in the previous section, the reason may be due to the comparatively higher Tg of BADABBA samples. With equal length of time at different temperatures, those samples cured

TABLE 2

TICA TEMPERATURE SCAN RESULTS OF ATS-G

Precure History °C/h	T_c °C	Tvit °C	Tg (∞) up °C	Tg (∞) down °C
N, Cure				
130/4.5	118	192	350	350
150/4.5	165	190	350	350
172/4.5	200	-	350	350
189/4.5	230	-	350	350
211/4.5	-	-	350	350
246/4.5	-	-	350	350
131/1.5	90	193	350	350
130/6.2	135	193	350	350
130/12	158	190	350	350
Air Cure				
131/4.5	96	193	341	341
150/4.5	152	193	327	334
170/4.5	203	-	314	326
190/4.5	227	-	306	322
210/4.5	-	-	308	328
229/4.5	-	-	315	333
247/4.5	-	-	316	334
131/1.7	70	198	348	350
131/14.3	140	194	323	333
131/30	166	194	316	330

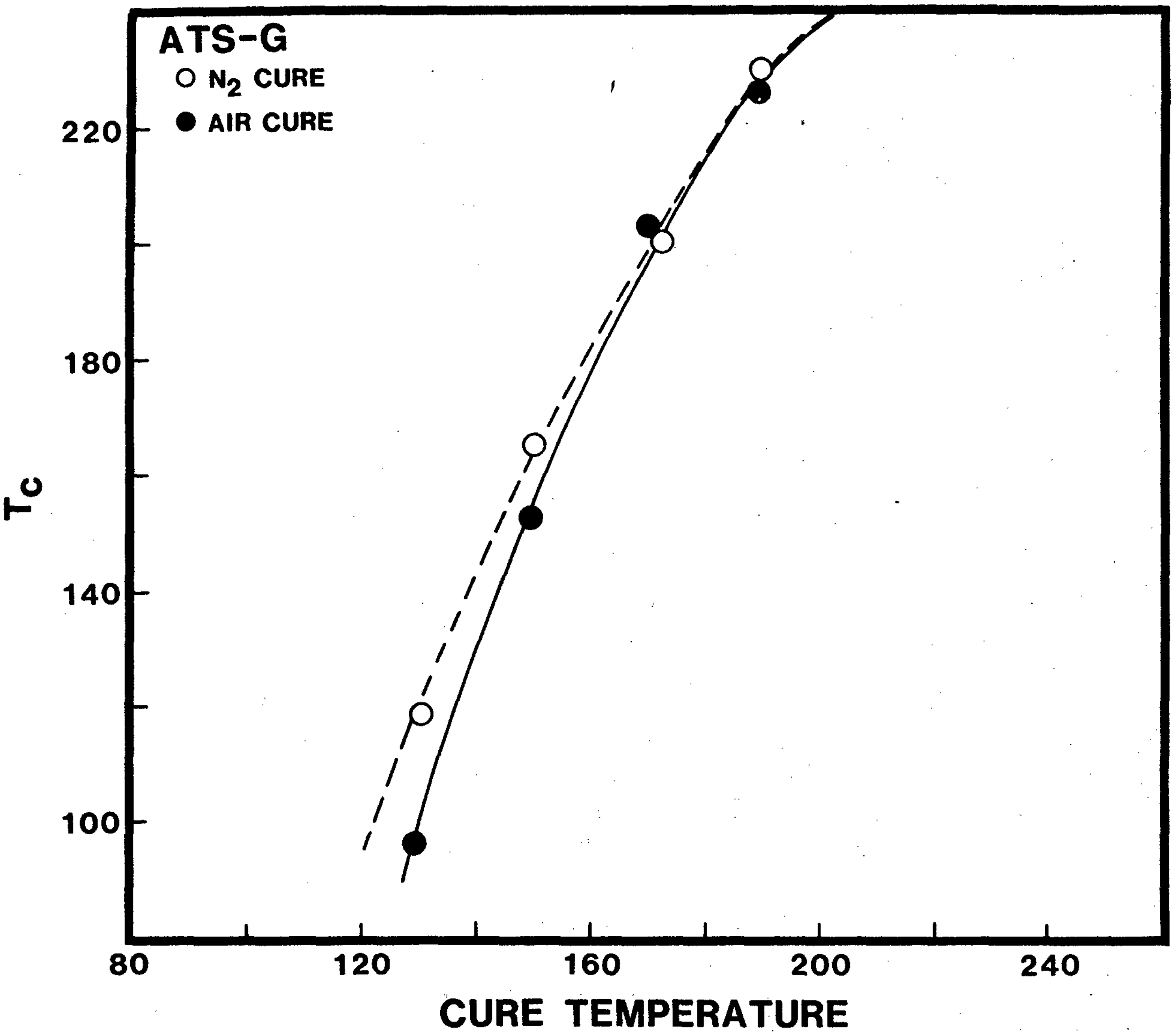

Figure 11. Plot of Tc vs Cure Temperature (4-1/2 h) of ATS-G

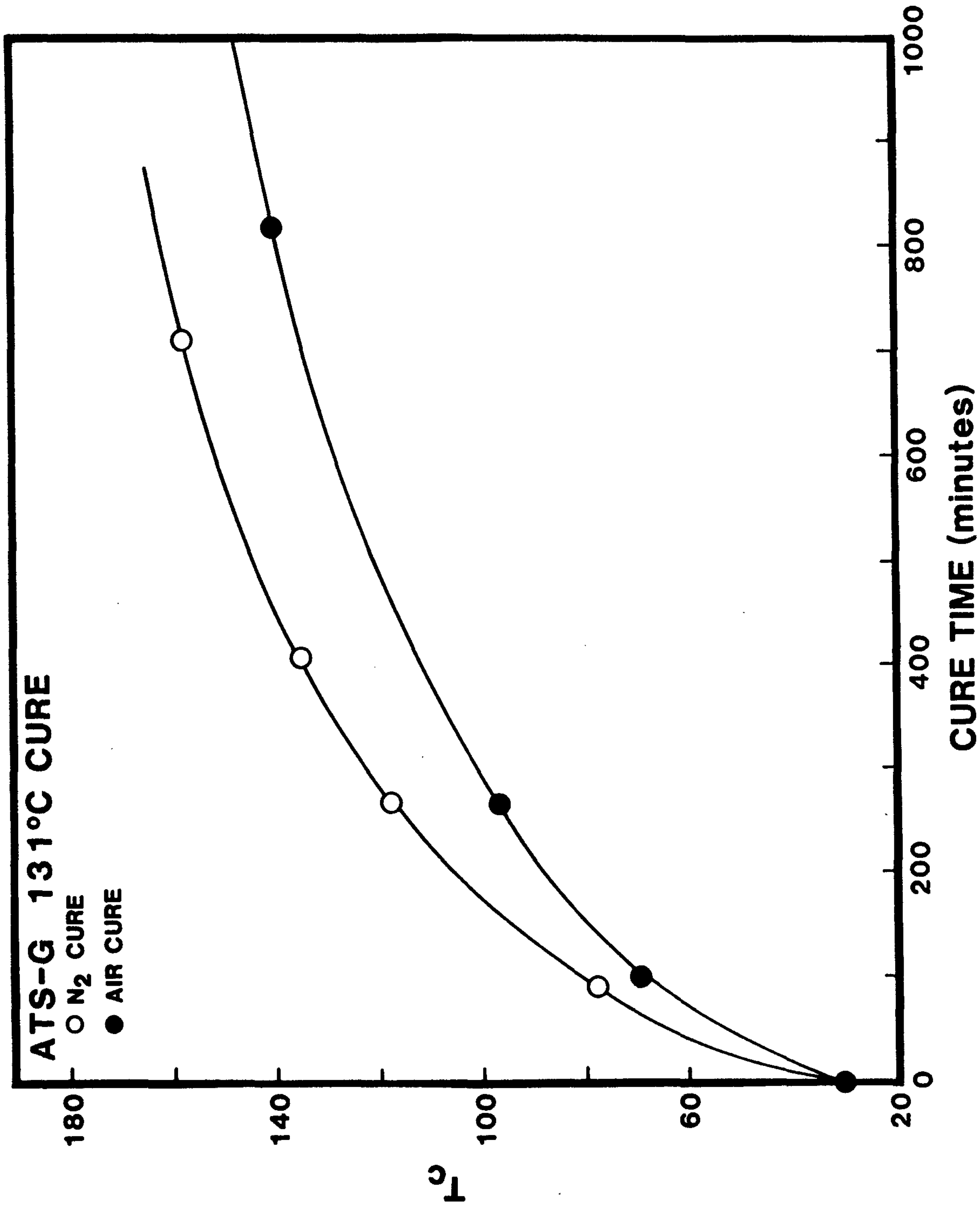

Figure 12. Plot of Tc vs Cure Time (131°C) of ATS-G

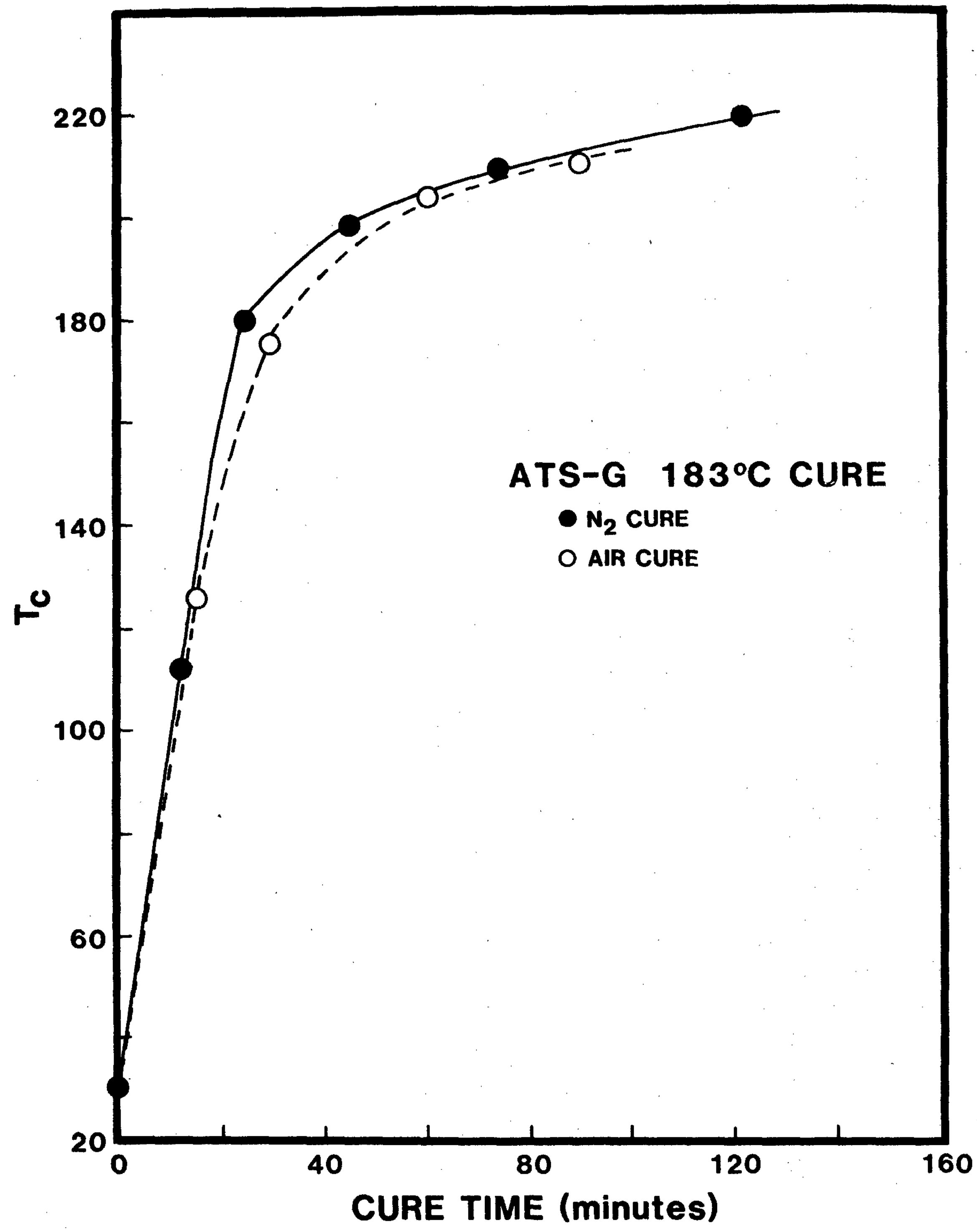

Figure 13. Plot of Tc vs Cure Time (183°C) of ATS-G

at higher temperatures will have higher partially cured Tg's. During the scans the samples with high Tg's will have more additional cure effect at Tc. The Tc peaks observed will not be a result of the partially cured Tg exclusively, but more likely will include additional cure effect, or even be owing to the rate conversion point. This point can be demonstrated by noting the times needed to reach "b" maximum at 131°C and 183°C isothermal experiments in the air and nitrogen environments.

