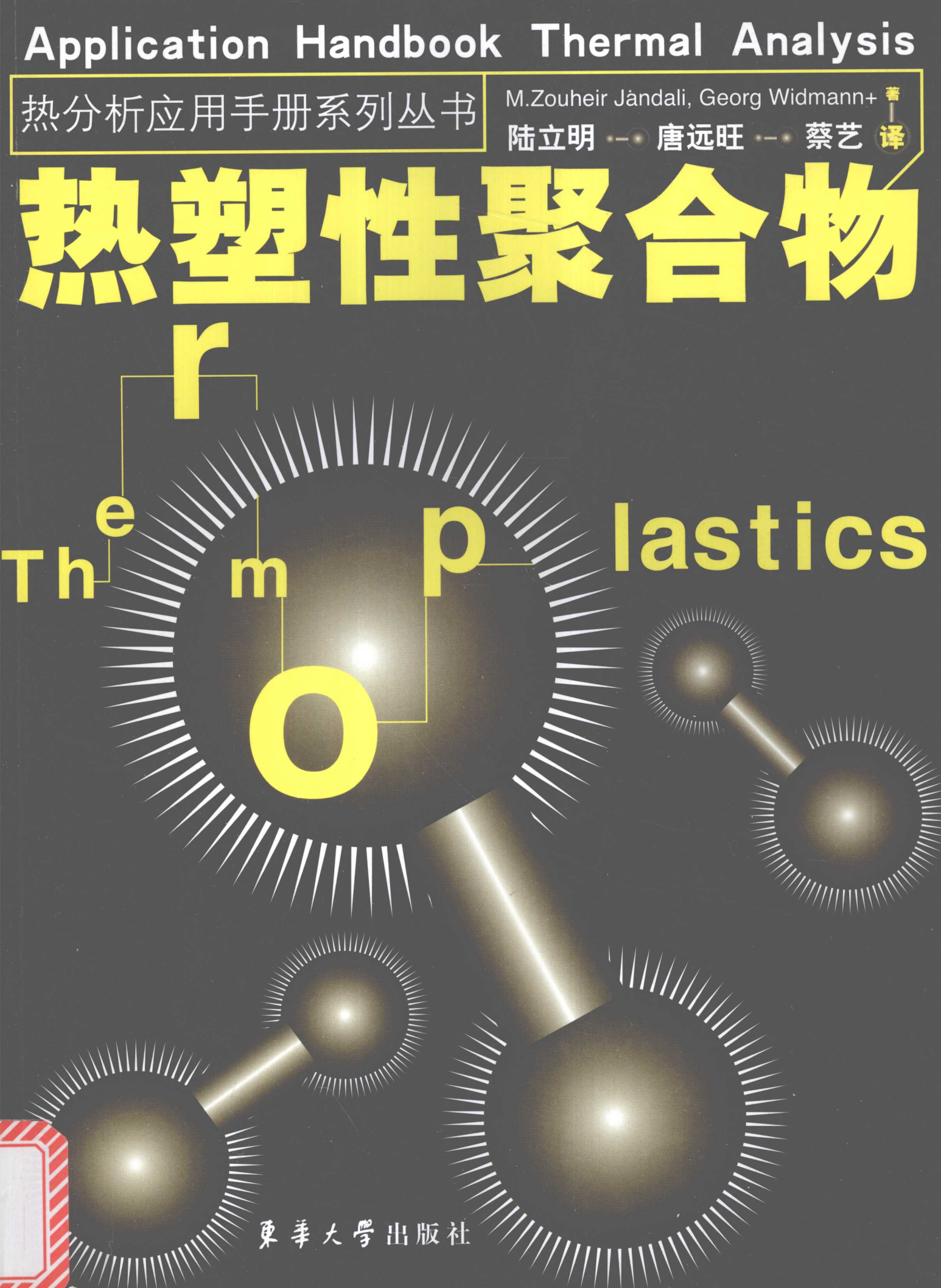
Application Handbook Thermal Analysis

热分析应用手册系列丛书

M.Zouheir Jandali, Georg Widmann+ 著
陆立明 唐远旺 蔡艺 译

热塑性聚合物

Thermoplastics



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本应用手册提供精选的应用实例。实验由瑞士梅特勒－托利多热分析实验室采用在每个应用中描述的特定仪器完成的，过程严谨，并以最新知识为依据对实验结果进行计算。

然而，这并非意味着读者无需用自己的适合样品的方法、仪器和用途进行亲自测试。由于对实例的效仿和应用是无法控制的，所以我们当然无法承担任何责任。

使用化学品、溶剂和气体时，必须遵循常规安全规范和制造商或供应商给予的使用指南。

This application handbook presents selected application examples. The experiments were conducted with the utmost care using the instruments specified in the description of each application at METTLER TOLEDO Themal Analysis Lab in Switzerland. The results have been evaluated according to the current state of our knowledge.

