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### Dynamic Thermal Analysis of Polymers. An Overview

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## **Dynamic Thermal Analysis of Polymers. An Overview**

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### **ABSTRACT**

Dynamic thermal methods of analysis are becoming increasingly important for polymer characterization. These techniques are based on measuring changes in certain physical properties continuously and automatically upon variation of the sample temperature. This presentation reviews thermal analysis in general, and briefly describes the features and applications of several commonly used thermal methods, such as differential thermal analysis, differential scanning calorimetry, thermogravimetry, thermo-mechanical analysis, electrothermal analysis, thermo-optical analysis, and thermal evolution analysis. General references are given for the various techniques.

### **INTRODUCTION**

Thermal methods used for polymer characterization can be traced to ancient times beyond memory, if we include all those techniques associated with a temperature measurement or a thermal treatment; for instance, a burning test to distinguish fibers, a capillary melting

point determination, or a dripping test. It will also be beyond the scope of this presentation to include such thermal methods as pyrolysis-gas chromatography, -mass spectrometry, and -infrared spectroscopy; hot-stage type of microscopy; classical calorimetry; or large-scale physical testing with temperature variation. We are here concerned with "dynamic thermal analysis," a family of rapidly growing analytical techniques based on monitoring changes in a physical property continuously and automatically as a function of temperature or as a function of time at a controlled temperature.

Most of the thermal techniques are old in principle but new in instrumentation. Besides the use of small sample size to achieve high resolution of thermal events, a recent trend in instrumentation is to provide modules to perform various functions, and to share some common components such as temperature programmer, recorder, atmosphere control, and even amplifiers. The present flourishing use of dynamic thermal methods in polymer chemistry started around 1961 when instruments with adequate resolution for polymer studies became available. Presently, at least 30 manufacturers are marketing thermal analyzers [1, 2]. The number of publications related to thermal analysis in basic chemical journals has been increasing at an exponential rate, and is now estimated at more than 5000 annually, 20% of which are probably associated with polymers [1, 3]. Two journals, Thermochimica Acta [4] and Journal of Thermal Analysis [5], are devoted to thermal analysis exclusively. Thermal analysis abstracts [6] are also becoming available.

The International Confederation for Thermal Analysis (ICTA) has held three conferences since its formation in 1965, the proceedings of which have been published [7-9]. Professional societies for thermal analysis have been formed in Japan, England, Italy, the Soviet Union, and other nations. Most thermal analysts in the United States join the North American Thermal Analysis Society (NATAS). The proceedings of the third annual NATAS meeting held in February 1972 have been published [10]. Several symposiums on thermal analysis were sponsored by various divisions of the American Chemical Society during national meetings in 1963 [11], 1965 [12], 1968 [13], and 1970 [14, 15]. These conferences contributed greatly to the exchange of research results among various workers. Interlaboratory tests are being conducted on several thermal techniques by ICTA, ASTM, International Organization for Standardization (ISO), and other national groups, and some results have been reported [16-21]. In collaboration with ICTA, the U.S. National Bureau of Standards has issued three sets of temperature standards (NBS-ICTA Standard Reference Materials 758, 759, and 760) for DTA in the three temperature ranges 125-435, 295-675, and 570-950°C, respectively. The program leading to the issuance of such standards and current activities of various organizations on standardization have been described [17, 22]. Recommendations on certain aspects of nomenclature in thermal analysis have

been published by ICTA [23], and should be consulted in preparing publications.

General descriptions of various thermal methods are provided in books by Wendlant [24] and Garn [25]. Fundamental developments in thermal analysis are reviewed biennially by Murphy [26].

### THERMAL ANALYSIS OF POLYMERS

Recent developments in the use of thermal methods for polymer characterization are reviewed biennially by Mitchell and Chiu [27]. Two volumes in a series of books on techniques and methods of polymer evaluation edited by Slade and Jenkins [28] are devoted to thermal techniques. Other review articles on thermal analysis of polymers in general include those by Ehlers and Fisch [29], Kambe [30], Miller [31], Manche and Carroll [32], and Nakamura [33]. Comprehensive thermal analysis data, mainly DTA and TGA, are included in books by Frazer [34] and Korshak [35].