From Figure 12, these times will show a Tc of 130°C and 131°C from the air and nitrogen curves which agree very well with the isothermal cure temperature. As explained in an earlier publication, this should be the case if no additional cure occurred during the scan. From Figure 13, however, the time to "b" maximum interpolated to a Tc value of 192°C and 194°C, which are about 10°C higher than the isothermal curing temperature. Clearly additional cure had occurred during the scan. Since the additional cure reactions are similar between the two sets of samples, the rate conversion point Tc will tend to decrease in difference in partially cured Tg. This could partially account for the decrease in difference between air- and nitrogen-cured Tc at higher temperature (Figure 11) and longer time (Figure 13).

Vitrification will quench the curing reaction rate because of hindrance to molecular motions in the glassy state. After the vitrification, the nitrogen-cured specimen, which had a faster reaction rate, will have a slower increase in Tg. The slower reaction-rate samples in air cure will then be able to catch up. Thus, in Figure 13 the difference between the air- and nitrogen-cured TR increases initially with cure time until both curves past the vitrification times which are around 30 to 50 minutes. After that, the difference decreases with increasing cure time after vitrification.

The third factor is the air diffusion effect. Air has to diffuse into the sample during the cure to cause changes in properties. So with increasing time of reaction, the effects between air and nitrogen cure will be more significant. For specimens cured to about the same Tc values, which should have similar extent of reaction, the samples cured at lower temperature exhibited much larger air effect (see Figures 12 and 13). This is because of the longer time needed to reach the same extent of cure, which increases the significance of the air effect. This air diffusion effect explanation is supported by the results from the study of neat specimens properties with different thicknesses. These results will be reported in a later technical report.

Figure 14 shows the TgB(∞) data from specimens that had been cured for 4½ hours at various temperatures. In BADABBA, all the runs except one showed identical "b" component peak locations on the scan-up and scan-down. For ATS-G, however, almost all scan-up results exhibit a lower "b" component peak temperature than the corresponding scan-down results. Comparing the curves linking the scan-up "b" maxima and the scan-down "b" maxima in Figure 14, one can observe two interesting features. Both curves show a minimum value at about 190°C; and the difference between the scan-up and scan-down increases with increasing cure temperatures.

The BADABBA results showed a trend of decreasing TgB(∞) with increasing air cure temperature, implying that air curing will lower the final Tg of the system. The data however, were in the range below 200°C. The ATS-G data which include the higher temperature range showed that TgB(∞) slightly increases after 200°C. This may be explained by the air diffusion factor again. At low temperature range, increasing temperature increases the air effect. But at higher temperature range, the shorter times to vitrification actually decrease the air effect.

The scan-up peak locations being lower than that of the scan-down indicates that at the peak maximum temperature during the scan-up,the system was in Stage II, or where $dT/dt > dTg/dt > 0$. For both BADABBA and ATS-G, if the specimens were precured in nitrogen, the (T-Tg) of the specimens were sufficiently negative (below Tg) in the range of 300°C to 350°C that it is difficult to say for sure what stage they were in. Judging from the difference in scanup and scan-down tan and "b" components curves in this region, it is likely that they were still in Stage II. For the BADABBA samples that were cured in air, the final Tg

