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A THERMAL EVOLUTION – DIFFERENTIAL TRAPPING – MASS SPECTROMETRIC TECHNIQUE FOR POLYMER CHARACTERIZATION

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ABSTRACT

The ability of thermal evolution techniques for polymer characterization is greatly enhanced when spectroscopic methods are combined, thus allowing identification of the off-gases. This work describes a thermal evolution–differential trapping–mass spectrometric technique for analysis of polymer systems. The technique involves heating the sample under controlled temperature and pressure conditions, condensing the evolved gases in traps maintained at various temperatures, continuously monitoring the pressure changes at strategic locations, and analyzing the selectively trapped volatiles by mass spectrometry. Both qualitative and quantitative aspects of the technique will be discussed.

INTRODUCTION

Various thermal evolution techniques have been effectively used for polymer characterization[1]. Volatile materials evolved from a sample upon controlled heating are continuously monitored by a suitable transducer such as a thermal conductivity detector, a flame ionization detector, etc. One of the less frequently used but potentially powerful transducers is that monitoring pressure changes. McNeill[2, 3] successfully employed vacuum gauges to study polymer degradation, and named the technique Thermal Volatilization Analysis. Similar applications were reported by others[4–7]. In general, such a detection system has the following features: (1) high sensitivity, (2) selectivity to distinguish products with different volatilities, (3) easy to operate, (4) products recoverable, (5) good baseline. McNeill[8] also suggested the use of several cold traps to differentially condense products to obtain information on the nature of the products based on their relative volatility. Murdoch and Rigby[9] used a thermal evolution–mass spectrometry technique for polymer characterization, in which the sample was heated below the electron beam of a time-of-flight mass spectrometer, and the thermal evolution curve was obtained by plotting the total ion current vs. the sample temperature.

The present work describes a thermal evolution analysis–differential trapping–

mass spectrometric (TEA-DT-MS) technique, which further extends the differential trapping capability described by McNeill, and analyzes the selectively trapped volatiles by mass spectrometry. Both qualitative and quantitative aspects of the technique will be discussed.

EXPERIMENTAL

The technique involves heating the sample under continuous vacuum at a programmed rate, condensing the evolved gases in traps maintained at different temperatures, continuously monitoring the pressure changes at strategic locations, and analyzing the trapped products by mass spectrometry. A schematic diagram of the apparatus is shown in Fig. 1. The sample furnace and the temperature programmer are those used in the DuPont 950 Thermogravimetric Analyzer without using the balance mechanism. Four U-shaped glass traps I, II, III, and IV are used, with three in series and one in parallel arrangement. The traps in series force the volatiles to completely pass through each trapping temperature, thus achieving maximum separation based on volatility. The one trap in parallel, III, is convenient in switching quickly to trap closely spaced components without interrupting heating. Five Pirani gauges (gag head G5C2, control unit model 14, Edwards High Vacuum Inc., Grand Island, N.Y.) are located after the sample furnace and the four traps. A 6-channel recorder (KA-62, Soltec Corp., Encino, Calif.) is used to record simultaneously the five pressure signals from the Pirani control units and the sample temperature. A duo seal oil pump (Model 1402, Welch Scientific Company, Skokie, Ill.) provides continuous vacuum during thermal evolution. For analysis, the product gases are directed to the mass spectrometer (Model 21-104, Instrument Products Division, DuPont Co., Wilmington, Del.) by turning stopcock F. The mass spectral data are collected and calculated by a computer (Model 21-MX, Hewlett-Packard, Cupertino, Calif.) and printed on paper tapes. These tapes are fed to a PDP-10 computer (Digital Equipment

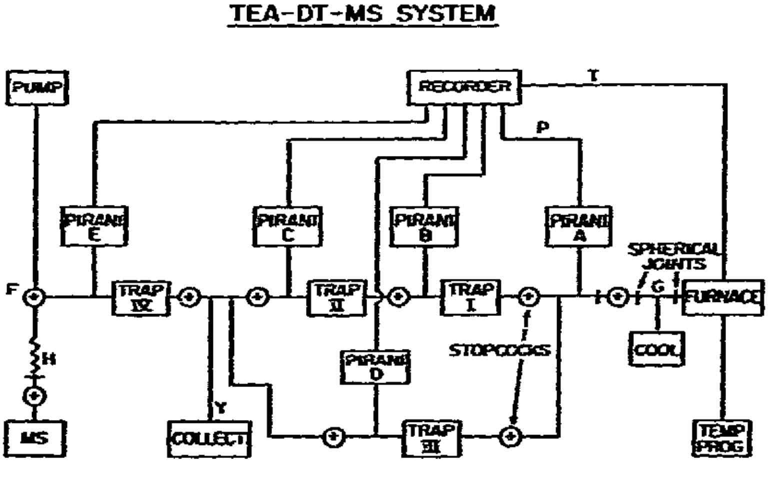


Fig. 1. Schematic diagram of thermal evolution–differential trapping–mass spectrometric system.