The applications of thermal analysis to polymer chemistry can be briefly summarized.

Monomers	polymerization	
	curing	
Solvents	←————→	Polymers
	depolymerization	
Additives	decomposition	

Polymerization and curing of monomeric systems can be studied by many thermal techniques with respect to enthalpy changes or kinetics and mechanism. In the opposite direction, depolymerization and decomposition of polymers under controlled conditions can be investigated and reaction products analyzed. For polymers, thermal techniques provide information on melting, crystallization, softening, shrinking, glass transition and other relaxations, crystalline transitions, adsorption, dissolution, thermal conductivity, crystallinity, heat capacity, dielectric properties, electrical conductivity, modulus, thermal expansion, thermal stability, oxidation and aging, chemical composition and structure, and chemical reactions. Thermal techniques are also used for studies of the components making polymers including monomers, solvents, additives, and initiators. Properties frequently studied include melting, freezing, crystalline transitions, glass transition, magnetic transition, boiling, sublimation, vapor pressure, heat capacity, purity, adsorption, electric behavior, thermal stability, solvation, complexation, oxidation and combustion, and other chemical reactions.

It is impossible and unnecessary to elaborate on these applications in this brief review. Many unique capabilities of thermal analysis for polymer characterization will be presented in this symposium.

However, some general comments will be made here on each of the more commonly used thermal techniques; namely, differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), thermomechanical analysis (TMA), electrothermal analysis (ETA), thermo-optical analysis (OTA), and thermal evolution analysis (TEA).

## DIFFERENTIAL THERMAL ANALYSIS (DTA)/ DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DTA and DSC are techniques monitoring enthalpy changes of a sample as a function of temperature. DSC or dynamic differential calorimetry (DDC) is considered a quantitative version of DTA, and therefore not distinguished in most discussions. DTA is probably the first dynamic thermal technique to arouse the enthusiasm of polymer chemists. General reviews on DTA include those by Smothers and Chiang [36], Mackenzie [37], Murphy [38], Wunderlich [39], and Schultze [40]. Reviews devoted to DTA of polymers have been written by Ke [41], Teitel'baum and Anoshina [42], Smith [43], Kanetsuna [44], and Barrall and Johnson [45].

DTA/DSC is mainly used for studies of physical transitions, although reactions such as degradation [46], polymerization [47, 48], oxidation [49-51], vulcanization [52], and chemical reactions [53] can readily be studied. Important applications of DTA/DSC to polymers and intermediates also include heat capacity [54, 55], crystallinity [56], and purity [57-62] measurements. Melting temperatures are frequently used for polymer identification on the basis that each polymer shows its characteristic melting endotherm in an incompatible mixture. This was demonstrated [63] by DTA of a physical mixture of seven commercial polymers; namely, high-pressure polyethylene, low-pressure polyethylene, polypropylene, polyoxymethylene, nylon 6, nylon 66, and polytetrafluoroethylene (Fig. 1). The melting peak area is a measure of the heat of fusion of the polymer, and can be used to determine the amount of the polymer present.

Qualitative analysis of polymers relies heavily on the resolution of thermal events. High resolution becomes possible only when a small sample is used. This is shown in Fig. 2 by DTA of a blend of linear polyethylene and isotactic polypropylene in a ratio of 25:75 by weight [64]. The two melting endotherms are completely resolved when a sample size of 2 mg is used. Another factor is heating rate. In general, a slower heating rate provides better resolution. Resolution of DTA peaks,  $R$ , can be defined, as shown in Fig. 3, in a manner similar to that in chromatography as the distance,  $T_2 - T_1$ , between the two peak maxima divided by the sum of the two half-peak widths,  $t_2 + t_1$ . The effect of sample size and scanning rate on resolution can then be