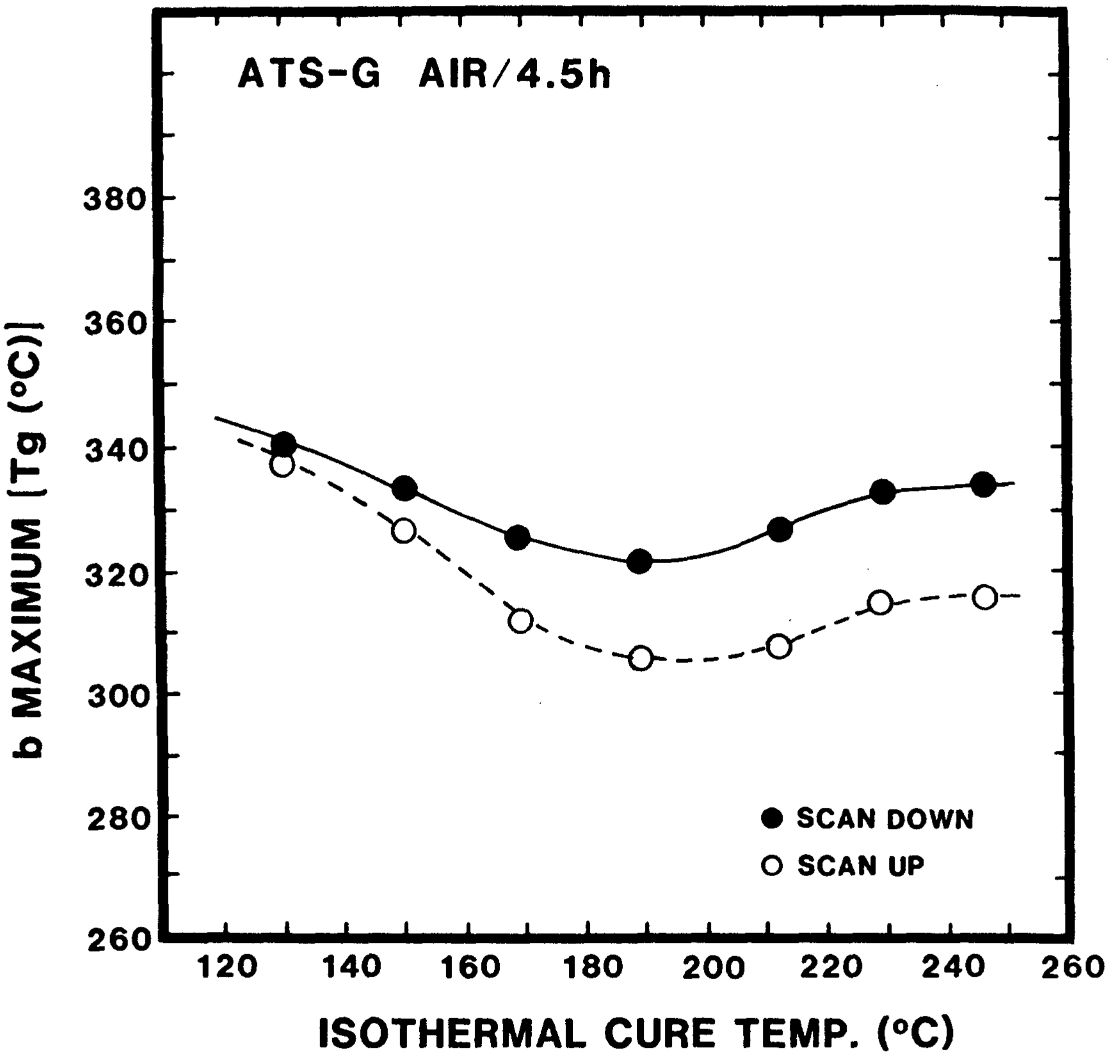

Figure 14. Plot of Final Tg of ATS-G vs Cure Temperature (4-1/2 h)

were all in the 350° to 400°C region, and the data show they were all in Stage I when the "b" component was at the peak, except one case where the "b" component was at 350°C. So it is not surprising to see the ATS-G data to show a difference in peak locations between the scan-up and scan-down curves, because their Tg's are below 350°C. What is unusual is the change in the difference with cure temperatures. The curves show that samples that were cured at 170°C and 230°C had the same Tg on the scan-up but different Tg on the scan-down. Similarly the sample that was cured at 150°C had the same scandown Tg as that of 230°C, but a different scan-up Tg.

These differences indicate that samples pre-cured at different temperatures had different reaction rates during the additional cure in this temperature range. The samples that were cured at higher temperatures have slower reaction rates. One plausible explanation is that the networks formed at different pre-curing temperature are different, thus causing the change in reaction rates. The chemistry can be different at different pre-cure temperatures as shown by contracting reports (Reference 7), thus leading to different products that will react differently in high temperature with different activation energies. Although the softening at 250° - 300°C region was proved not owing to a two-step reaction mechanism, the idea of a secondary reaction at high temperature is still possible. Recent preliminary DSC data by I. Goldfarb (Reference 13) have shown the presence of another weak exotherm at high temperature that normally would have been masked out by the main exotherm.

Observation of changing additional curing rates with different pre-cure temperatures can be explained by other postulations as well. Note that the specimens cured at lower temperatures experienced a lower viscosity level at the rate conversion point during the temperature scan. The low viscosity level will allow the strains on the network built up during the isothermal cure to relax. Thus at the temperature range near the completely cured Tg, these specimens have networks that were less strained than those from the high-temperature-cured specimens; thus allowing freer motions of the reactive groups. This may account for the difference in overall kinetic rate. The validity of any of these postulations will have to await further experimentation.

