

AFML-TR-77-43

ADA 044532

OFFICIAL FILE COPY

THE EFFECT OF AGING ON THE GLASS TRANSITION TEMPERATURE OF SOME POLYMERS

Polymer Branch
Nonmetallic Materials Division

June 1977

TECHNICAL REPORT AFML-TR-77-43

Final Report for Period November 1974 - November 1975

Approved for public release; distribution unlimited.

Best Available Copy

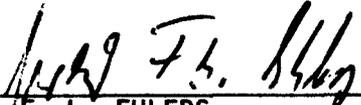
AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

2004 0301 053

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (ASD/OIP) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be releasable to the general public, including foreign nations.



G. F. L. EHLERS
Project Engineer

FOR THE COMMANDER



R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. G. F. L. Ehlers (AFML/MBP) as Project Scientist.

This report covers work conducted from November 1974 to November 1975 by G. F. L. Ehlers and K. R. Fisch. It was submitted for publication by the authors in January 1977.

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	DISCUSSION	2
III	CONCLUSIONS	7
REFERENCES		9

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	DTA Signals ($\Delta T=20^{\circ}\text{C}/\text{min}$) of PPO I after Aging in the Dupont DTA Cell in Air	10
2	DSC Signals ($\Delta T=20^{\circ}\text{C}/\text{min}$) of PPO I after Aging in the Perkin-Elmer DSC-1 in Nitrogen	11
3	DSC Signals ($\Delta T=20^{\circ}\text{C}/\text{min}$) of PPO I after Aging in the Perkin-Elmer DSC-1 in Air	12
4	Aluminum Block for the Thermal Aging of Polymer Samples	13
5	DSC Signals ($\Delta T=20^{\circ}\text{C}/\text{min}$) of P_3O after Aging in Air	14
6	Glass Transition Temperatures of WRD-412 after Aging in Nitrogen	15
7	Glass Transition Temperatures of WRD-412 after Aging at 425°C in Nitrogen and in Air	16
8	Glass Transition Temperatures of WRD-401 after Aging in Nitrogen	17
9	Glass Transition Temperatures of WRD-401 after Aging in Air	18

LIST OF TABLES

TABLE		PAGE
1	Glass Transition Temperatures of PPO I after Aging in Nitrogen	19
2	Glass Transition Temperature of PPO I after Aging in Air	20
3	Glass Transition Temperatures of PPO II after Aging in Air	21
4	Glass Transition Temperatures of P_3O after Aging in Nitrogen	22
5	Glass Transition Temperatures of P_3O after Aging in Air	23
6	Glass Transition Temperatures of WRD-412 after Aging in Nitrogen	24
7	Glass Transition Temperatures of WRD-412 after Aging in Air	24
8	Glass Transition Temperatures of WRD-401 after Aging in Nitrogen	25
9	Glass Transition Temperatures of WRD-401 after Aging in Air	25

SUMMARY

Three polyphenylene oxides and two polyphenylquinoxalines were subjected to aging in nitrogen and in air, at temperatures below and above their glass transition temperatures, and the change of Tg was determined by DSC. Tg increases of up to 70°C were observed. Formation of a second Tg, and widening of the Tg interval in one instance, can be connected to the formation of new polymer species during the initial decomposition, and to the formation of crosslinked systems. The effect of aging in air was, as expected, more rigorous than aging in nitrogen.

SECTION I

INTRODUCTION

The exposure of polymers to high temperatures, especially in the presence of oxygen, results in fragmentation and/or in the formation of crosslinked networks. Fragmentation of the "unzipping" type, as observed for a number of vinyl polymers, leads to small, volatile fragments, while the molecular weight and the structure of the residual polymer remains essentially unchanged. Consequently, no change in the glass transition temperature is expected to occur. However, random chain scission may produce large fragments which may, at least temporarily, stay with the polymer and cause plasticization. This would cause the glass transition temperature to decrease. Crosslinking, on the other hand, is known (References 1, 2) to increase the glass transition temperature, a fact which is being utilized during the curing of polymers. It is during crosslinking that the most significant changes of the glass transition temperature can be expected.

Very little work has been done to systematically explore the effect of aging on the glass transition temperature. One reason was the lack of equipment sensitive enough to detect the relatively weak Tg signals of crosslinked polymer systems. Only with the development of highly sensitive differential scanning calorimeters, and especially torsion braid analyzers, torsion pendulums and viscoelastometers, these studies became feasible. Augl and coworkers (References 3-5) subjected polyquinoxalines, polyquinoxaline amides, and polyquinoxaline imides to temperatures above their glass transition temperatures over a period of up to 33 hours in inert atmosphere and determined the Tg after aging by torsion braid analysis. Increases of up to 90°C have been observed.

The limited information on aging-Tg relationships of polymers suggested own studies with several polymers in inert atmosphere and in air, using the differential scanning calorimeter for the determination of the glass transition temperature.

SECTION II

DISCUSSION

To study the effect of aging on the glass transition temperature, we initially selected polyphenylene oxides since we had observed that oxygen pronouncedly affects these polymers; therefore, the influence of oxidative crosslinking on T_g should be readily visible. For example, we noticed that poly-m-phenylene oxide became partially insoluble during drying at 110°C in air, and that PPO showed a distinct weight gain above 200°C during thermogravimetric analysis in air; furthermore, oxygen absorption of PPO has been observed with specially designed equipment (Reference 6).

1. Poly-2,6-dimethyl-1,4-phenylene oxide (PPO I)

The first polymer selected by us was a PPO in the form of a white powder, received by the General Electric Company in 1965 and named "PPO I" by us in the following studies. Initially, we aged polymer samples in the Pyrex sample tubes (3mm dia.) of the Dupont 900 Differential Thermal Analyzer in an air atmosphere. At the end of the aging time, the sample was cooled to room temperature without removing it from the DTA cell, and then reheated at a heating rate of $\Delta T=20^\circ\text{C}/\text{min}$, while recording the DTA trace. A composite plot of typical DTA curves can be seen in Figure 1. These results are rather unsatisfactory; the reason for this may be the loss of contact between thermocouple and sample during aging. Nevertheless, it can be seen that the T_g (extrapolated onset of baseline shift) moves from 193°C for the original polymer to 209°C for the sample aged 16 hours at 150°C and to 223°C for the sample aged 16 hours at 200°C in air. Also, it can be noted from the plots that the onset of the oxidation exotherm shifts to increasingly lower temperatures with increased aging times (from about 200°C for the unaged sample to 170°C for the sample aged 16 hours at 250°C in air). This suggests that structures with increased susceptibility to oxygen form with increased aging times.

Better results were obtained when approximately 10 mg samples were aged in aluminum sample cups in the Perkin-Elmer DSC-1 and then analyzed in the Dupont 990 Differential Scanning Calorimeter (DSC). A typical

composite plot of aging results in nitrogen which can be seen in Figure 2. The numerical Tg values of series of aging runs in nitrogen are listed in Table 1. Figure 2 shows that a shoulder forms on the Tg baseline shift, while the original baseline shift disappears. Finally, a transition is no longer identifiable. The two transitions increase slightly with aging (Table 1). In air, the same changes occur as in nitrogen, only much faster, so that the presence of two transitions could be detected only in two cases. Strong baseline drift due to oxidation occurs above Tg, leading to an oxidation exotherm around 340°C. A representative, composite plot is shown in Figure 3, and Table 2 summarizes the results of the aging studies in air.