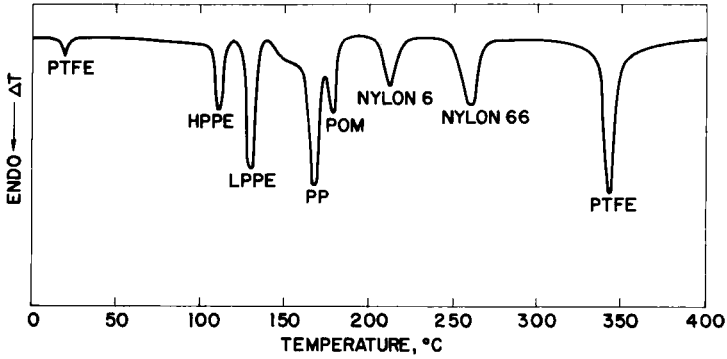


FIG. 1. DTA of seven component polymer mixture. Sample weight, 8 mg; heating rate, 15°C/min.

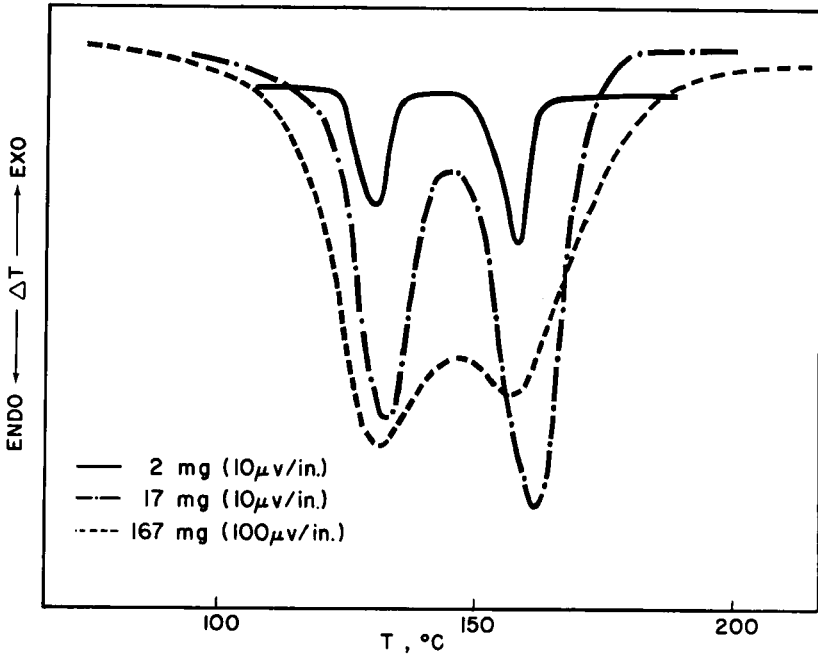


FIG. 2. DTA of 25:75 polyethylene:polypropylene blend. Heating rate, 45°C/min.

represented by the relationship

$$RS^a W^b = C$$

where S and W represent scanning rate and weight of sample, respectively, and a, b, and C are empirical constants. In the meantime, the effect of sample size and scanning rate on the transition temperature can be represented by

$$T = T_0 \pm k_1 S \pm k_2 W$$

where T is the observed transition temperature,  $T_0$  is the equilibrium transition temperature, and  $k_1$  and  $k_2$  are instrumental constants. Plus signs are used for heating and minus signs for cooling. The above two relationships have been tested with experiments on resolution of the two closely spaced transitions of n-dotriacontane, chain rotation and fusion. The results obtained using a Perkin-Elmer DSC-1B instrument are shown in Tables 1 and 2 and plotted in Figs. 4-7. Infinite resolution is thus obtained at zero scanning rate or zero sample size. True transition temperatures are obtained when both scanning rate and sample size approach zero. We obtained the thermogram for dotriacontane shown in Fig. 8(C) by using a sample size of 0.1 mg, a heating rate of  $10^\circ\text{C}/\text{min}$ , and a chart speed of 6 in./min. A resolution of 4.7 was achieved with peak temperatures at  $65.1$  and  $70.4^\circ\text{C}$  for rotation and fusion, respectively. This resolution contrasts dramatically with the scan in Fig. 8(B) obtained under normal operating conditions and the scan in Fig. 8(A) obtained under somewhat extreme conditions.