Tc AS A CURE STATE PARAMETER

The value Tc can be used as a parameter to denote the extent of cure. In the BADABBA data, specimens that have the same Tc values resulting from different cure histories do not have the same final Tg values. Therefore the Tc values is not a unique parameter to describe the cure state. For the ATS-G air cure data available in this report, the Tc values appear to correlate with the final Tg's from the scan-down. By plotting the Tc vs TgB(∞) from different cures, the points fall into a curve. These data are plotted in Figure 15. By using the Tc values as cure-state parameters, final Tg's from different cure temperatures as well as different cure times can be composed into a single curve.

One can view Figure 15 as showing how different pre-curing histories in air affect the final Tg of the systems. For a virgin specimen, the Tc would have been 30^oC (see Figure 1). The data in Figure 15 can be extrapolated to Tc of 30^oC to find out what the final Tg would be if no air-curing effect is present. By using a least squares curve fitting routine, the scan-up TgB(∞) curve gave a value of 371^oC.

This value is very close to the scan-up TgB(∞) value of 366^oC in Figure 1. This agreement, inspite of the different temperature scan range, supports the interpretation that only insignificant amount of degradation had occured up to 366^oC.

CALCULATION OF THE TG DNCREASE AS A FUNCTION OF REACTION

Kaelble and Leung had recently calculated the theoretical Tg increase of ATS-G (Reference 14) as a function of the extent of cure. Two curves were obtained: one by assuming a linear polymerization reaction and the other through crosslinking reaction. Experimental data were used to check the curves. Samples were isothermally cured for different periods of time. The extent of reaction of these samples were