This does not however absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility.

When chemicals,solvents and gases are used,general safety rules and the instructions given by the manufacturer or supplier must be observed.

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应用列表 Application list

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目 录

1 热分析导论 Introduction to Thermal Analysis

热分析是测试材料的物理和化学性能与温度的函数关系的一类技术的总称。在所有方法中，样品受控于加热、冷却或恒温温度程序。
测试可在不同气氛中进行，通常使用惰性气氛（氮气、氩气、氦气）或氧化气氛（空气、氧气）。某些情况下，在测试中气体从一种气氛切换到另一种气氛。有时另一个可选择变化的参数是气体压力。

Thermal analysis is the name given to a group of techniques used to measure the physical and chemical properties of materials as a function of temperature. In all these methods, the sample is subjected to a heating, cooling or isothermal temperature program.
The measurements can be performed in different atmospheres. Usually either an inert atmosphere (nitrogen, argon, helium) or an oxidative atmosphere (air, oxygen) is used. In some cases, the gases are switched from one atmosphere to another during the measurement. Another parameter sometimes selectively varied is the gas pressure.

DSC 还可与能同步观察样品的仪器联用（DSC 显微镜方法）或用不同波长的光照射（光量热法）。

DSC can also be used in combination with instruments that allow the sample to be simultaneously observed (DSC microscopy) or exposed to light of different wavelengths (photocalorimetry).

1.1 差示扫描量热法(DSC) Differential Scanning Calorimetry

在 DSC 中，测量样品吸收和放出的热量。DSC 可用于研究物理转变（玻璃化转变、结晶、熔融和挥发成分的蒸发）和化学反应这样的热效应，所获得的信息表征样品的热性能和组成。此外，还可测定热容、玻璃化转变温度、熔融温度、反应热和反应程度这样的性能。

In DSC, the heat flow to and from the sample is measured. DSC can be used to investigate thermal events such as physical transitions (the glass transition, crystallization, melting, and the vaporization of volatile compounds) and chemical reactions. The information obtained characterizes the sample with regard to its thermal behavior and composition. In addition, properties such as the heat capacity, glass transition temperature, melting temperature, heat and extent of reaction can also be determined.

1.1.1 常规 DSC Conventional DSC

常规 DSC 采用线性温度程序，样品和参比物（或只是空坩埚）以线性速率加热或冷却，或在某些情况下保持在恒定温度（即恒温）。经常几部分程序即所谓的程序段连接在一起生成一个完整的温度程序。聚合物的典型 DSC 曲线如图 1.1 所示。
测试开始时曲线上的变化是由于初始的“启动偏移”（1）。在该瞬变区域，状态突然从恒温模式变为线性升温模式。启动偏移的大小取决于样品热容和升温速率。在玻璃化转

Conventional DSC employs a linear temperature program. The sample and reference material (or just an empty crucible) are heated or cooled at a linear rate, or in some cases, held at a constant temperature (i. e. isothermally). Often several partial programs or so-called segments are joined together to form a complete temperature program. A typical DSC curve of a polymer is shown schematically in Figure 1.1.
The change in the curve at the beginning of the measurement is due to the initial “startup deflection” (1). In this transient region, the conditions suddenly change from an isothermal mode to a linear heating mode. The magnitude of the startup deflection depends on the heat capacity of the sample and the heating rate.

变区(2),样品的热容增加,因而可观察到一个吸热台阶。冷结晶(3)发生在玻璃化转变以上。结晶容易的聚合物被加热至熔点以上,然后骤冷以遏制微晶的形成。这样的聚合物在玻璃化转变之上重结晶。继续加热时,发生熔融(4)。在较高的温度开始分解(6)。在熔融和分解之间有些物质可能汽化(5)。

实验中使用的保护气氛的种类经常对涉及的反应有影响。

At a glass transition (2), the heat capacity of the sample increases and therefore an endothermic step is observed. Cold crystallization(3) occurs above the glass transition. Polymers that crystallize readily are heated to above the melting point and quench-cooled to suppress the formation of crystallites. Such polymers recrystallize above the glass transition. On further heating, melting (4) takes place. At higher temperatures, decomposition (6) begins. Some substances may vaporize(5) between the melting and decomposition.