The evolution of a new Tg at a lower temperature may be connected to the formation of a methyl-free polyphenylene oxide structure. Methane is the first major volatile product to form during the thermal decomposition of PPO in inert atmosphere (Reference 7). In air, oxygen absorption, connected to the oxidation of the methyl groups, has been observed below 200°C (Reference 6). With increased aging time/temperature, crosslinking occurs, which raises the Tg's of the methyl containing and methyl-free polymer species.

Schoff and Gillham (Reference 8) subjected samples of PPO I to isothermal aging in air at temperatures between 201° and 267.5°C in the Torsion Braid Analyzer and determined rigidity and mechanical damping index at intervals. A log-log plot of rigidity versus aging time shows a step increase of the rigidity after a certain aging time, while a log-log plot of the mechanical damping index versus time reaches a maximum. The authors postulate that the inflection point of the rigidity curve and the peak of the damping index signify the vitrification point, or the aging time needed to raise the Tg of the material to the temperature of the experiment. This would mean that the polymer reached a Tg of 230°C after 88 minutes at 230°C, a Tg of 250°C after 41 minutes at 250°C, and a Tg of 260°C after 24 minutes at 260°C. These results do not agree with our own data in Table 2. However, it can be expected that aging of the polymer on the braid, with its large surface area, is

much more rigorous than that of a compacted powder in the DSC sample holder. Furthermore, differential scanning calorimetry probably was not sensitive enough to detect Tg's beyond the values listed in Table 2.

2. Poly-2,6-dimethyl-1,4-phenylene oxide (PPO II)

A more recent sample of PPO, in the form of pellets, was obtained from the General Electric Company under the code No. GE 534-80 in 1973. The sample was reprecipitated from chloroform-methanol and was used in a series of aging studies in air under the code name "PPO II". For these, and all future aging studies, 50 to 100 mg of polymers was aged under controlled temperature and atmospheric conditions in an apparatus as shown in Figure 4, with the temperature control provided by an F&M Scientific 240 Temperature Programmer. Sufficient amounts of the aged polymer were then packed into the DSC aluminum sample holders. This procedure was more satisfactory than aging in the sample holders, since weight loss and shrinking of the polymer during aging often resulted in insufficient quantity and contact for good DSC signals.

The aging of PPO II was performed in air at temperatures of 175°, 200°, 230°, 250°, and 260°C for periods up to 120 hours. Only the 260°C runs (Table 3) showed a Tg increase with aging. At the lower aging temperatures, the obtained Tg values, as determined from the extrapolated onsets of the glass transition intervals, scattered and for all practical purposes, remained unchanged. However, the extrapolated end of the interval increased with increased aging time, thereby widening the interval. Ueberreiter and Kanig (Reference 2) explain the widening of the transition region (in a copolymer system styrene-divinyl-benzene) with the presence of chain units of varying mesh width, while Karasz (Reference 9) related the increase of width of the glass transition interval of copolymers to the extent of phase heterogeneity. Both mechanisms may apply after aging of PPO: The formation of crosslinked polymers of varying mesh width, and the formation of less compatible structures without methyl, or with carboxy groups.

3. Poly-2,6-diphenyl-1,4-phenylene oxide (P_3O)

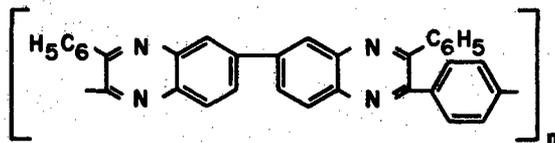
This polymer sample was obtained from the General Electric Company in 1969, in the form of a white, fluffy powder. The polymer was partially crystalline and had a glass transition temperature, a crystallization temperature, and a crystalline melting point.

Early aging trials in the DTA cell (as described for PPO I) had shown that a significant change of T_g with aging in air did not occur below 235°C. Aging experiments in nitrogen and in air were then carried out in the equipment shown in Figure 4. In nitrogen, aging first increases glass transition temperatures slightly. With increased aging, they cannot be detected any more by DSC (Table 4). At the same time, the crystallization temperature decreases and the crystallization exotherm becomes smaller with increased aging temperature. Once the aging temperature exceeds the crystallization temperature, no crystallization exotherm can be observed.

The results are essentially the same after aging in air. Here, the DSC runs were carried to sufficiently high temperatures to detect the melting transition, and in Table 5 it can be seen that the T_g increases slightly, and T_{cryst} and T_m decrease with increased aging temperature and time. At the same time, the crystallization exotherm becomes smaller, and, as a result of crosslinking, the melting endotherm also becomes smaller (Figure 5).

4. Poly[2,2'-(1,4-phenylene)-6,6'-bis(3-phenylquinoxaline)] (WRD-412)

This polymer,



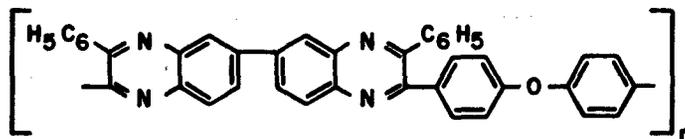
was obtained from the Whittaker Corporation with the code WRD-412. The same polymer has been studied by Augl and Booth (Reference 3) in nitrogen.

One main objective in investigating this polymer was to see if we could duplicate the results of Augl and Booth. These authors used the highly sensitive torsion braid analysis for their work, while our studies were limited to the less sensitive differential scanning calorimetry. Since this polymer has a highly rigid structure, Tg signals were expected to be rather weak after thermal or oxidative crosslinking through aging. However, it turned out that aging in the equipment shown in Figure 4 and using relatively large amounts of the aged polymer in pellet form for the DSC runs gave satisfactory results which compare well with the results obtained by the above authors (Table 6 and Figure 6). Only limited data, however, were obtained after aging in air (Table 7). It seems that the detection limit is reached when the Tg exceeds 400°C, while the before mentioned authors were able to detect Tg's as high as 457°C by TBA.

Figure 7 represents a comparison of the glass transition temperatures after aging in nitrogen and in air at 425°C. The results are indicative of the accelerating effect of oxygen on aging and crosslinking.

5. Poly[2,2'-(4,4'-biphenylene oxide)-6,6'-bis(3-phenylquinoxaline)]
(WRD-401)

This polymer,



received from Whittaker (WRD-401), was expected to give better DSC signals after aging than WRD-412, as a result of its more flexible structure. This proved to be the case. The data obtained from aging in nitrogen and in air are tabulated in Tables 8 and 9 and plotted in Figures 8 and 9. One can see that the Tg of WRD-401 is lower than that of WRD-412, but that aging (in inert atmosphere) has a stronger effect on the former than on the latter. On the other hand, the difference between aging in oxidative and in inert atmosphere is less pronounced for WRD-401 than it is for WRD-412.

SECTION III

CONCLUSIONS

Several polymers were subjected to temperatures slightly below to above their glass transition temperatures for periods up to 168 hours in nitrogen and in air and the change of the Tg with aging was determined by differential scanning calorimetry.

1. Poly-2,6-dimethyl-1,4-phenylene oxide (PPO)

Two different samples of PPO were investigated. The first, "PPO I", was subjected to aging in nitrogen and in air between 175° and 260°C. Behavior was essentially the same in both atmospheres, but air aging proved to be more rigorous. The Tg (223°C) increased by 5 to 10 degrees during aging before it could not be detected. At the same time, a second Tg formed at a lower temperature (in nitrogen 203°C; in air 213°C) which also increases slightly with aging and can still be detected while the original Tg becomes unrecognizable. It is believed that the second Tg is the result of the formation of a new polymer structure, possibly a methyl-free polyphenylene oxide as the initial decomposition product of PPO.