A question often raised by polymer chemists is how to determine the melting point of a sample from its melting endotherm obtained by DTA or DSC. For metals and monomeric substances, the extrapolated onset temperature, found by extrapolating the base line, prior to the peak, and the leading side of the peak to their intersection is the closest

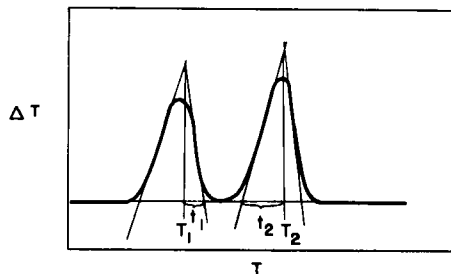


FIG. 3. Resolution.

TABLE 1. Sample Size Effect (scanning rate = 40°C/min)

Sample size (mg)	Heating			Cooling		
	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)	[R]	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)	[R]
10.0	73.0	82.0	0.53	-	-	-
5.0	70.8	78.0	0.71	54.8	60.0	0.43
1.0	68.7	74.8	1.10	57.0	63.2	1.41
0.2	66.8	73.0	1.44	57.0	63.0	1.90
0.05	67.5	72.9	2.18	57.3	63.3	2.87

TABLE 2. Scanning Rate Effect (sample size = 5.0 mg)

S (°C/min)	Heating			Cooling		
	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)	[R]	T <sub>1</sub> (°C)	T <sub>2</sub> (°C)	[R]
40	71.0	77.0	0.78	55.0	60.0	0.41
20	68.0	74.2	1.04	59.1	64.3	0.96
10	66.5	72.8	1.53	60.9	65.8	1.70
5	65.8	71.3	2.00	62.0	66.8	2.86
2.5	65.2	70.6	2.84	62.4	67.6	3.84
1.25	65.4	70.8	3.76	63.2	68.4	6.58

to the equilibrium transition temperature [17]. However, this is inapplicable for polymers. Melting of a polymer occurs over a broad temperature range, and the melting point observed varies greatly with the sensitivity of the method used for the determination. The use of the deviation point or the extrapolated onset point in a DTA/DSC scan could cause great chaos. An interlaboratory study of melting point methods for polyamides, sponsored by ISO, was made on seven nylons using Fisher-Johns method of ASTM D 789, Kofler hot stage method of ASTM D117, Leitz polarizing microscope, Antes capillary, Culatti capillary, x-ray diffraction, and DTA. The results reported by laboratories in Italy, France, Germany, The Netherlands, and the United States are summarized and shown in Fig. 9 [21]. The spread of the data even within similar methods is indeed disappointing. However, it is of interest to note that the DTA extrapolated end and end temperatures are close to those by x-ray diffraction, and the DTA peak temperatures are essentially the averages of the other methods. Since the



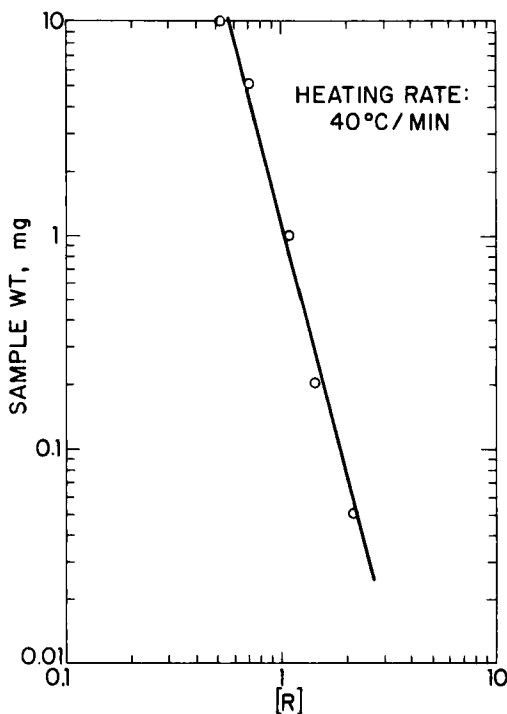


FIG. 4. Sample size effect on resolution on n-dotriacontane transitions.

x-ray method measures a more definitive temperature of disappearance of the last traces of crystallinity, and is more objective and sensitive than the optical methods, the extrapolated end point or the end point seems to be the temperature of choice as the DTA melting point of a polymer sample.