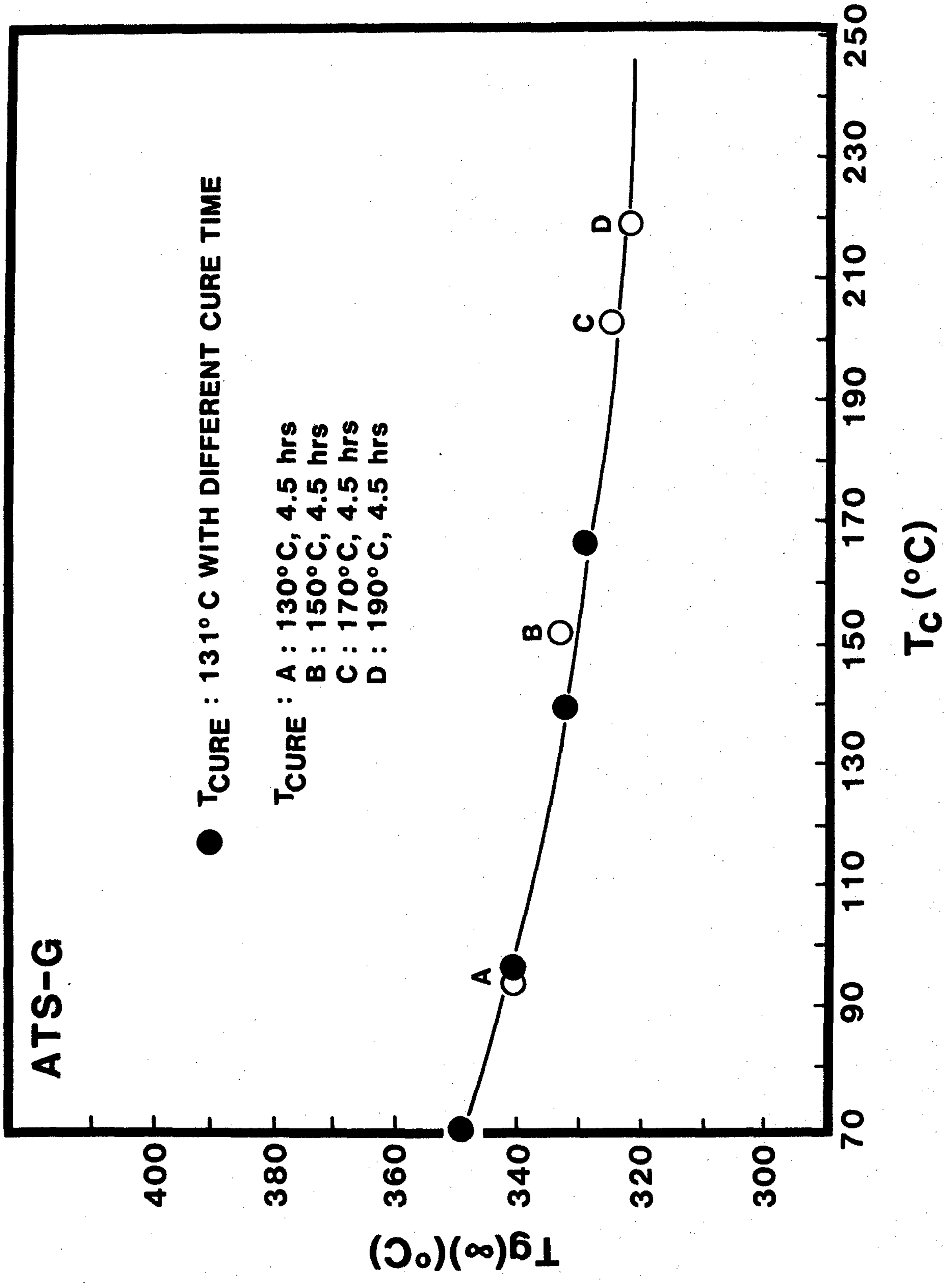

Figure 15. Plot of Tg vs Tc of ATS-G

measured by the remaining heat of reaction through DSC and Tg's were measured with TMA. All experimental data followed the uncrosslinked curve.

The data used in the calculation in Reference 14 are 40°C for the uncured sample, 344°C for the fully crosslinked system. A theoretical Tg for a linear ATS was calculated to be 267°C. The theoretical Tg of a partially cured system was calculated by the equation:

$$Tg = Tg^{\infty} \frac{r(Z-2)}{r(Z-2-\frac{2c}{r})+2Z} \qquad (1)$$

Where Z = 10 defines the local lattice coordination number in the liquid state, Tg^{∞} is the theoretical linear polymer ATS glass transition temperature, r is a parameter relating to the degree of chain extension, c is a parameter relating to the degree of crosslinking. The parameter r can assume either one of the following equations:

$$r = r_o \left(\frac{1}{1-F^{2}}\right) \qquad (2)$$

or

$$r = r_o \left(\frac{1}{1-F}\right) \qquad (3)$$

Equation 2 is used if the reaction is assumed to be purely chain extention polymerization; and Equation 3 is for the case where crosslinking occurs. The data from Rockwell generated a r_o of 3.45 and a c/r ratio of 0.5.

We have attempted to do similar calculation with the data obtained from the TICA experiments. The theoretical Tg of the linear ATS (267°C) calculated by Kaeble and Leung was used in the calculation. The TICA scans showed an uncured Tg of 30°C. The fully cured Tg of the crosslinked system was assumed to be 366°C (see discussion in previous section). Using these values and the equation given by Kaeble et al., we calculated a r_0 value of 3.21, and the c/r ratio for the crosslinked system to be 0.63. Two curves showing the theoretical Tg increase via an extension reaction and a crosslinking reaction were calculated and plotted in Figure 16.

In Figure 1, the tan δ gel peak occur at 169°C. From the 2°C/min DSC data, there should be a 19% reaction at this temperature. From previous discussion, the system at this gel peak should hmve a Tg of 70°C. This point is plotted in Figure 16. Obviously the point falls on the crosslinking curve, disagreeing with the Rockwell observation. The disagreement may be due to the different ways the glass transition temperature and extent of reaction were measured.

