

3 THERMAL DEGRADATION STUDIES OF SEVERAL PYRRONE FILMS* 6

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SYNOPSIS

The thermal degradation of several polyimidazopyrrolone (Pyrrone) films was studied in air and in vacuum over the range of 100° C to 1,000° C by thermogravimetric analysis (TGA), using both isothermal heating and programmed heating rates of 2°, 3°, 5°, and 7.5° C/minute. At pressures of 10⁻⁶ torr or less, maximum weight losses average 30 percent at 800° C. Rates of volatilization and activation energies were derived to provide comparison between these ladder-type polymers. Mass spectrometric analysis of the pyrolysis gases evolved under vacuum conditions showed that CO, CO₂, and H₂O were the primary volatile products and that they were formed throughout the period of weight loss. Approximate correlation between changes in weight and changes in the total pressure for the vacuum tests indicates that mass spectrometric results could provide quantitative as well as qualitative data. The importance of sample history prior to heating and of sample geometry in developing meaningful and reproducible TGA results is aptly demonstrated. The ability of these materials to absorb readily 5 to 7 percent, by weight, of water under ambient conditions and the effect of this property upon weight loss measurements are shown.

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THERMAL DEGRADATION STUDIES OF SEVERAL PYRRONE FILMS

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INTRODUCTION

The thermophysical behavior of several polyimidazopyrrolone (Pyrrone) polymers (ref. 1), was investigated (1) to relate chemical structure to thermal stability, and (2) to aid the direction of exploratory synthesis of this class of aromatic/heterocyclic materials. Combining some of the desirable chemical and physical properties of the polyimides and the polybenzimidazoles, the Pyrrones hold considerable potential for specialized aerospace and terrestrial uses.

Thermogravimetric analysis (TGA) in air and in vacuum of four films from these "step-ladder" materials suggests some preliminary indication of ways to improve their thermal stabilities. Both isothermal and dynamic heating were used to derive rates of volatilization and activation energies. The comparison of TG curves, as well as the results from other measurements such as differential thermal analysis (DTA) and residual gas analysis, were used to detail the modes of thermal degradation.

EXPERIMENTAL

Description of Materials

The polyimidazopyrrolones were prepared using two aromatic dianhydrides: pyromellitic dianhydride (PMDA) and 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride (BTDA). Two tetraamines were polymerized with each of

the two dianhydrides: 3, 3'-diaminobenzidine (DAB), and 3, 3', 4, 4'-tetraaminodiphenyl ether (TADPO). Their proposed structural repeating units are shown in table 1. Synthesis and characterization of these polymers have been reported elsewhere (ref. 2).

Films were formed by casting polymer solutions onto glass plates and by drying them to soluble films in a forced airflow oven at 125° C for 1 hour. After the films were stripped from the plates, they were postcured at 350° C in air for 2 hours. Test specimens 0.635 cm in diameter, with a nominal thickness of 0.0025 cm and initial weights of 2.05 mg ± 0.03 mg were cut from the films.

Description of Equipment and Test Procedures

The TG equipment used for vacuum exposures was an essentially all metal-glass system, with ion pumps maintaining sample environmental pressure at 10⁻⁶ torr or less at all times. The main components were (1) a Cahn RG null-type electrobalance, (2) quartz suspension fibers, (3) 3/8-inch-o.d. by 1/8-inch-high platinum sample pan, (4) chromel-alumel thermocouples within the vacuum chamber, and (5) a 2-inch-diameter by 12-inch-long furnace with adjustable tapping to guarantee a large evenly heated reaction zone. In addition to the necessary ion gages, power programmer, and recorders, an R-C circuit provided an instantaneous first derivative of the weight-loss curve, and a Vanderslice type mass spectrometer permitted partial pressure measurements. Separate electrobalance equipment similarly arranged was used for tests made in air. DTA data were obtained with a DuPont 900 DTA unit.

In each test the initial weight was determined after preconditioning the sample at 100° C for 30 minutes. Isothermal temperatures in the 400° to

460° C region required an average of 8 minutes to reach thermal equilibrium and were maintained within ±0.5° C. Nonisothermal heating rates of 2, 3, 5, and 7.5° C/min were held within ±1.5° C during the entire period of heating. The large surface-to-volume ratio of the small specimens and the large uniformly heated reaction zone were felt to justify the use of the sample pan temperature as the temperature of the material (ref. 3). Dummy runs, where a thermocouple was electron-beam welded to a pan, provided the means to correlate surrounding temperature to pan temperature.

Activation energies E were derived by employing the method of H. Anderson (ref. 4). Data from multiple isothermal tests can provide for the complete solution of the equation:

$$\log(\dot{w}/\dot{t}) = \log A + n \log(w_i - w) - E/2.3RT \quad (1)$$

where

w	weight lost during time t at temperature T (°K)
A	Arrhenius preexponential factor
n	order of decomposition
w_i	initial sample weight
R	gas constant
E	activation energy

For data from tests using constant rates of heating the left side of equation (1) becomes

$$\log \left[\left(\frac{dw}{dT} \right) \left(\frac{dT}{dt} \right) \right]$$

By varying either temperature T or rate of heating dT/dt , all unknowns in the equation can be determined. The major limitation relates to the complex manner of degradation of Pyrrone films, so that the derived value E , is really an effective value of all the individual E 's involved.

DISCUSSION

Results in Air

Isothermal TG results in air are presented in figures 1, 2, and 3. As seen in figure 1, weight-loss curves for BTDA-DAB, the most thermally stable of the four films tested, show that initially there is a rather large fraction volatilized. Since the films had been postcured at 350° C, this loss suggests thermal instability in air above 400° C, rather than further polycondensation.

In figure 2, the plateaus in the curves show that at least 40 percent of the sample was lost at a nearly constant maximum rate, which denotes optimization of test parameters.

Figure 3 presents the data from the plateau regions (48 to 53 percent of volatilization) of figure 2 as Arrhenius plots. The three temperatures involved are 440° C, 450° C, and 460° C. By using the slopes of the lines of figure 3, activation energy E values were calculated from equation (1). Numerical values of E ranged from 28 to 34 Kcal/mole and are listed individually for the four polymers in figure 3.