For amorphous polymers, glass transitions can sometimes be used for qualitative and quantitative analyses [65]. More recent developments in DTA/DSC include high-pressure operations [66-68], simultaneous DTA/DSC and electrical conductivity measurements [69-71] simultaneous DTA and photothermal analysis [72], thermal diffusivity determination [73], combined DTA/DSC-mass spectrometry [74, 75], and computer reduction of DSC data [76-78]. Computer interface and programs are also commercially available.

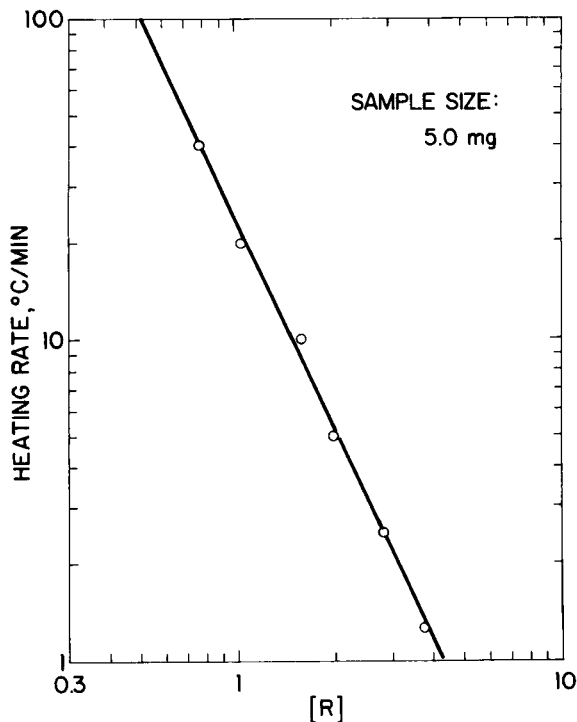


FIG. 5. Heating rate effect on resolution of n-dotriacontane transitions.

### THERMOGRAVIMETRY (TG)

Thermogravimetry or thermogravimetric analysis (TGA) monitors the weight changes in a sample as a function of temperature. General reviews on TG of polymers include those by Chiu [79], Anderson [80], Reich and Levi [81], Zimmermann and Budisch [82], Reich [83], and Reich and Stivala [84].

TG is considered the most important method for studying polymer stability. However, there are other unique applications of this technique not well recognized, such as determination of additives [79, 85] and characterization of polymer blends and copolymers [79, 86, 87]. TG has also been used for studies on flame retardance [88-93], cross-linking [94, 95], track resistance [96], and thermal life [97, 98].

Derivative thermogravimetry (DTG) shows improved resolution of thermal events and precise comparison of thermal stability [99-101].