"PPO II" behaved somewhat differently. The original Tg at 169°C increased only at the highest aging temperature (260°C) in air (by 6°C). However, the transition interval widened from 18°C to maximal 41°C. This widening may be the result of formation of different polymer structures and/or crosslinked systems of different mesh width.

2. Poly-2,6-diphenyl-1,4-phenylene oxide (P₃O)

This polymer is partially crystalline and has a glass transition temperature, a crystallization temperature, and a crystalline melting point. With increased aging time and temperature, the Tg (224°C) increased only 7 to 12 degrees before it became undetectable. The crystallization temperature decreases up to 5°C, while the crystallization exotherm decreases in size with increased aging temperature and finally was no longer visible. Once the aging temperature exceeded

the crystallization temperature, no crystallization exotherm could be observed. The melting temperature also decreases distinctly at aging temperatures above the T_g , and the endotherm decreases in intensity. The reason for the decreasing signal strength of the crystallization exotherm and the melting endotherm is increased crosslinking during aging.

3. Poly[2,2'-(1,4-phenylene)-6,6'-bis(3-phenylquinoxaline)] (WRD-412)

The T_g of 364°C increased to 404°C during aging in nitrogen, and to 396°C during aging in air. Beyond these temperatures, a glass transition could not be detected. As expected, the increase is more pronounced in air than in nitrogen. Aging at 465°C in nitrogen causes about the same T_g increase as aging at 425°C in air. The increase is rapid during the first 100 to 300 minutes; after that the increase remains fairly constant over the time.

4. Poly[2,2'-(4,4'-biphenylene oxide)-6,6'-bis(3-phenylquinoxaline)] (WRD-401)

This polymer is more sensitive to aging than WRD-412 as the result of the ether linkage, and lower temperatures are needed to effect the same changes in T_g as in WRD-412. After aging at 440°C for 120 minutes, the T_g increases from 290° to 323°C in nitrogen, to 358°C in air.

REFERENCES

1. T. G. Fox and S. A. Loshaek, J. Polymer Sci. 15, 371 (1955).
2. K. Ueberreiter and G. Kanig, J. Chem. Phys. 18, 399 (1950).
3. A. M. Augl and H. J. Booth, J. Polymer Sci. Polym. Chem. Ed. 11, 2179 (1973).
4. A. M. Augl and H. J. Booth, J. Polymer Sci. Polym. Chem. Ed. 11, 2195 (1973).
5. A. M. Augl, J. V. Duffy, and S. E. Wentworth, J. Polymer Sci. Polym. Chem. Ed. 12, 1023 (1974).
6. G. F. L. Ehlers and K. R. Fisch, unpublished results.
7. G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, J. Polymer Sci. A-1, 7, 2931 (1969).
8. C. K. Schoff and J. K. Gillham, AFML-TR-73-230, Part II (1974).
9. F. E. Karasz, private communication.

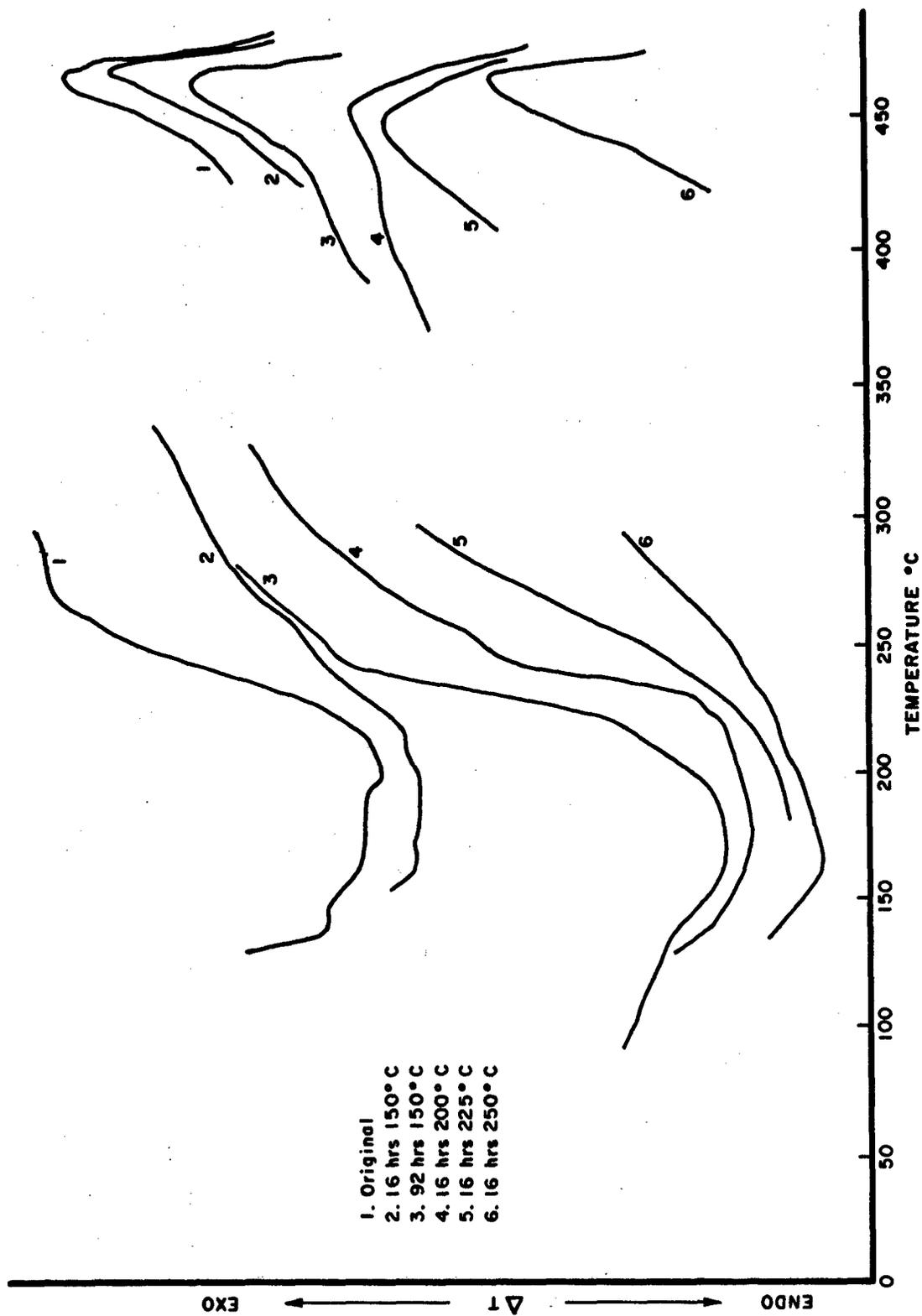
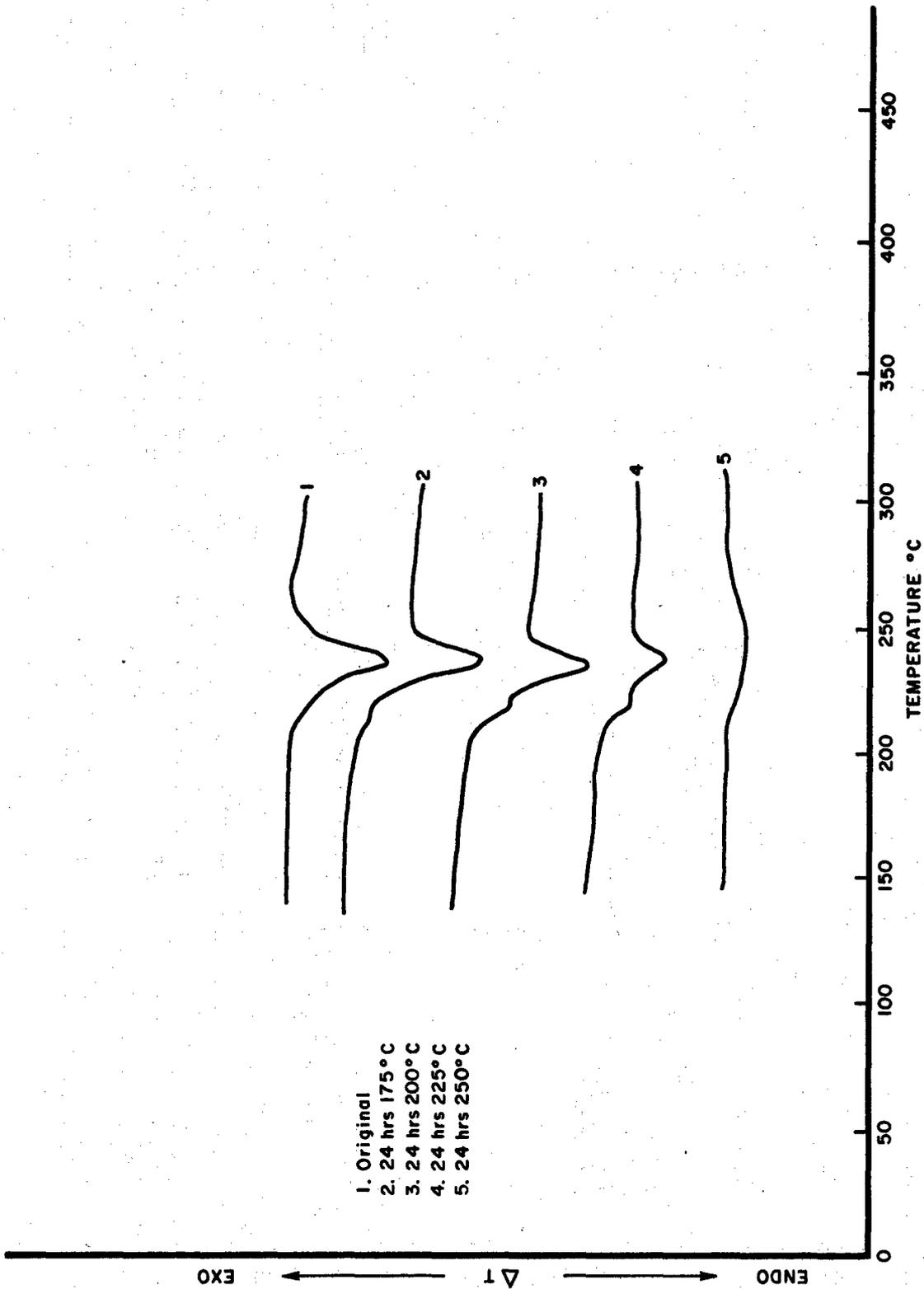