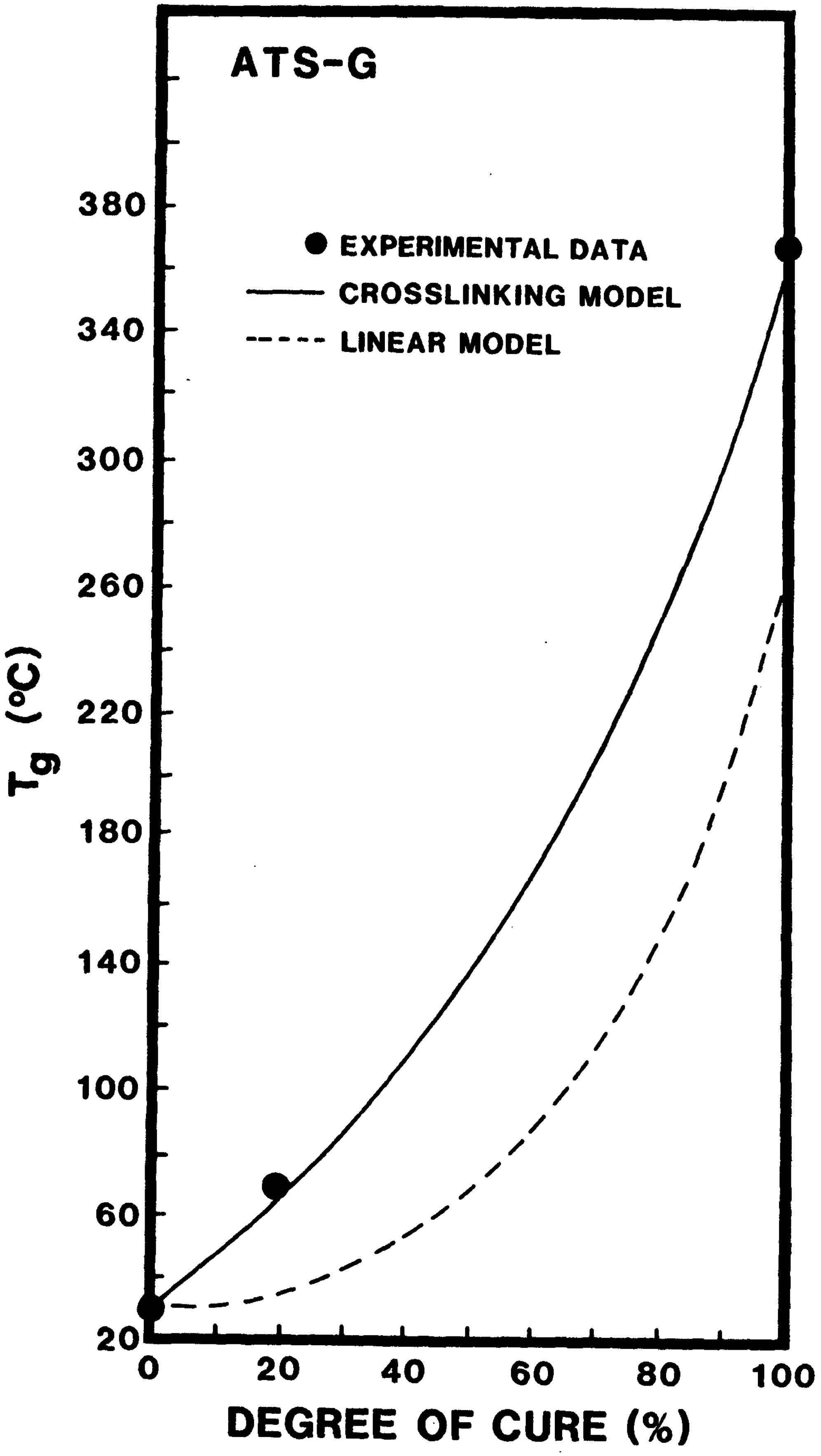

Figure 16. Theoretical Tg Increase Cure of ATS-G as a function of extent of cure

CONCLUSIONS

The air/nitrogen cure results are consistent with that observed with the BADABBA data. But because of the lower Tg before cure as well as the lower Tg after cure of ATS-G, the air cure effects are amplified so additional information about curing effects was gained from the study. The findings are summarized as followed:

1. The ATS-G data showed clearly that the kinetic rate in air cure is slower than nitrogen cure.
2. The air/nitrogen cure effects on the volatile coming off the cloth at the 250° - 300°C range are similar between BADABBA and ATS-G.
3. The ATS-G is thermally less stable than the BADABBA system, and high temperature degradation was observed.
4. High temperature oxidative crosslinking occurs like BADABBA and its effect predominates that from thermal degradation.
5. Air diffusion rate into the sample during cure is an important factor controlling the total air cure effect.
6. The reaction rate of high temperature additional cure is shown to vary with cure temperature and cure time.
7. The final Tg of ATS-G was determined to be 366°C.
8. A theoretical curve of Tg increase as a function of extent of cure was calculated based on an equation developed by D. Kaeble. Comparison of a gel point datum with the theoretical value indicates that crosslinking occurs early in the reaction.

The findings from this report will be used as a framework to explain tensile and fracture properties of ATS-G cured under air and nitrogen environments. The mechanical measurement results will be presented in a later technical report.

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