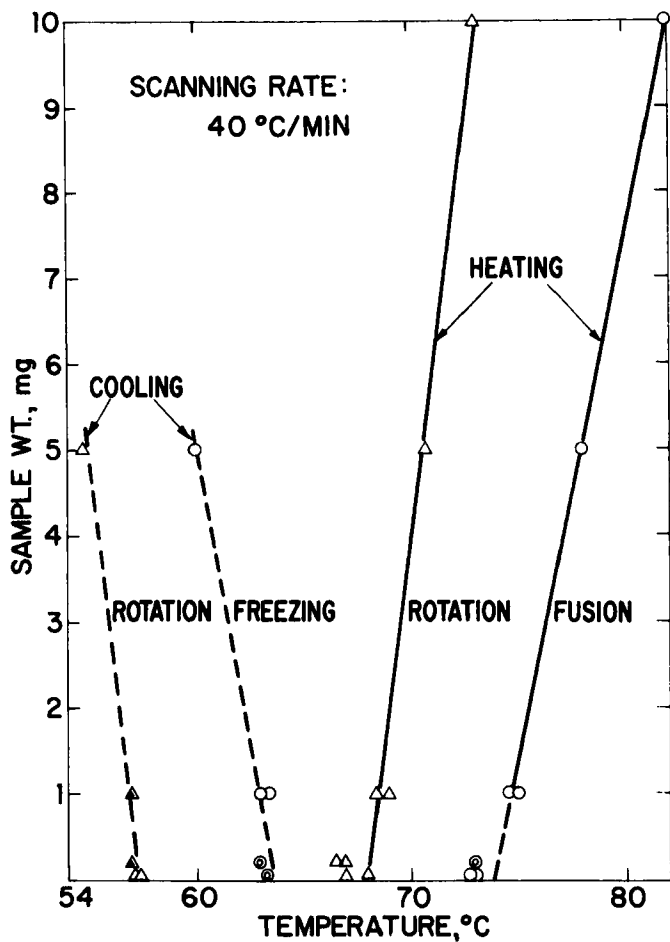


FIG. 6. Sample size effect on peak temperatures of n-dotriacontane transitions.

Kinetic studies by TG have been reviewed [102, 103]. Isothermal and dynamic TG methods for kinetic studies of polymer degradation have been compared [104, 105]. The dynamic methods provide more rapid measurements over a wide temperature range, whereas the isothermal technique is more reliable and applicable to most systems. Computers have been used for processing TG data, particularly in kinetic studies [106-114].

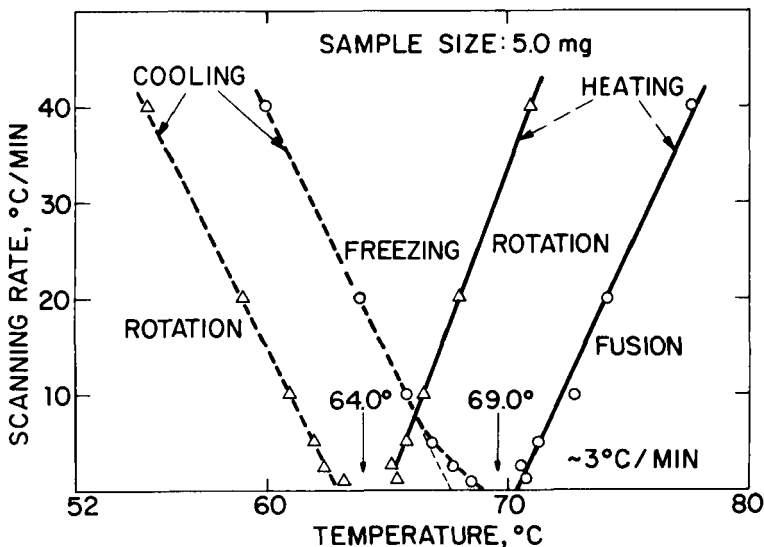


FIG. 7. Scanning rate effect on peak temperatures of n-dotriacontane transitions.

TG is basically a means for studying behavior, and not an absolute identification tool. For investigation of complex systems, it is often desirable to couple TG with other analytical techniques such as DTA, DTA-ETA [115], DTA-TMA [116], TOA [117], gas chromatography (GC) [118], mass spectrometry (MS) [119-121], GC-MS [122, 123], and GC-IR [124].

#### THERMOMECHANICAL ANALYSIS (TMA)

Thermomechanical analysis is a name broadly used to describe a group of thermal techniques which measure the mechanical strength of a material as a function of temperature. Such techniques are useful in obtaining information on softening, modulus, shrinkage, glass transition, segmental motions, and expansion coefficients. Commercial instruments are available to allow dynamic measurements performed in expansion, compression, and extension modes [125-127]. The TMA method for relating modulus and temperature has been shown to be comparable to ASTM tests such as deflection temperature under load, VICAT softening temperature, and Clash-Berg  $T_F$  [128].