Figure 1. DTA Signals ($\Delta T=20^\circ\text{C}/\text{min}$) of PPO I after Aging in the Dupont DTA Cell in Air



- 1. Original
- 2. 24 hrs 175°C
- 3. 24 hrs 200°C
- 4. 24 hrs 225°C
- 5. 24 hrs 250°C

Figure 2. DSC Signals ($\Delta T=20^\circ\text{C}/\text{min}$) of PPO I after Aging in the Perkin-Elmer DSC-1 in Nitrogen

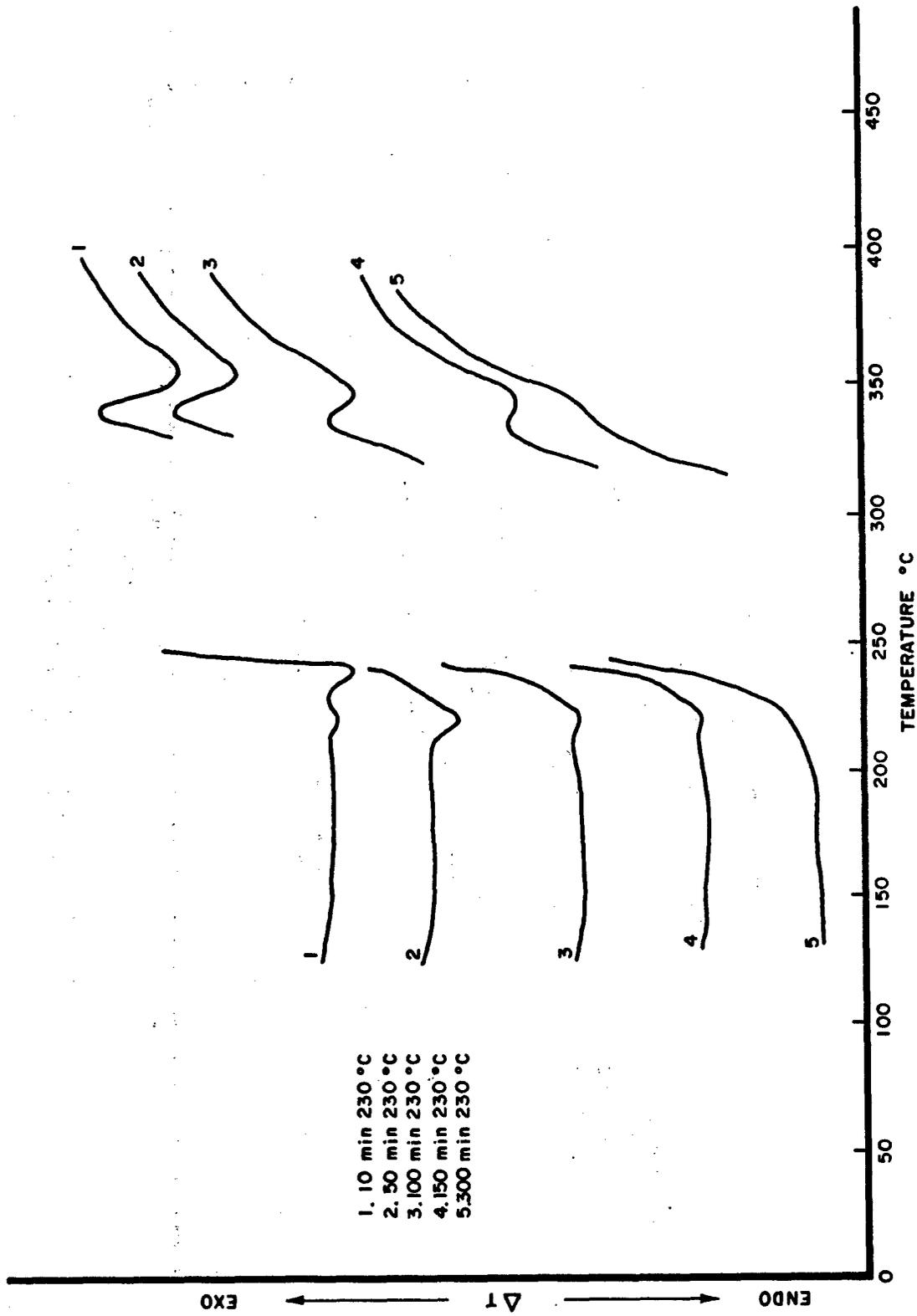


Figure 3. DSC Signals ($\Delta T=20^\circ\text{C}/\text{min}$) of PP0 I after Aging in the Perkin-Elmer DSC-1 in Air