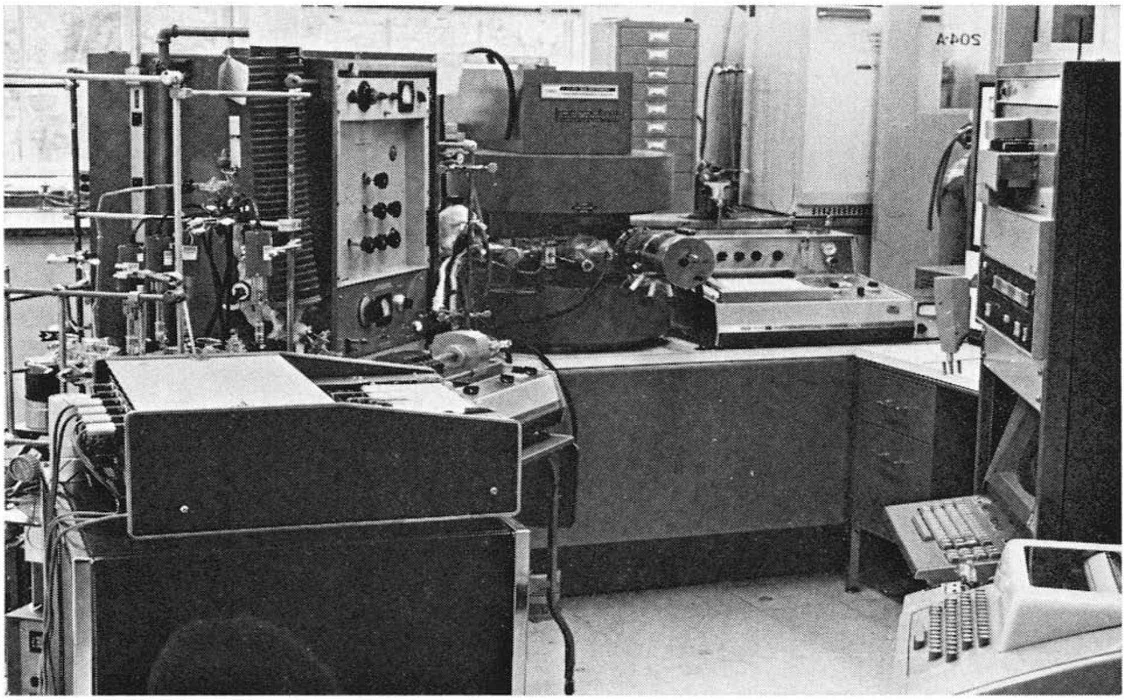
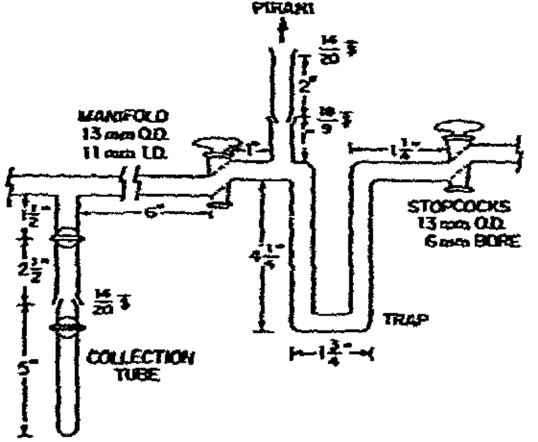


Fig. 2. Layout of thermal evolution-differential trapping-mass spectrometric system.