Results from nonisothermal heating tests are shown as thermograms in figures 4 and 5. Figure 4 shows the effect of varying the heating rate on the thermograms of the polymer, PMDA-DAB. As heating rate increases, the indicated temperature stability increases which is consistent with the fact that volatilization proceeds at a finite rate.

As was done for the isothermal data, Arrhenius plot treatment was given the data depicted in figure 4 in the vicinity of 50 percent volatilization.

The average value of E approximated 31 Kcal/mole, which agrees with the value obtained from isothermal data.

In figure 5 thermograms generated at a heating rate of 5° C/min reveal that the two polymers made from BTDA exhibit identical behavior from 100° C to 480° C, where a knee develops. The two curves separate at approximately 500° C, with the BTDA-DAB polymer exhibiting slightly greater temperature stability.

Examination of the curves in figure 5 for the two polymers made from PMDA reveals that the initial weight change experienced by the PMDA-TADPO polymer represents loss through further polycondensation, suggesting an incompletely cured sample. This conclusion was confirmed by an experiment in which another PMDA-TADPO sample was postcured at 350° C for 2 hours before its thermogram was determined. The more stringently postcured sample produced a thermogram which coincided with the curve for PMDA-DAB until commencement of rapid degradation at 460° C.

In order to eliminate the effect of adsorbed moisture, each film was preconditioned at 100° C for 30 minutes before its thermogram was determined. The importance of this step is shown in figure 6. The data of figure 6 were obtained by alternately heating a PMDA-DAB film to 100° C and then cooling it to 25° C, with a total period of 1 hour. As shown in table 2, the ratio of the percent of water lost on heating to 100° C to the theoretical percent of water of conversion is a constant with a value of 0.342.

DTA thermograms were determined in air on a BTDA-DAB polymer to ascertain whether thermal effects such as phase changes were occurring which would not appear in TGA thermograms. As shown in figure 7, the DTA results did not

reveal any such changes, but rather substantiated the TG data. In figure 8 the maximum exotherm generated during the 5° C/min run equated to a differential sample temperature increase of 1.2° C. Since surrounding temperatures rather than sample temperatures were monitored, the TG thermograms were corrected accordingly.

Results in Vacuum

Figure 8 shows that, of the four Pyrrones which were heated in vacuum at 5° C/min, the BTDA-DAB film had the greatest thermal stability. In air, the two BTDA-derived polymers were the most stable, while under vacuum the two most stable polymers were made from the DAB amine. The early weight loss experienced by the PMDA-TADPO again reflects the use of a sample cured below 350° C. Incorporating data from a cured PMDA-TADPO test, all runs begin to level out at 800° C, and at this point, weight losses range from 28 percent to 38 percent of initial weight. At a 15-percent weight change, the activation energies vary between 47 and 50 Kcal/mole.

Since several weight loss steps or semisteps occur in each thermogram, an attempt was made to relate these changes to the mode of structural decomposition through the simultaneous use of TGA and qualitative residual gas analysis (ref. 5). Figure 9 combines the weight loss curve and the prominent mass peaks observed upon heating BTDA-DAB in vacuum at 2° C/min. The slow rate of weight loss from 100° C to 380° C was accounted for by the evolution of water only (m/e values of 17 and 18 predominate). Both balance and spectrometer indicated a plateau from 380° C to 420° C. At 420° C a knee in the thermogram commences, leading into a steep rate of change at 520° C, which reaches a maximum rate at 550° C, and sharply declines at 620° C. Concurrently, carbon monoxide (m/e = 28) and carbon dioxide (m/e = 44) begin "

to evolve in great quantities at 420° C, peaking at 550° C and disappearing at 620° C. At about 500° C, the mass 40 peak, perhaps the NCN grouping, emerges. With increasing temperature, this NCN species increases together with masses 26 and 27 (CN and HCN). Beyond 650° C, mass 27 predominates. A trace of ammonia (mass 17) is evident during the main period of decomposition.

These results demonstrate: (1) an early period of dehydration and (2) a subsequent simple thermal breakdown of the bonds separating the benzene rings. Theoretically, CO and NCN groups in BTDA-DAB account for 28 percent of the repeating unit weight, which is the same percentage of weight loss observed experimentally upon reaching the plateau at 800° C.

CONCLUSIONS

Some conclusions drawn from thermophysical measurements of several polyimidazopyrrolone films are:

1. Pyrrone films show a good degree of thermal stability, particularly under vacuum conditions.
2. The films are hygroscopic.
3. Of four structural compositions studied, the BTDA-DAB polymer is the most thermally stable.
4. A combination of thermogravimetric and mass spectrographic data can be used to outline the route of thermal degradation and partially substantiate the proposed polymeric structure.

ACKNOWLEDGEMENT

The author expresses appreciation to Dr. V. L. Bell who provided the Pyrrone films used in this study, and thanks Drs. G. F. Pezdirtz and V. L. Bell for their suggestions. The assistance of P. R. Young and J. R. Tyeryar, who made the thermal physical measurements is acknowledged.