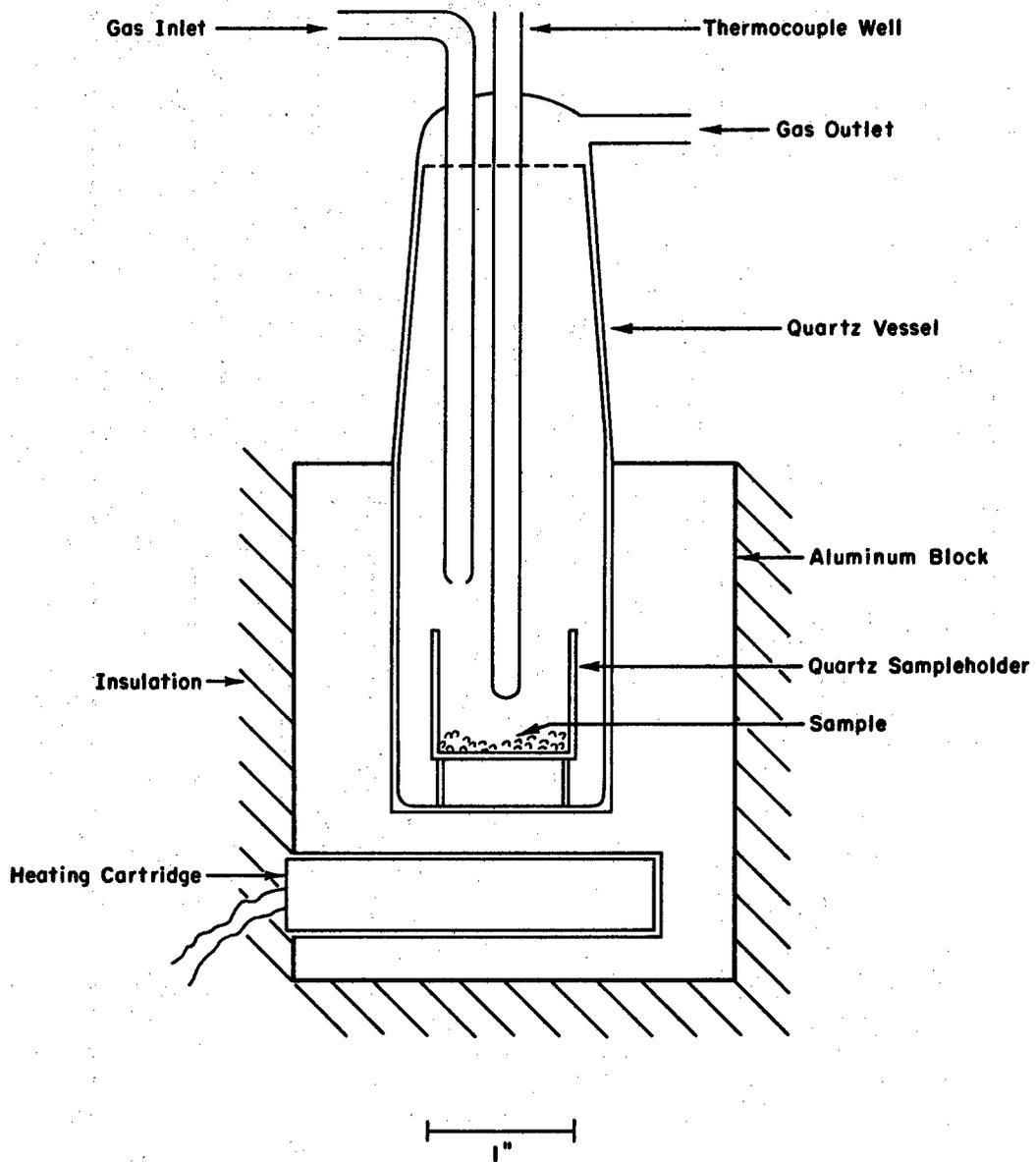


Figure 4. Aluminum Block for the Thermal Aging of Polymer Samples

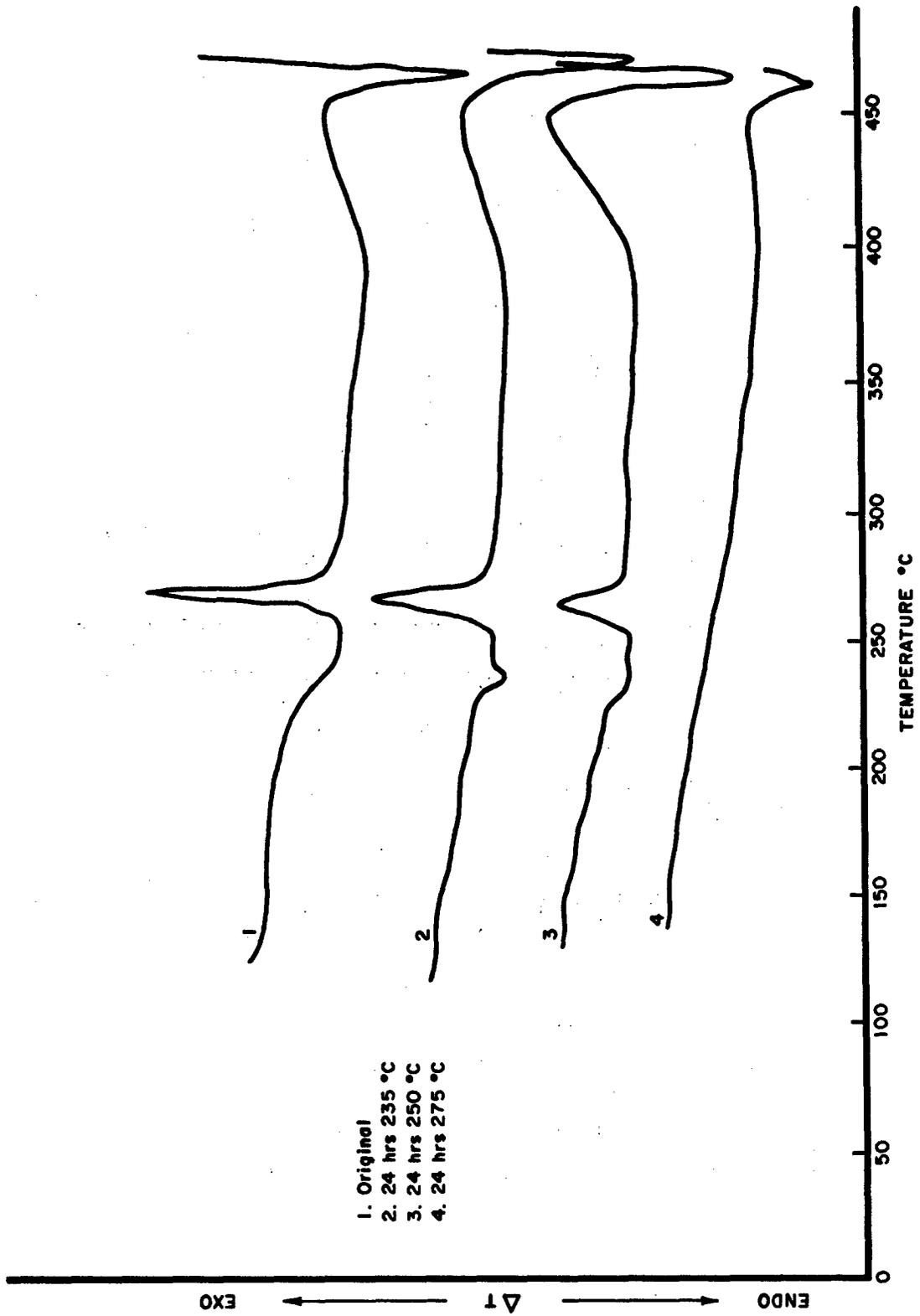


Figure 5. DSC Signals ($\Delta T=20^\circ\text{C}/\text{min}$) of P₃₀ after Aging in Air