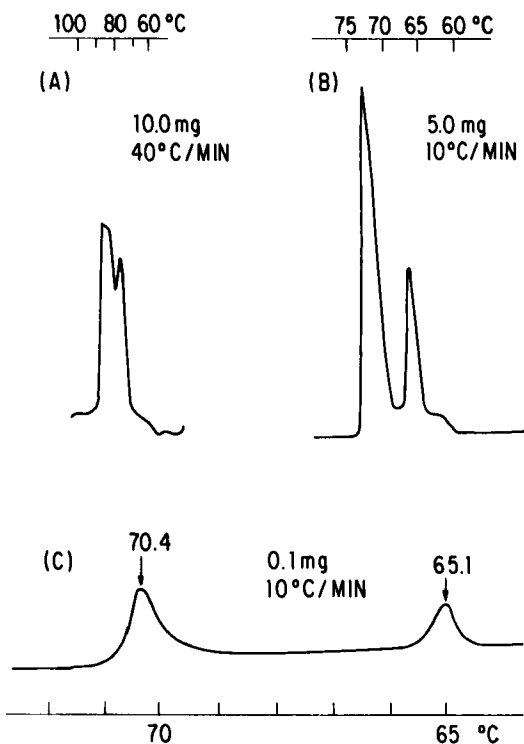


FIG. 8. DSC scans of n-dotriacontane.

TMA has been used for studies of phase transitions [129-132], swelling and dissolution [133, 134], curing [135, 136], and rheological compatibility of polymer blends [137].

Another thermomechanical technique, named torsional braid analysis (TBA) by Gillham [138], is an extension of the conventional torsion pendulum method for dynamic mechanical studies. The method employs a glass braid substrate, impregnated with a solution of the material under investigation, and subjected to free torsional oscillations under programmed temperature conditions. The frequency and decay of the oscillating pendulum provide information on the modulus and mechanical damping of the sample, allowing studies of polymer transitions, resin curing, and degradations. TBA has been recently used for determination of the effectiveness of polymer additives [139]. A similar method using a dynamic spring has been used for following cross-linking reactions with higher sensitivity than TBA [140].

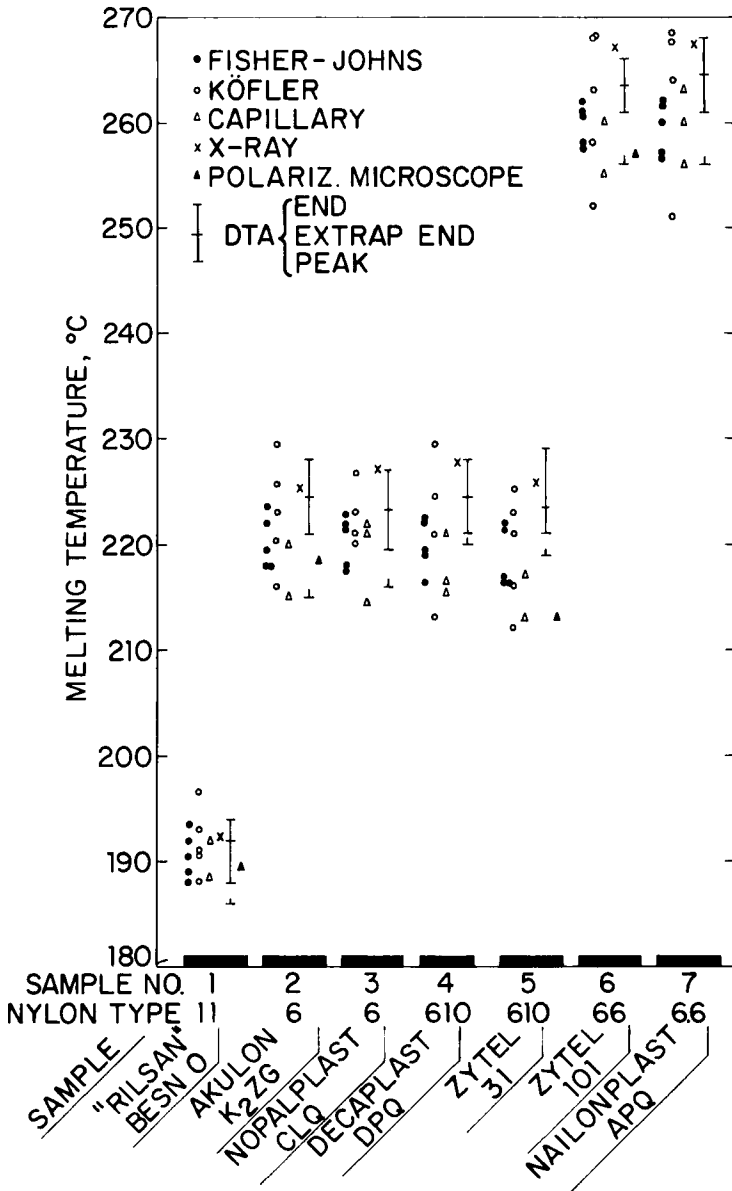


FIG. 9. Melting points of polyamides by different methods.