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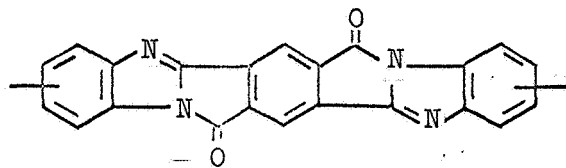
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LIST OF FIGURES

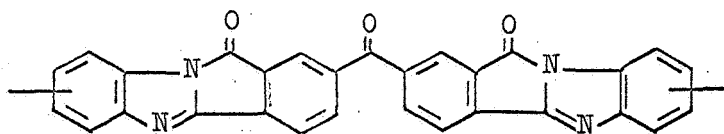
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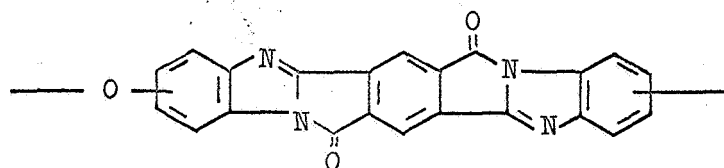
TABLE 1.- POLYIMIDAZOPYRROLONE REPEAT UNITS



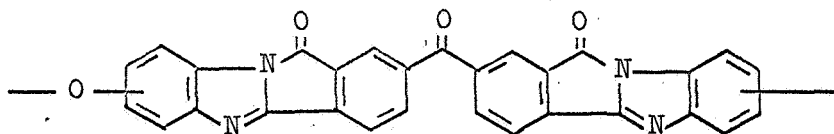
PMDA-DAB



BTDA-DAB



PMDA-TADPO



BTDA-TADPO

TABLE 2.- A COMPARISON OF MOISTURE CONTENT OF PYRRONE FILMS

Material	Theoretical		Experimental	Ratio of column C to column B
	Molecular weight of repeat unit A	Percent of water of condensation B	Percent weight change on heating to 100° C C	
PMDA-DAB	360	20.0	6.90	0.345
PMDA-TADPO	376	19.2	6.55	.337
BTDA-DAB	452	15.9	5.41	.340
BTDA-TADPO	468	15.4	5.32	.345

SAMPLE WEIGHT: 2.05 mg \pm 0.03 mg
SAMPLE SIZE: 0.25 IN. DIAM. \times 0.001 IN. THICK.
FILM CURED AT 350°C/2 HR/AIR
PRECONDITIONING: 100° FOR 30 MIN

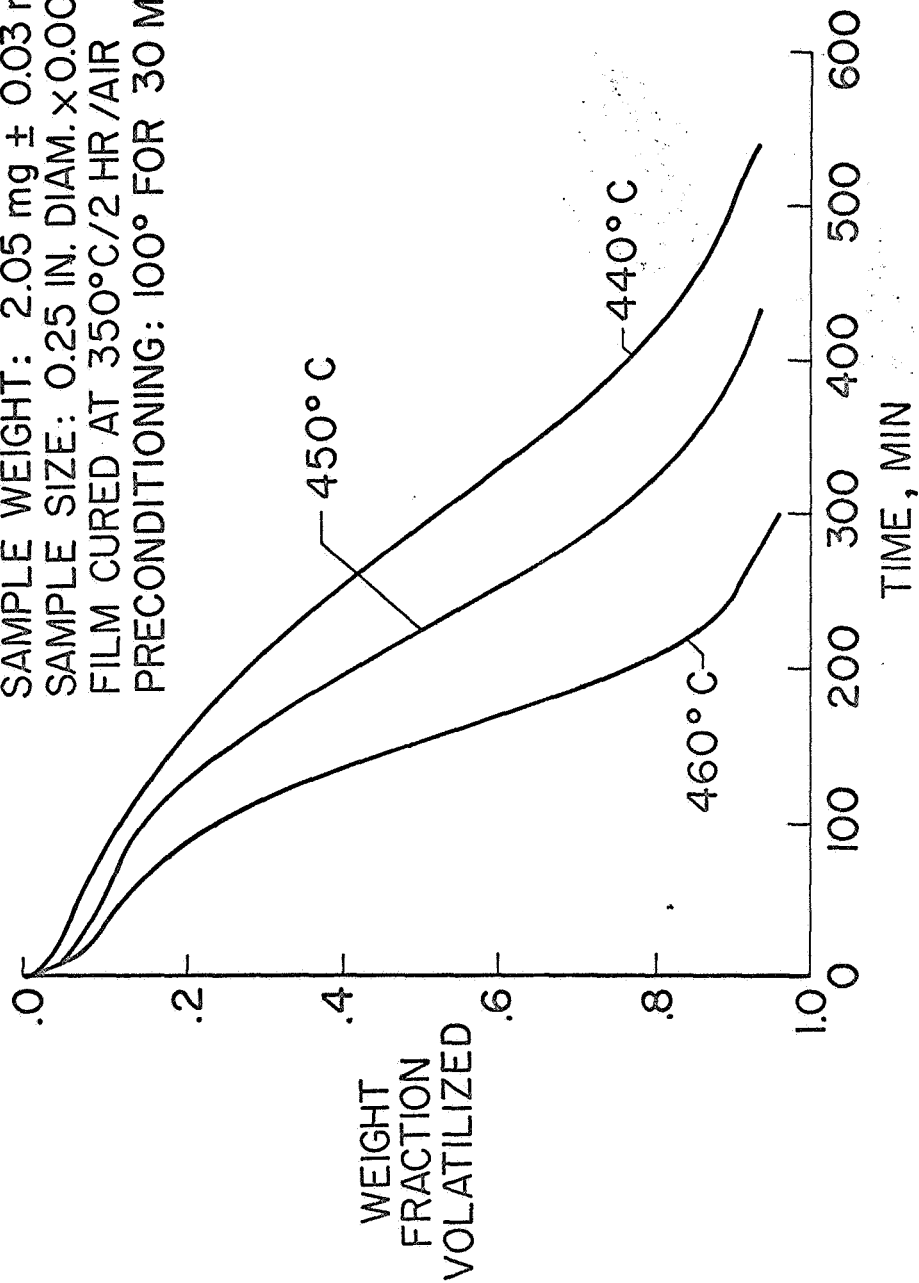


Figure 1.- Isothermal TG results in air for BTDA-DAB film.