The type of purge gas used in the experiment often has an influence on the reactions involved.

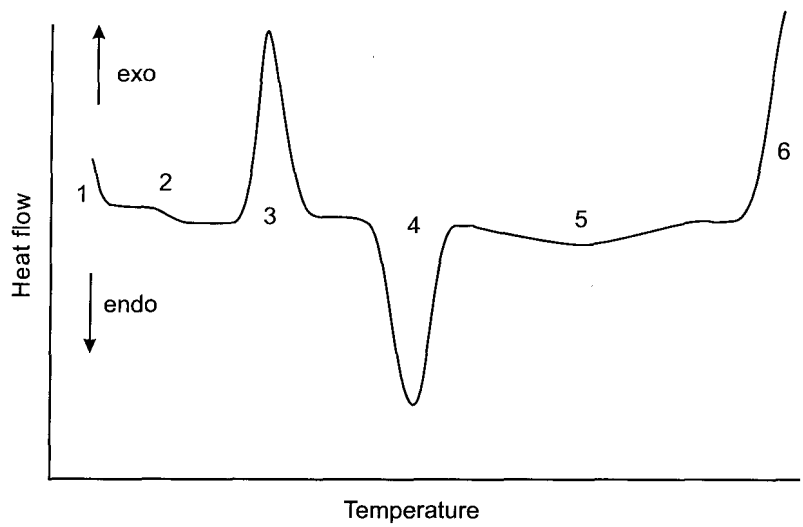

图 1.1 图示聚合物 DSC 曲线:1 初始启动偏移;2 玻璃化转变;3 冷结晶;4 熔融;5 汽化;6 分解

Fig. 1.1 Schematic DSC curve of a polymer: 1 initial startup deflection; 2 glass transition; 3 cold crystallization; 4 melting; 5 vaporization; 6 decomposition

转变和反应可通过冷却样品和再次测试它来区分——化学反应是不可逆的,而熔化了的结晶材料当冷却或二次加热时会重新结晶。玻璃化转变也是可逆的,但经常在玻璃化转变的第一次加热测试中观察到的焓松弛是不可逆的。

Transitions and reactions can be differentiated by cooling the sample and measuring it again-chemical reactions are irreversible whereas crystalline materials melt then crystallize again on cooling or on heating a second time. Glass transitions are also reversible but not the enthalpy relaxation often observed in the first heating measurement of a glass transition.

1.1.2 温度调制 DSC Temperature- modulated DSC

1.1.2.1 ADSC

调制 DSC(ADSC)是一种特别类型的温度调制 DSC(TMDSC)。与常规 DSC 不同,小周期温度变化叠加在线性温度程序上。温度程序的特

Alternating DSC (ADSC) is a particular type of temperature-modulated DSC (TMDSC). In contrast to conventional DSC, the linear temperature program is overlaid with a small periodic temperature change. The temperature program is characterized

征为基础加热速率、温度振幅和周期性变化温度的持续时间(图 1.2)。采用准恒温测试,基础加热速率也可为零。

by the underlying heating rate, the temperature amplitude and the duration of the periodically changing temperature (Fig. 1.2). With quasi-isothermal measurements, the underlying heating rate can also be zero.

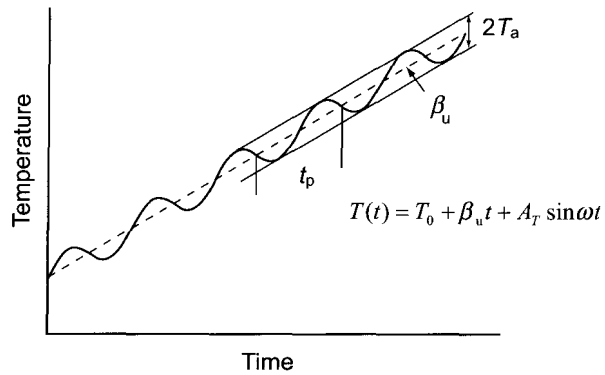

图 1.2 典型 ADSC 温度程序:β_U 为基础加热速率,A_T 为温度振幅,t_P 为周期,$2\pi/P$ 为角频率 ω,P 为正弦波的周期

Fig. 1.2 Typical ADSC temperature program: β_U is the underlying heating rate, A_T the temperature amplitude, t_P period, The angular frequency ω is defined as $2\pi/P$ where P denotes the period of the sine wave.