## ELECTROTHERMAL ANALYSIS (ETA)

Electrothermal analysis is defined as a thermoanalytical technique for studying the nature and behavior of a material by monitoring the changes in resistivity or dielectric parameters automatically and continuously as a function of temperature. Thus electrical properties can be used in polymer characterization in a manner similar to DTA or TMA. Although this technique has not yet been widely used, potential applications of ETA to polymer problems evidently include studies of physical transitions and segmental relaxations, analysis of additives and contaminants, elucidation of structures, identification of polymer blends and copolymers, and investigation of polymerization, curing, and degradation reactions.

Principles and applications of direct current (dc) ETA or resistivity measurements have been reviewed [141, 142]. Recent developments include simultaneous DSC-ETA [71], DTA-ETA [69, 70, 143], and DTA-TG-ETA [115].

Dielectric measurements performed as a function of temperature have shown promise in elucidation of structure and stereoregularity of acrylics [144]. Sacher [145] used a continuously nulling capacitance bridge to obtain both capacitance and dissipation factor vs temperature curves for a variety of polymers. Hedvig, Kisbenyi, et al. used the dielectric method to study degradation [146], efficiency and compatibility of plasticizers [147], and curing [148]. Wrasidlo and co-workers [149] and Chiu [150] developed apparatus for dynamic dielectric measurements, and applied the technique to several polymer systems. The correlation among ETA, DTA, and other methods was discussed.

## THERMO-OPTICAL ANALYSIS (TOA)

Thermal depolarization analysis (TDA), depolarized light intensity analysis (DLI), and thermo-optical analysis (TOA) are names used to describe thermal techniques based on measuring light intensity as a function of temperature. Generally, this technique is more sensitive than DTA in detecting partial melting, pre-melting, and recrystallization phenomena. The use of changes in optical properties for studying fusion has been discussed [151]. A general discussion of the use of thermal optical measurements for polymer characterization has been presented [152-154]. Major applications of TOA include studies on glass transition [155], melting [156], mobility transitions in polymer blends [157], and smoke generation [117]. A technique based on light emanation from sample upon heating has also been reported [72].

## THERMAL EVOLUTION ANALYSIS (TEA)

Evolved gas analysis (EGA) and evolved gas detection (EGD) generally refer to techniques which determine the nature or amount of volatiles formed, or detect whether or not a volatile product is formed. Here the name thermal evolution analysis is coined to include techniques which monitor continuously the amount of volatiles thermally evolved from the sample upon programmed heating. The resulting record is essentially equivalent to a weight loss curve. In fact, this technique provides information similar to that obtained by TG. The advantages of TEA over TG are potentially higher sensitivity, less expensive equipment, and more flexibility in sample handling. Commercial units are presently available.

Transducers used in TEA include vacuum gauge [158], flame ionization detector [159, 160], and thermal conductivity detector [161]. These techniques have shown promise in studies of thermal degradation, analysis of trace impurities and additives, and elucidation of polymer structures. Another potential application is in the area of vapor pressure measurements for flame retardants and other additives in polymer systems [162].

## CONCLUSION

The above discussion provides a brief overview of the various dynamic thermal methods more commonly used today. More detailed information can be found in the general references given. Thermal analysis is now generally recognized as one of the basic analytical tools for polymer characterization. Its future expansion can only be limited by the usefulness of the property of the material to be measured. With the rapid development and improvement of commercial instrumentation, and the increasing awareness of the capabilities of thermal techniques by industries and research institutes, the continued growth of thermal analysis is expected for years to come.

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