SAMPLE WT: 2.05 mg \pm 0.03 mg
SAMPLE SIZE: 0.25 IN. DIAM \times 0.001 IN. THICK

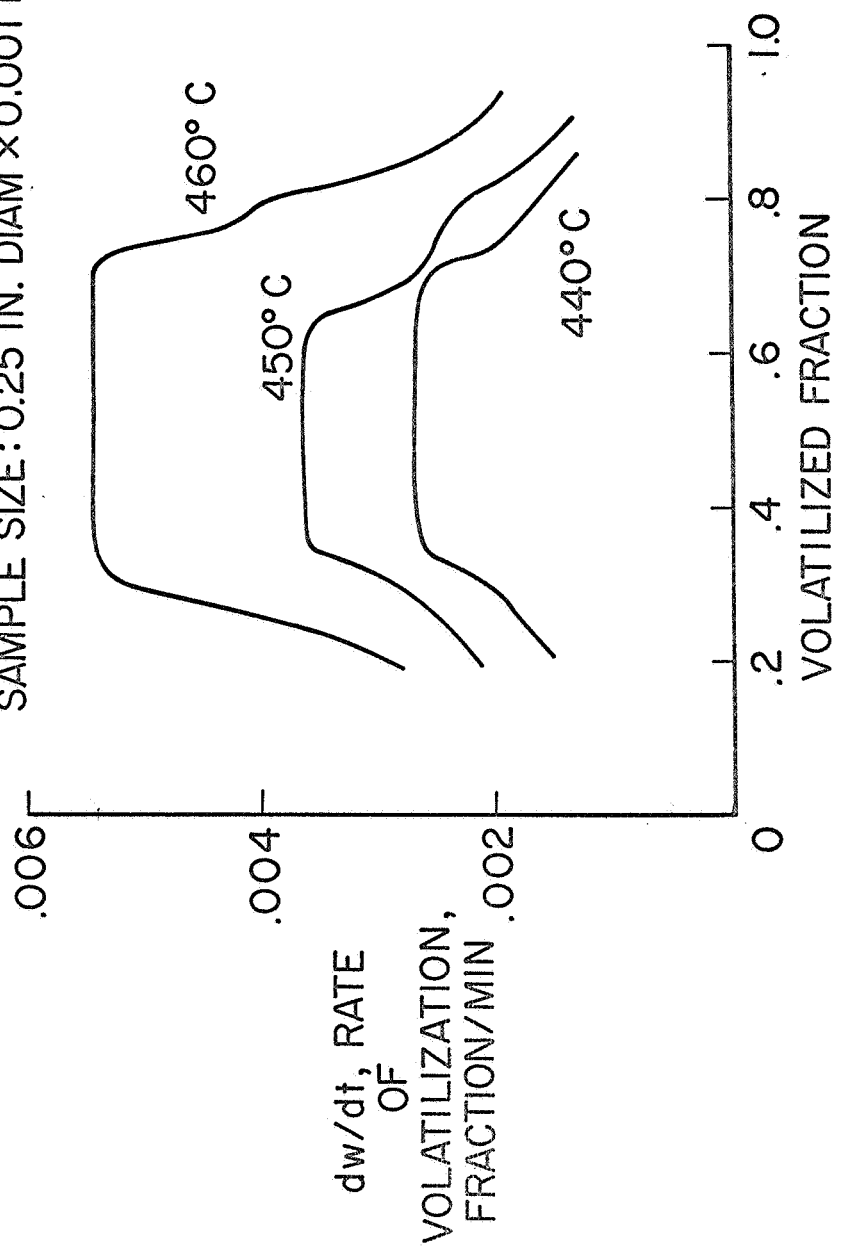


Figure 2.-- Volatilization rates of BTDA-DAB films heated isothermally in air.