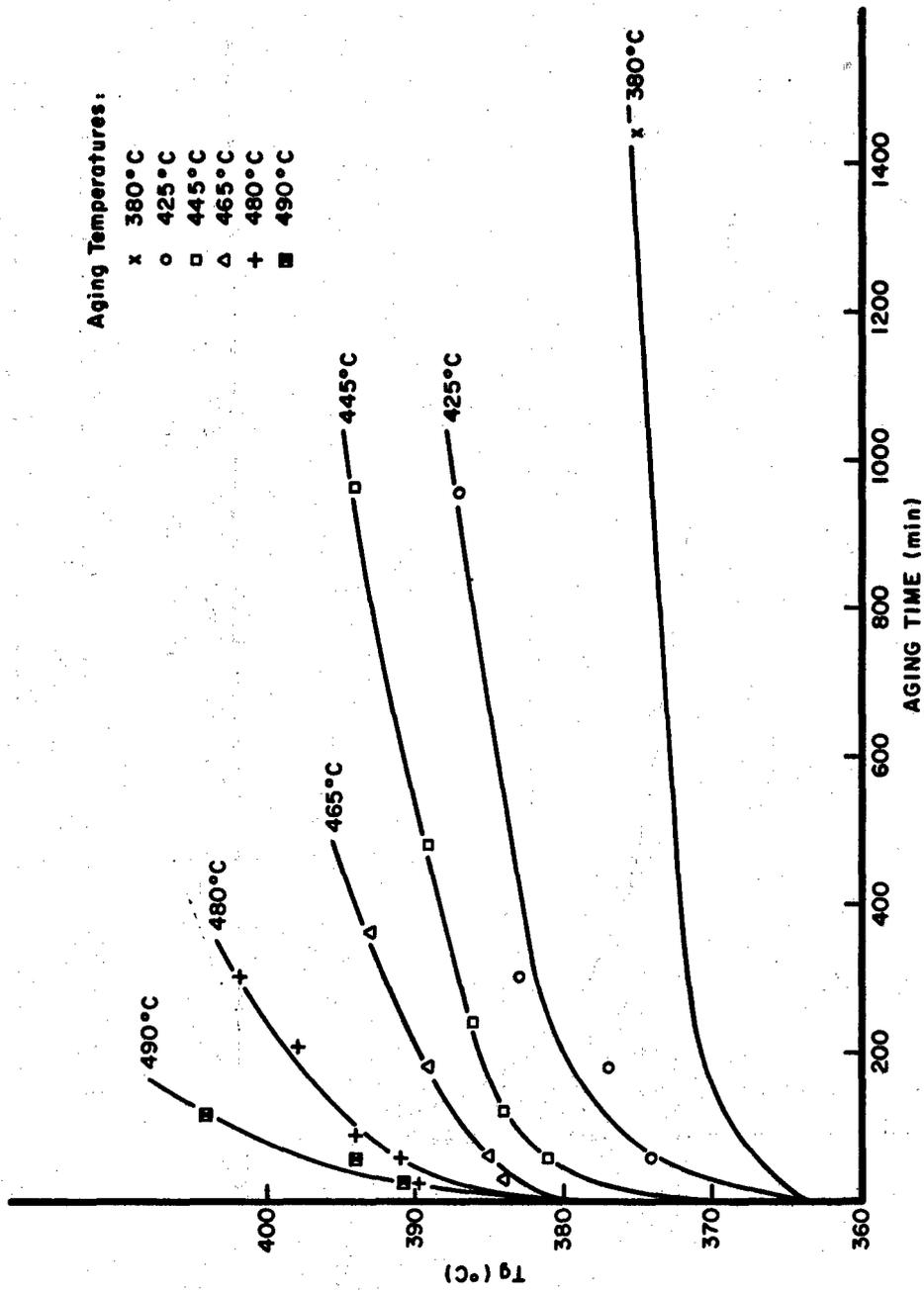


Figure 6. Glass Transition Temperatures of MRD-412 after Aging in Nitrogen

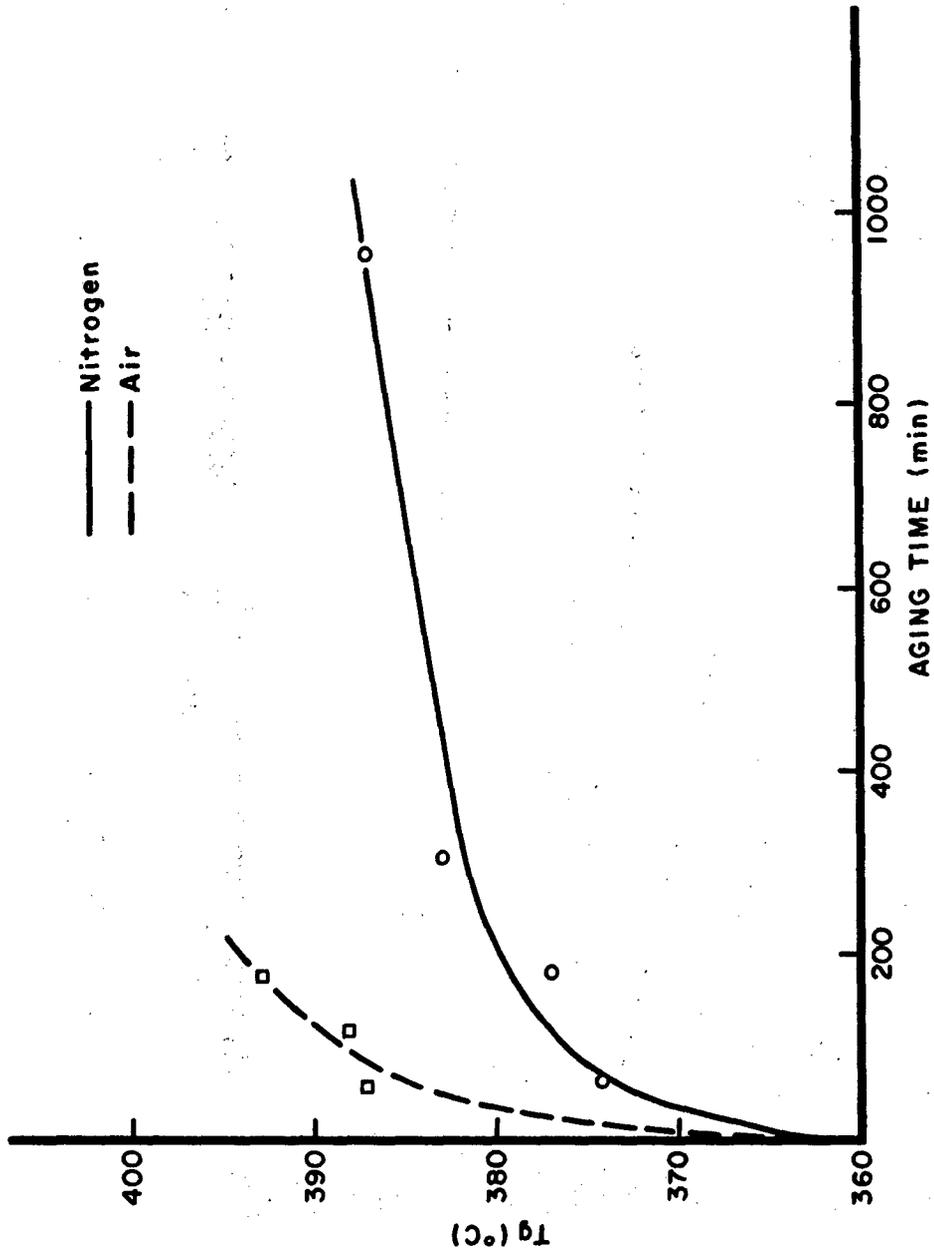


Figure 7. Glass Transition Temperatures of WRD-412 after Aging at 425°C in Nitrogen and in Air