(a) TRAP



(b) FURNACE INSERT AND SAMPLE TUBE

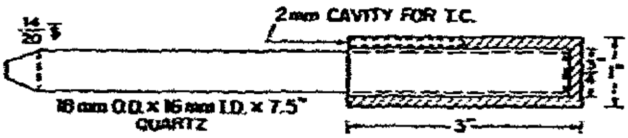


Fig. 3. Schematic diagrams of sample trap (a), and furnace insert and sample tube (b).

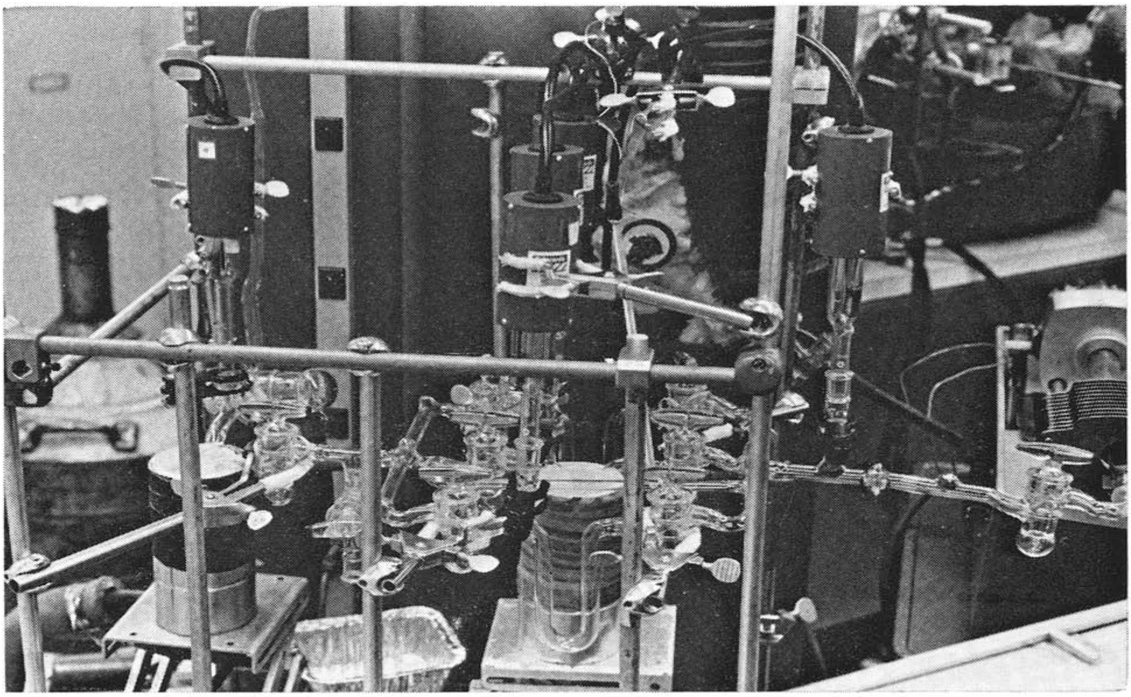


Fig. 4. Layout of sample trapping system.

Corp., Maynard, Mass.) for quantitative calculations. Relatively non-volatile components are condensed in the extended portion, G, of the sample tube cooled by room air or a cooling jacket and are collected for other analyses. The trapped volatiles can be transferred to a collection tube, Y, by proper heating and cooling. The laboratory layout of the complete system is shown in the photograph in Fig. 2.

The trapping system is constructed from borosilicate glass with a wall thickness of 2 mm and a bore diameter of 11 mm. to provide adequate strength and easy evacuation. The traps, as shown in Fig. 3 (a), are U-shaped, and immersed in cooling Dewars to maintain different condensation temperatures. The last trap, IV, is usually maintained at liquid nitrogen temperature to remove moisture and air from the oil pump. A Pirani gauge is mounted between the trap and the stopcock to provide good response. The trapping system is connected to the mass spectrometer by a flexible glass-end tubing, H, (G321-4-G-X-G-2, Cajon Company, Cleveland, Ohio). A photograph of the trapping system is shown in Fig. 4.

The quartz sample tube snugly fits into a stainless steel furnace insert shown in Figure 3(b). The sample, in milligram or gram quantities, can be placed either directly in the sample tube or in a platinum boat. The sample temperature is taken by a chromel–alumel thermocouple contained in a 2 mm diameter cavity in the furnace insert.