由于温度的调制,所测得的热流呈周期性变化。该热流能分离成两部分,如图 1.3 所示。信号平均生成基本信号(总热流),它相当于常规

As a result of temperature modulation, the measured heat flow changes periodically. This can be separated into two parts as shown in Figure 1.3. Signal averaging yields the underlying signal (total heat flow), which corresponds to the conventional DSC

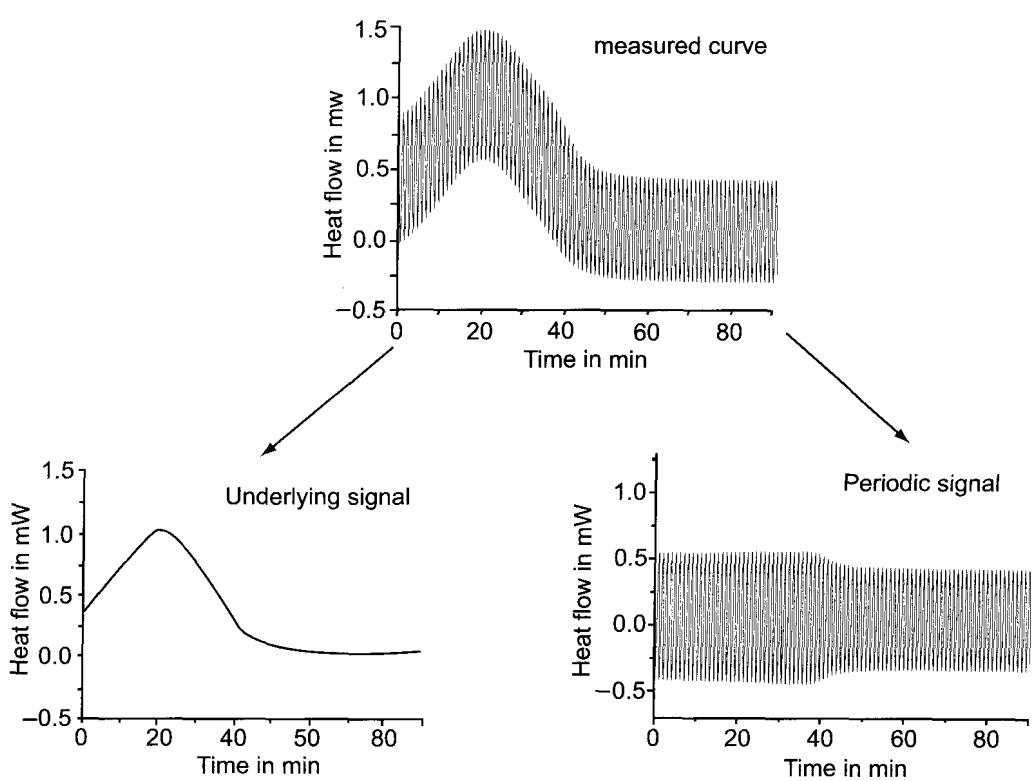

图 1.3 测得的 ADSC 曲线分离成基础和周期性信号成分

Fig. 1.3 Separation of the measured ADSC curve into the underlying and the periodic signal components

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DSC 曲线。作为附加信息，还得到周期性信号成分。可逆热流为能够直接跟上加热速率变化的热流成分，从同相比热计算得到。总热流与可逆热流的差值得到不可逆热流。本技术的一个优势是能将同时发生的过程分开。例如，化学反应过程中的热容变化可直接测量。

curve. As additional information, one also obtains the periodic signal component. The reversing heat flow corresponds to the heat flow component that is able to follow the heating rate change directly and is computed from the in-phase heat capacity. The difference between the total heat flow and the reversing heat flow yields the non-reversing heat flow. One advantage of this technique is that it allows processes that occur simultaneously to be separated. For example, the change in heat capacity during a chemical reaction can be measured directly.