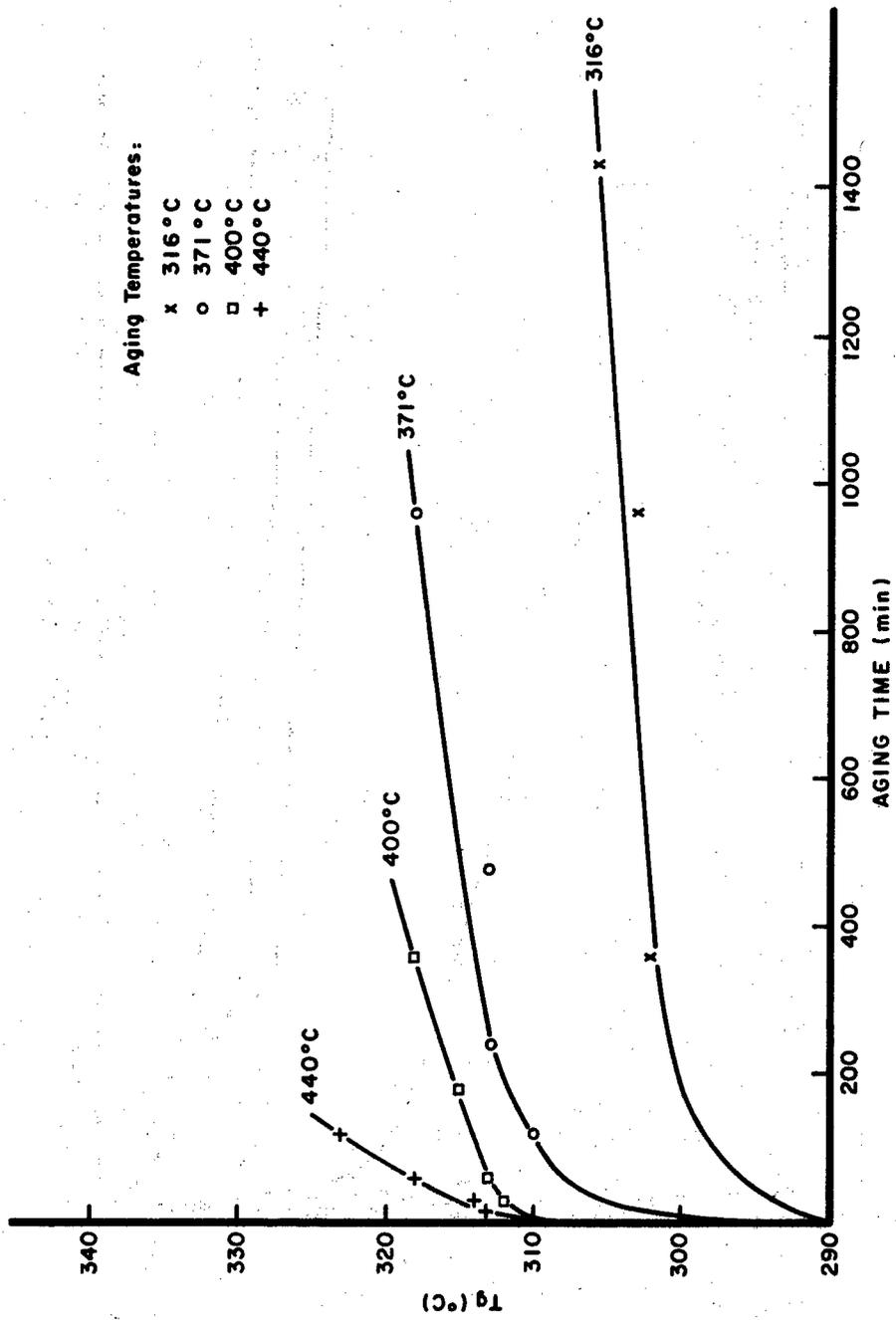


Figure 8. Glass Transition Temperatures of WRD-401 after Aging in Nitrogen

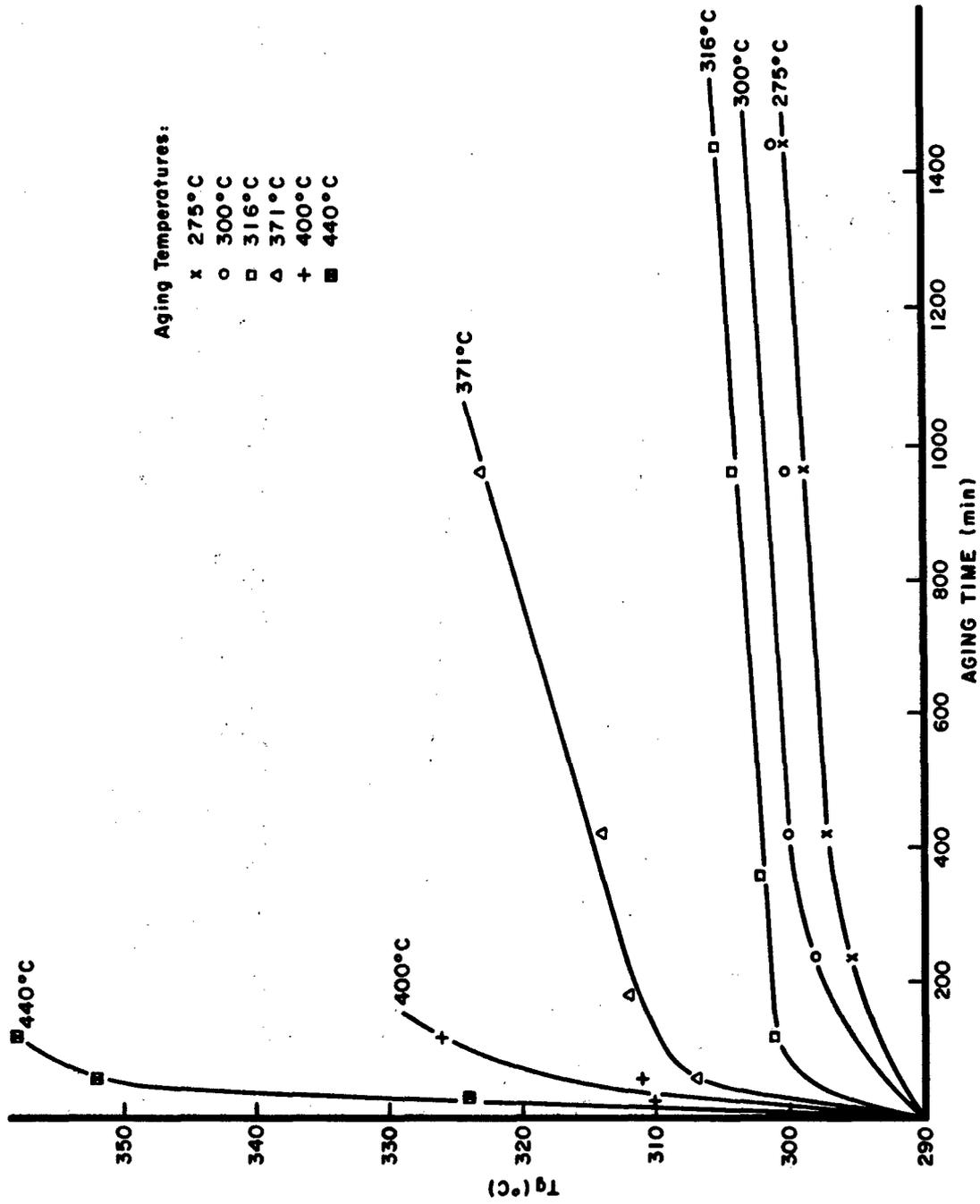


Figure 9. Glass Transition Temperatures of MRD-401 after Aging in Air

TABLE 1
GLASS TRANSITION TEMPERATURES OF PPO I AFTER AGING
IN NITROGEN

Aging Time (hrs)	Aging Temperature (°C)	T _g °C	
---	---		223
24	175	(203)	223
24	200	(209)	226
24	225	212	228
24	250	~ 212	

---	---		223
24	200	(208)	226
73	200	208	223
168	200	218	227

---	---		223
1	250	208	(228)
5	250	209	
24	250	~ 213	

(in parenthesis: transition barely detectable).

TABLE 2

GLASS TRANSITION TEMPERATURES OF PPO I AFTER AGING IN AIR

Aging Time		Aging Temperature (°C)	T _g (°C)	
(hrs)	(min)			
---	---	---		223
24		175		223
72		175		229
120		175		~ 233

---	---	---		223
24		200	(212)	233
72		200	---	---
120		200	---	---

	---	---		223
	10	230	214	232
	50	230	213	---
	100	230	214	---
	150	230	215	---
	300	230	---	---

	---	---		223
	10	250	213	
	30	250	215	
	50	250	215	
	80	250	215	
	200	250	---	

	---	---		223
	5	260	213	
	10	260	213	
	30	260	214	
	60	260	215	

TABLE 3

GLASS TRANSITION TEMPERATURES OF PPO II AFTER AGING IN AIR

Aging Time		Aging Temperature (°C)	Glass Transition Interval (°C)	
(hrs)	(min)		Onset (T _g)	End
24		175	169	187
72		175	168	185
120		175	170	190

24		200	168	201
72		200	169	206
120		200	167	206

	10	230	168	200
	50	230	165	200
	100	230	168	202
	150	230	168	204
	300	230	169	210

	10	250	171	202
	30	250	167	202
	50	250	165	207
	80	250	167	206
	200	250	164	216

	5	260	168	200
	10	260	169	201
	30	260	170	203
	60	260	170	206
	100	260	174	215

TABLE 4
GLASS TRANSITION TEMPERATURES OF P_3O AFTER AGING
IN NITROGEN

Aging Time (hrs)	Aging Temperature ($^{\circ}C$)	Tg ($^{\circ}C$)	Tcryst ($^{\circ}C$)
---	---	224	270
24	235	225	266
64	235	226	266
120	235	226	265

---	---	223	270
24	250	225	265
70	250	226	265

---	---	223	270
24	235	225	266
24	250	225	265