RESULTS AND DISCUSSIONS

One of the primary objectives of this study was to explore the possibility of using the thermal evolution peaks to derive quantitative information on the basis of pressure change detection. The Pirani gauge is based on thermal conductivity of heated filaments, the temperature, and therefore the resistance, of which changes with gas pressure. The relationship between the recorder output in millivolts of the Pirani gauge and the logarithm of the pressure in torrs is an S-shaped curve. A 10-mV linear

In order to correlate quantitatively residual gases after various traps, all the gauges in use should be calibrated to the same scale. As shown in Fig. 5 for four gauges, the system was evacuated to the best vacuum to set zero points. A small leak of air was then introduced to provide pressure readings. The gauge heads were adjusted at half-scale and also at the top-scale when atmospheric pressure was reached. This procedure was repeated several times until all gauges agreed with each other within acceptable limits.

The quantitative aspects of the Pirani gauge detection was tested with Teflon* 6 (E. I. duPont de Nemours & Co., Wilmington, Del.). Polytetrafluoroethylene is known to depolymerize completely to produce essentially the monomer by a first-order reaction[10]. Thermal evolution analysis was performed at a heating rate of 10°C per minute with traps II and IV in liquid nitrogen Dewars. A typical scan is shown in Fig. 6. Gauge A showed a single smooth evolution peak associated with the

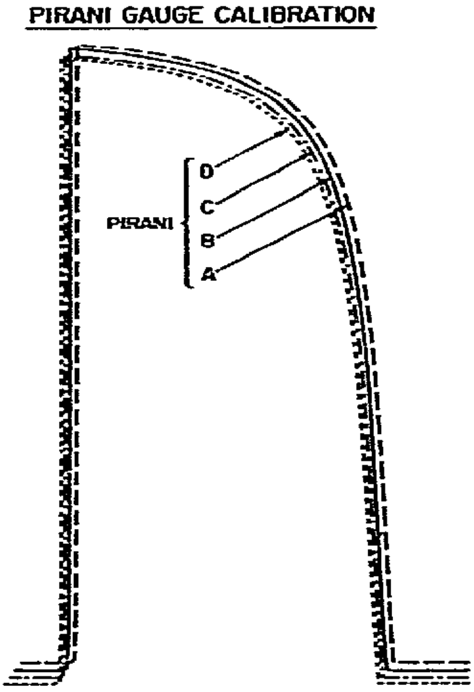


Fig. 5. Pirani gauge calibration curves.

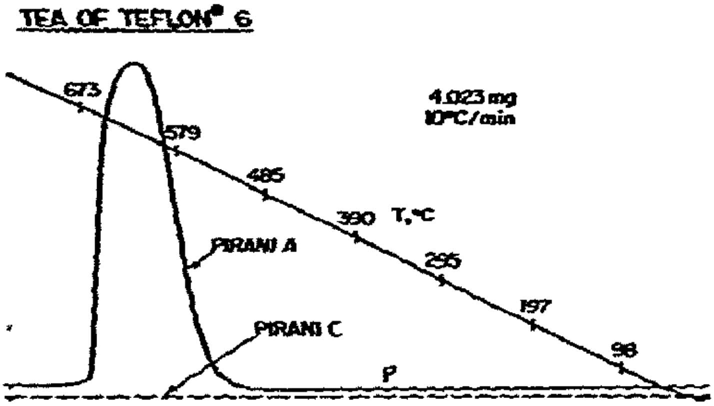


Fig. 6. Thermal evolution curves of Teflon® 6. Sample weight, 4.023 mg; heating rate, 10°C min^{-1}; *P*, total pressure; *T*, sample temperature in °C.

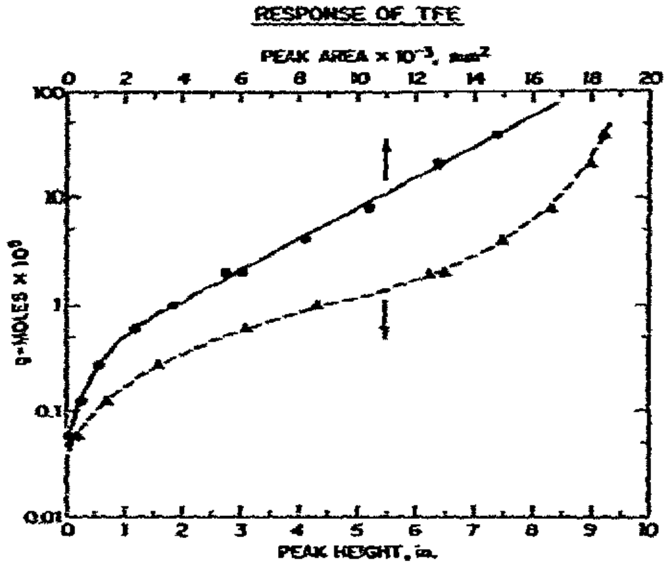


Fig. 7. Response of TFE.