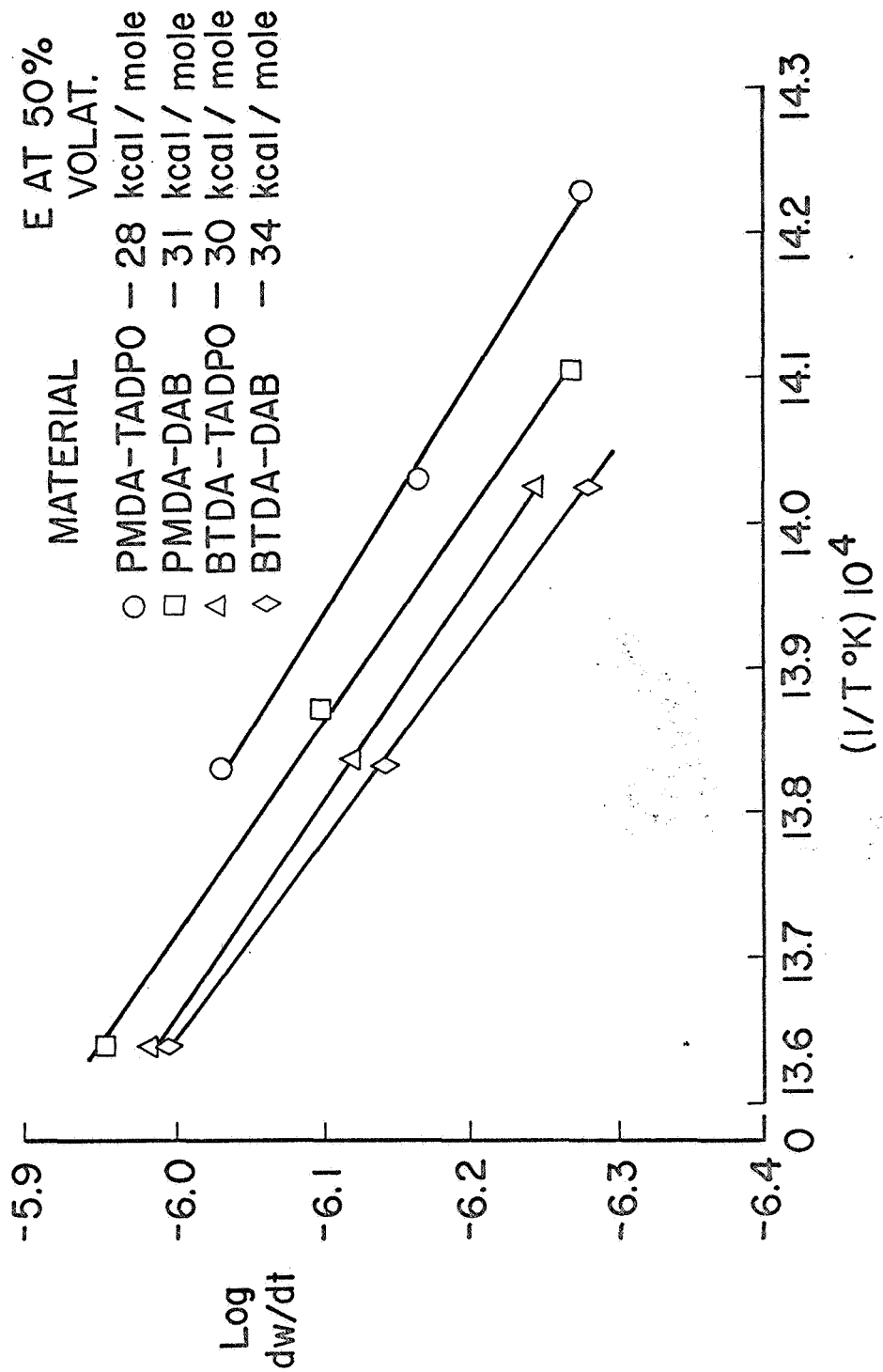


Figure 3.- Arrhenius plots of maximum volatilization rates of four Pyrrone films heated isothermally in air.

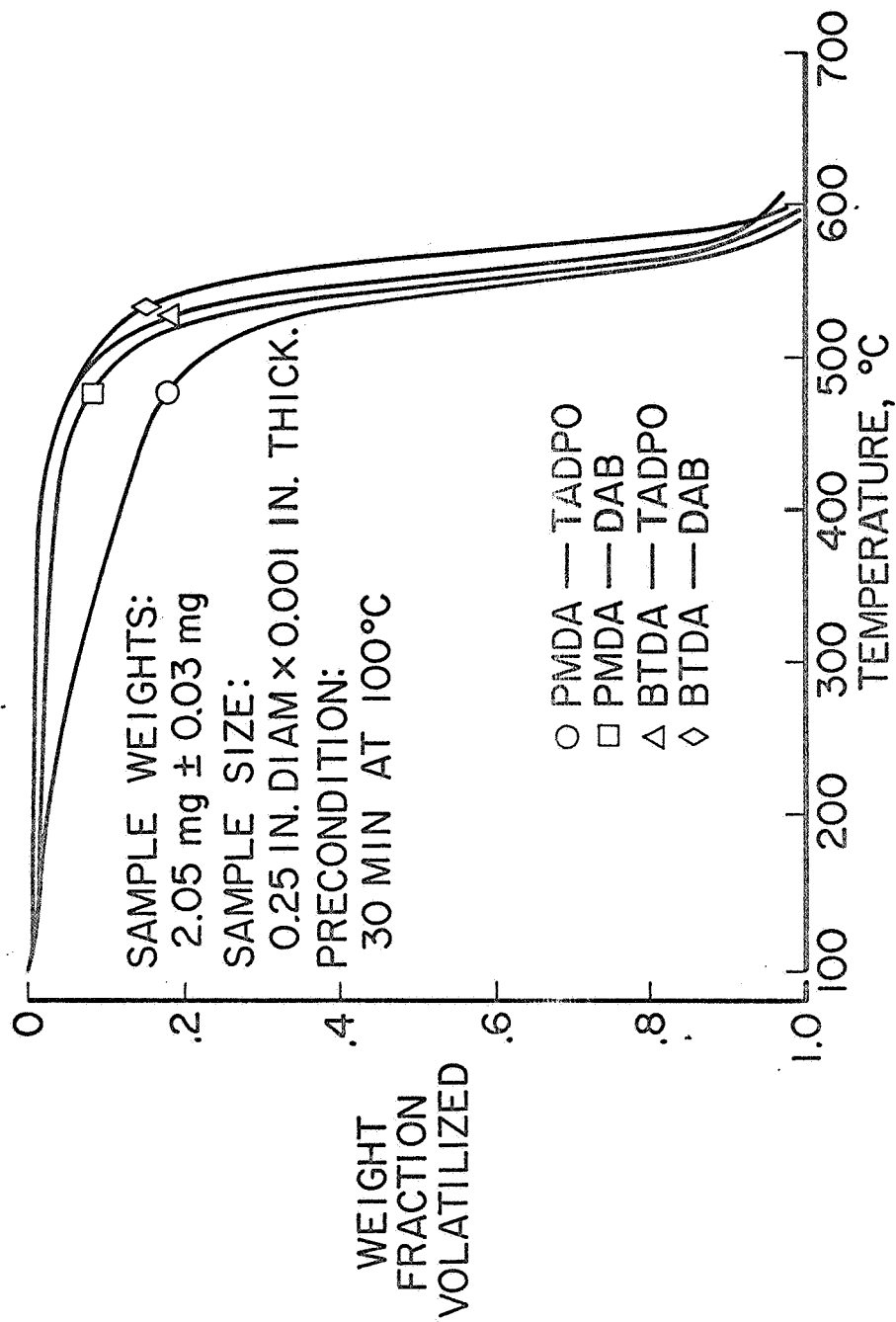


Figure 4.-- TG thermograms of EMDA-DAB film.