24	275	?	---
24	300	~ 235	---

TABLE 5
GLASS TRANSITION TEMPERATURES OF P_3O AFTER AGING IN AIR

Aging Time		Aging Temperature	Tg	Tcryst	Tm
(hrs)	(min)	(°C)	(°C)	(°C)	(°C)
---	---	---	224	270	465
24		235	229	267	470
24		250	224	265	463
24		275	---	---	461

---		---	227	270	465
24		235	229	267	470
48		235	231	266	469
72		235	234	266	467

---	---	---	227	270	465
	100	350	---	---	458
	200	350	---	---	455
	400	350	---	---	451
	500	350	---	---	448

	---	---	227	270	465
	5	440	---	---	467
	10	440	---	---	465
	20	440	---	---	462

TABLE 6

GLASS TRANSITION TEMPERATURES OF WRD-412 AFTER AGING

Aging Temperature (°C)	IN NITROGEN	Tg (°C)
	[in brackets: aging time (min.)]	
340	364 [0]; 364 [16]	
350	364 [122]	
380	375 [1440]	
425	374 [60]; 377 [180]; 383 [300]; 387 [960]	
445	381 [60]; 384 [120]; 386 [240]; 389 [480]; 394 [960]	
465	384 [30]; 385 [60]; 389 [180]; 393 [360]	
480	390 [30]; 391 [60]; 394 [90]; 398 [210]; 402 [300]	
490	390 [30]; 394 [60]; 404 [120]; ? [240]	

TABLE 7

GLASS TRANSITION TEMPERATURES OF WRD-412 AFTER AGING IN AIR

Aging Temperature (°C)	Tg (°C)	
	[in brackets: aging time (min.)]	
425	364 [0]; 387 [60]; 388 [120]; 393 [180]	
445	399 [60]; 396 [120]; ? [240]	
465	? [30]	
480	? [30]	

TABLE 8
GLASS TRANSITION TEMPERATURES OF WRD-401 AFTER AGING
IN NITROGEN

Aging Temperature (°C)	Tg (°C)
	[in brackets: aging time (min.)]
316	290 [0]; 302 [360]; 303 [960]; 306 [1440]
371	310 [120]; 313 [240]; 313 [480]; 318 [960]
400	312 [30]; 313 [60]; 315 [180]; 318 [360]
440	313 [15]; 314 [30]; 318 [60]; 323 [120]

TABLE 9
GLASS TRANSITION TEMPERATURES OF WRD-401 AFTER AGING IN AIR

Aging Temperature (°C)	Tg (°C)
	[in brackets: aging time (min.)]
275	290 [0]; 295 [240]; 297 [420]; 299 [960]; 300 [1440]
300	298 [240]; 300 [420]; 300 [960]; 301 [1440]
316	301 [120]; 302 [360]; 304 [960]; 305 [1440]
371	307 [60]; 312 [180]; 314 [420]; 323 [960]
400	310 [30]; 311 [60]; 326 [120]
440	324 [30]; 352 [60]; 358 [120]