total amount of the original sample. Gauge C detected no residual gas after liquid nitrogen trap II. Results obtained with a wide range of sample weights are shown in Fig. 7, with the logarithm of gram-moles of tetrafluoroethylene plotted vs. both peak heights and peak areas. Expectedly, the peak height shows an S-shaped response to pressure, and therefore, the number of moles of the volatile products. This type of curve is not ideal for quantitative work. However, the peak area plot appears to be linear except at very small amounts of materials. Thus, the use of peak area measurement is recommended for quantitative determinations based on thermal evolution. Different calibration curves will have to be constructed for components of widely different thermal conductivities.

One obvious advantage of coupling mass spectrometry to thermal evolution

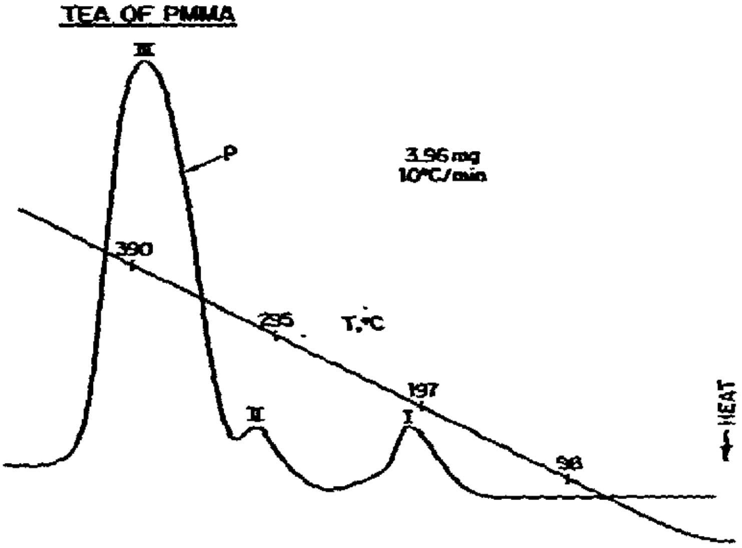


Fig. 8. Thermal evolution curve of polymethyl methacrylate. Sample weight, 3.96 mg; heating rate, 10°C min^{-1}; *P*, total pressure; *T*, sample temperature in °C.

TABLE I

MASS SPECTRAL RESULTS FOR DEGRADATION OF PMMA

Component	*mole %*		
	Peak I	*Peak II*	*Peak III*
MMA	61.1	91.6	97.7
H_2O	38.9	8.4	0.7
CO_2	trace	—	0.8
Methanol	—	—	0.8

is the capability of identifying products evolved at various temperature stages. This can be illustrated by the degradation of an experimental sample of polymethyl methacrylate made by a free-radical mechanism shown in Fig. 8. The thermal evolution scan obtained at a heating rate of 10°C per minute showed three peaks I, II, and III at 206, 310, 380°C, respectively. Volatile products during peak I were collected in liquid nitrogen trap II. While trap II was warmed up and analyzed by mass spectrometer, peak II products were collected in liquid nitrogen trap III. The collection was rapidly switched from trap III to trap II at a point between peak II and peak III. The mass spectral results are summarized in Table I. Peak I shows mainly residual monomer and moisture. Peak II represents degradation of an unstable fraction initiated at chain ends, while peak III, degradation of the more stable fraction undergoing random chain scissions[11, 12]. Both processes produce mainly the monomer.