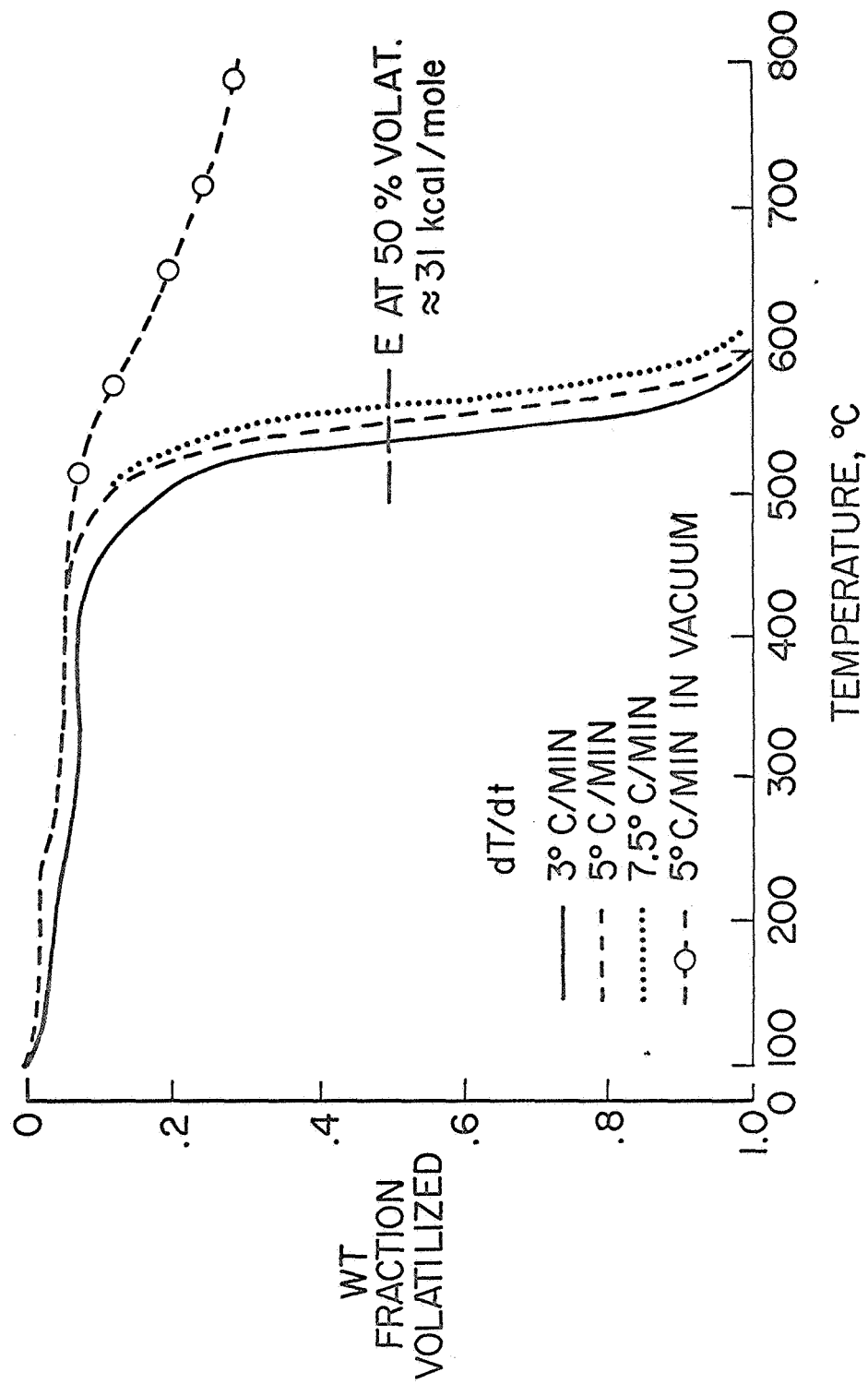


Figure 5.- TG thermograms for four Pyrrone films heated in air at 5° C/minute.

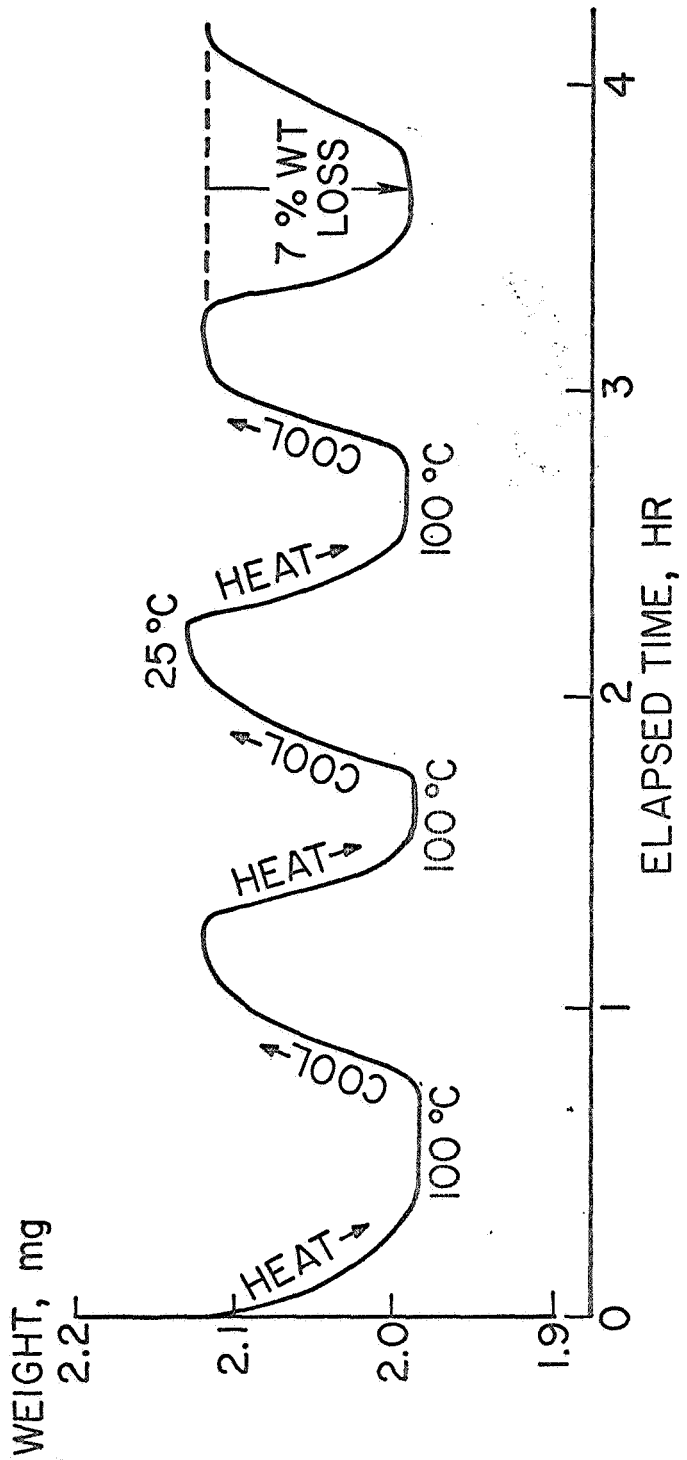


Figure 6.- Ability of EMDA-DAB film to absorb moisture.