The present TEA–MS technique is essentially a combination of controlled pyrolysis and mass spectrometry ideally suited for polymer characterization. The

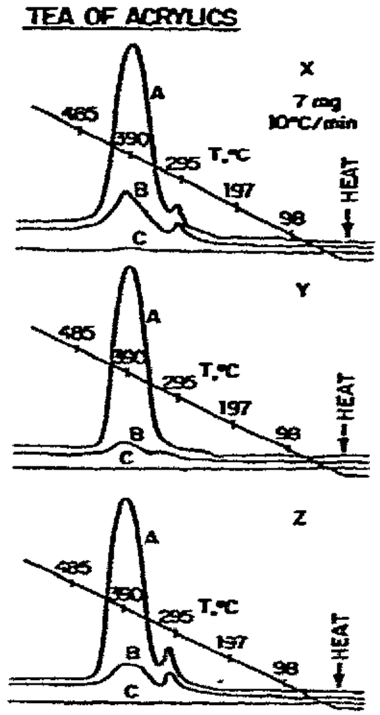


Fig. 9. Thermal evolution curves of acrylics. Sample weight, 7 mg; heating rate, 10°C min^{-1}; A, total pressure, B, after dry ice–acetone trap I; C, after liquid N_2 trap II.

TABLE 2

MASS SPECTRAL RESULTS FOR ACRYLICS

Component[a]	*Mole%*					
	Resin X		*Resin Y*		*Resin Z*	
	Dry-ice	*Liq N*	*Dry-ice*	*Liq N*	*Dry-ice*	*Liq N*
MMA	99.3	46.6	100.0	73.0	99.9	80.0
EA	0.7	29.0	0.0	11.9	—	0.2
MA		4.3		1.7	0.1	10.4
MIB		0.9		0.7		0.7
CO_2		5.9		4.6		3.5
MP		1.5		2.0		1.3
EtOH		0.6		—		0.3
MeOH		8.3		5.7		3.4
C_2H_4		2.9		0.4		0.2
MOLE% IN TRAP		4.0		5.4		4.3
% YIELD		34		34		43
MOLE% COMONOMER		3.4		1.9		1.0

[a] MMA = methyl methacrylate; EA = ethyl acrylate; MA = methyl acrylate; MIB = methyl isobutyrate; MP = methyl propionate.

thermal evolution profile provides a means for preliminary separation of thermal events, thus avoiding the complex mass spectra resulting from all the products by conventional total pyrolysis. The added feature of differential trapping has the advantages of further separation of the products according to their volatilities, and selective removal of certain components before mass spectrometric analysis. Barnes and Kirton[13] successfully combined differential freezing, differential thermal analysis, and evolved gas detection (based on thermal conductivity detector) to identify and determine carbonate impurity in silver oxide at levels below 1% CO_2. The present TEA–DT–MS technique has been found to be very effective in identification and determination of small amounts of comonomer in methyl methacrylate copolymers.

Figure 9 shows thermal evolution scans for three commercial acrylic resins X, Y, and Z, obtained with a sample weight of ca. 7 mg and a heating rate of 10°C per minute. Traps I and II were immersed in dry ice–acetone mixture and liquid nitrogen, respectively. Trap IV, also in liquid nitrogen, was used for protection against moisture and air back diffusion from the oil pump. The mass spectral results for the trapped products are shown in Table 2. The thermal evolution scans showed that almost 95% of the volatile products were condensed in the dry ice–acetone trap for all three resins, which were identified by mass spectrometry as mainly methyl methacrylate monomer. The remaining products were entirely condensed in the liquid nitrogen trap, and showed differences in composition. Resins X and Y were apparently methyl methacrylate (MMA)–ethyl acrylate (EA) copolymers, while resin Z was methyl methacrylate copolymerized with small amounts of methyl acrylate (MA). The amount of total volatiles in % mole condensed in the liquid nitrogen trap was estimated from the ratio of the thermal evolution peak areas B to A by assuming the same pressure response factors for all the components. By further assuming pyrolysis yields of 34% EA and 43% MA for such copolymers[14], the comonomer content of the three resins X, Y, and Z was calculated to be 3.4, 1.9 and 1.0 mole %, respectively, by multiplying the mole % comonomer from MS analysis by mole % total volatiles in the liquid nitrogen trap, and dividing the product by the % pyrolysis yield. Experiments to verify this calculation are now in progress. It should be noted that, prior to the removal of most MMA by the dry ice–acetone trap, such an analysis would be most difficult.

CONCLUSION

A new thermal evolution analysis technique has been described. The use of such a technique for polymer characterization has been illustrated. Preliminary results showed promise in using this technique for quantitative determinations. Further modification of the apparatus should allow investigation in inert or reactive atmospheres other than vacuum.

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