SAMPLE: BTDA-DAB
SIZE: 2mg
ATM. AIR
PRECONDITIONING:
100° C FOR 30 MIN

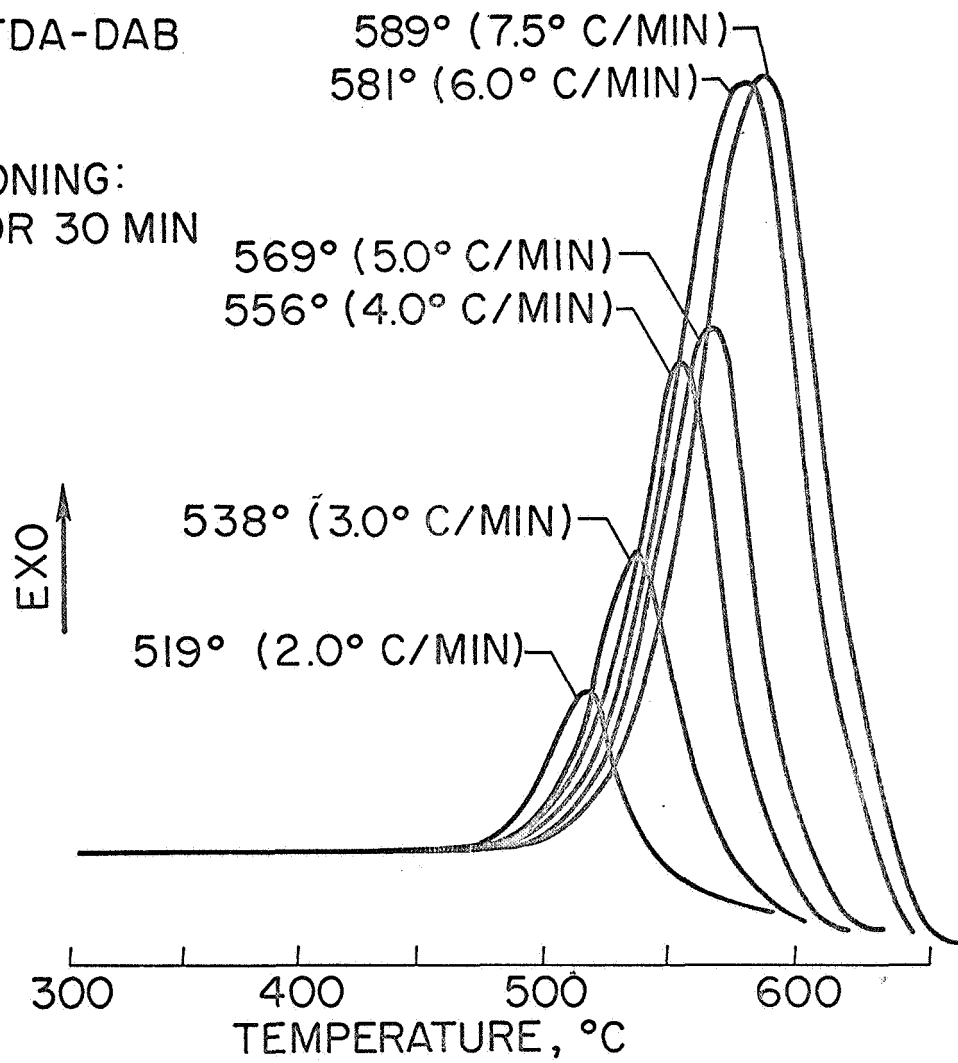


Figure 7.- DTA thermograms in air for BTDA-DAB film.

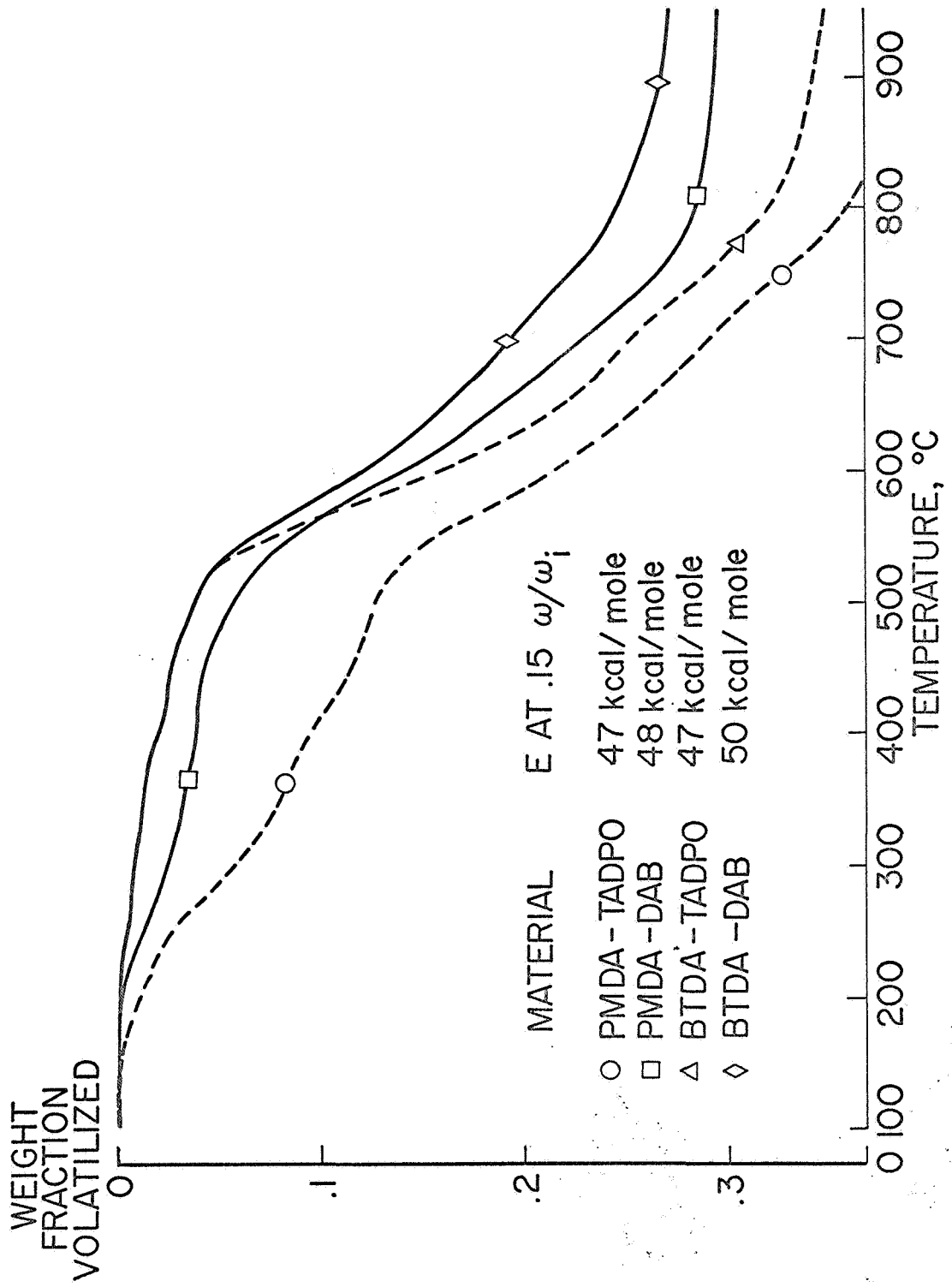


Figure 8.- TG thermograms of four Pyrrone films heated in vacuum at 5° C/minute.

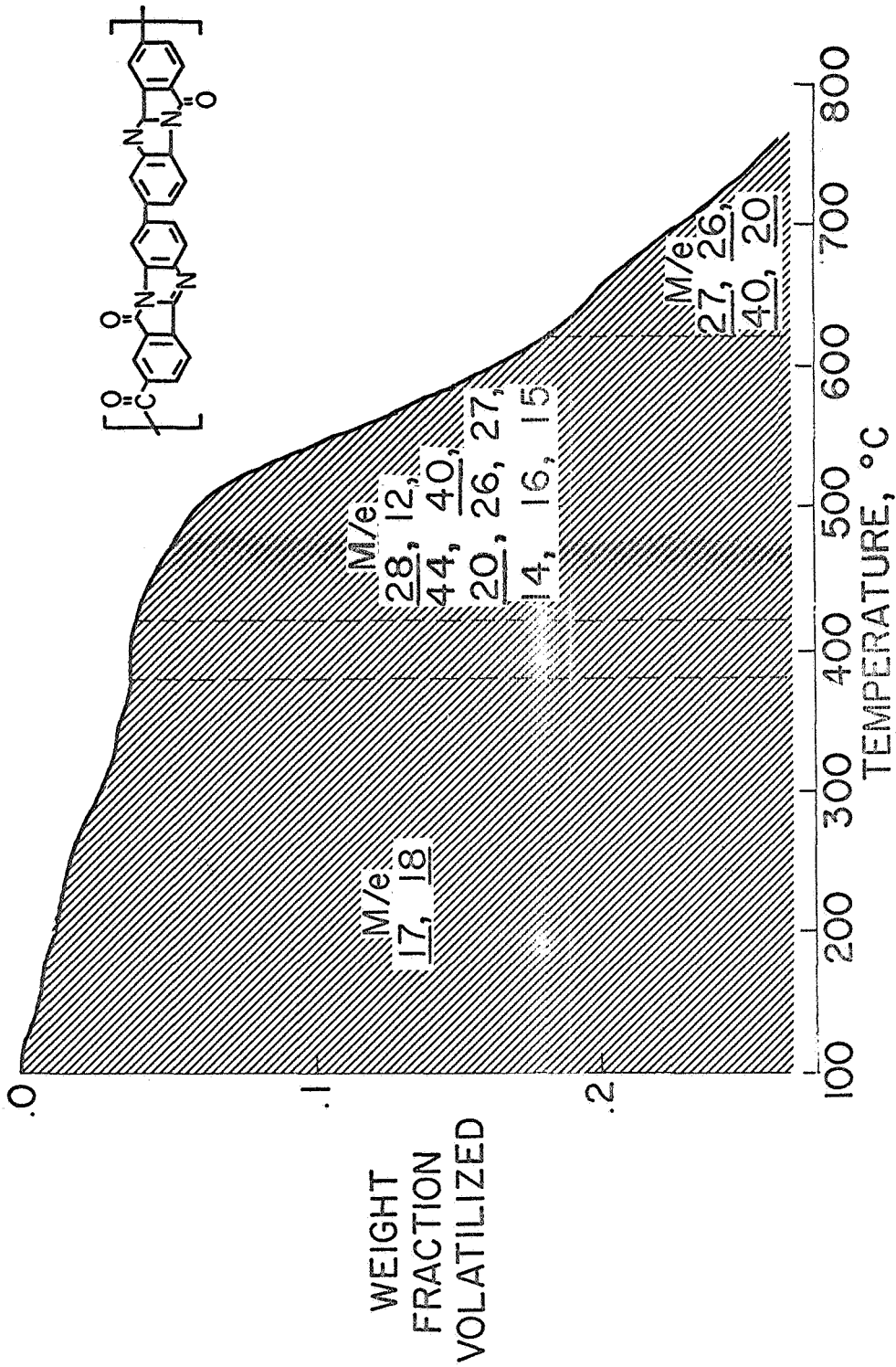


Figure 9.- Residual gas analysis of volatiles from BTPDA-DAB films heated in vacuum at 2° C/minute.