ADSC 曲线的数值计算基于傅立叶分析。复合比热 c_p^* 的模量用下面的等式计算：

The evaluation of the ADSC curves is based on Fourier analysis. The modulus of the complex heat capacity c_p^* is calculated using the equation,

$$|C_p^*| = \frac{A_\Phi}{A_\beta} \cdot \frac{1}{m}$$

式中 A_Φ 和 A_β 为调制热流和加热速率的振幅，m 为样品质量。ADSC 热流信号与加热速率之间的相角用于计算同相 c_p。

where A_Φ and A_β denote the amplitudes of the modulated heat flow and heating rate, and m the sample mass. The phase angle between the ADSC heat flow signal and the heating rate is used to calculate the in-phase c_p.

1.1.2.2 IsoStep

IsoStep 是一种特殊类型的温度调制 DSC。在该方法中，温度程序由很多开始和结束为恒温段的动态程序段组成(图 1.4)。

IsoStep is a special type of temperature-modulated DSC. In this method, the temperature program consists of a number of dynamic segments that begin and end with an isothermal segment (Fig. 1.4).

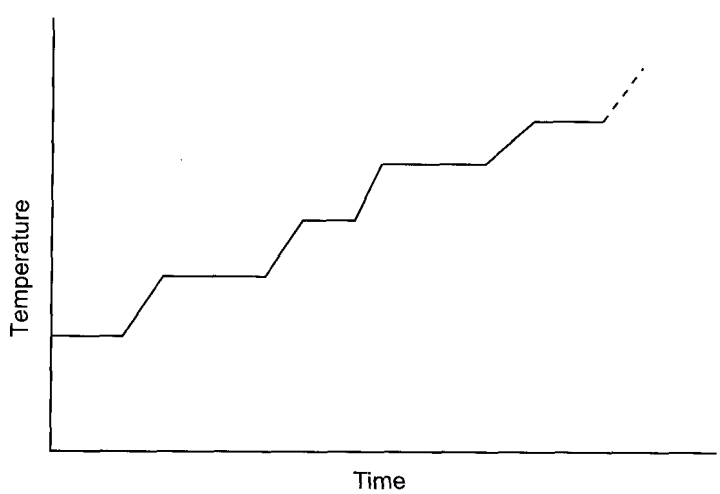

图 1.4 IsoStep 温度程序由不同的恒温和动态段组成

Fig. 1.4 IsoStep temperature program consisting of different isothermal and dynamic segments

恒温段能让动态段的恒温漂移获得修正，结果得到更好的热容准确性。恒温台阶还可能包含动力学信息，

The isothermal segments allow the isothermal drift of the dynamic segments to be corrected. This results in better heat capacity accuracy. The isothermal step may also contain kinetic

例如化学反应。比热可用蓝宝石参比样进行测定，而动力学效应能从热容变化中分离开。

information, for example of a chemical reaction. Heat capacity determinations can be made using a sapphire reference sample, and kinetic effects can be separated from changes in heat capacity.

1.1.2.3 TOPEM™

TOPEM™是高级温度调制 DSC 技术，基于对 DSC(仪器和样品两者)对随机调制基础温度程序响应的全面数学分析(图 1.5)。由于温度脉冲是随机分布的，系统在宽频范围而不是只在某单一频率(ADSC)内服从于温度振荡。振荡式输入信号(加热速率)和响应信号(热流)的相关分析能得到比常规温度调制 DSC 多得多的信息，不仅能将可逆与不可逆效应分开，而且还能测量样品的准稳态热容和测定频率依赖的热容值。这可用来在一次测试中就区分开频率依赖的松弛效应(例如玻璃化转变)和非频率依赖的效应(例如化学反应)。

TOPEM™ is an advanced temperature-modulated DSC technique that is based on the full mathematical analysis of the response of a DSC (both the apparatus and the sample) to a stochastically modulated underlying temperature program (Fig. 1.5). Due to the randomly distributed temperature pulses, the system is subjected to temperature oscillations over a wide frequency range and not just at one single frequency (ADSC). An analysis of the correlation of the oscillating input signal (heating rate) and the response signal (heat flow) provides much more information than can be obtained using conventional temperature-modulated DSC. Not only can reversing and non-reversing effects be separated, but the quasi-static heat capacity of the sample is also measured and frequency-dependent heat capacity values are determined. This can be used to distinguish between frequency-dependent relaxation effects (e. g. glass transitions) and frequency-independent effects (e. g. chemical reactions) in one single measurement.

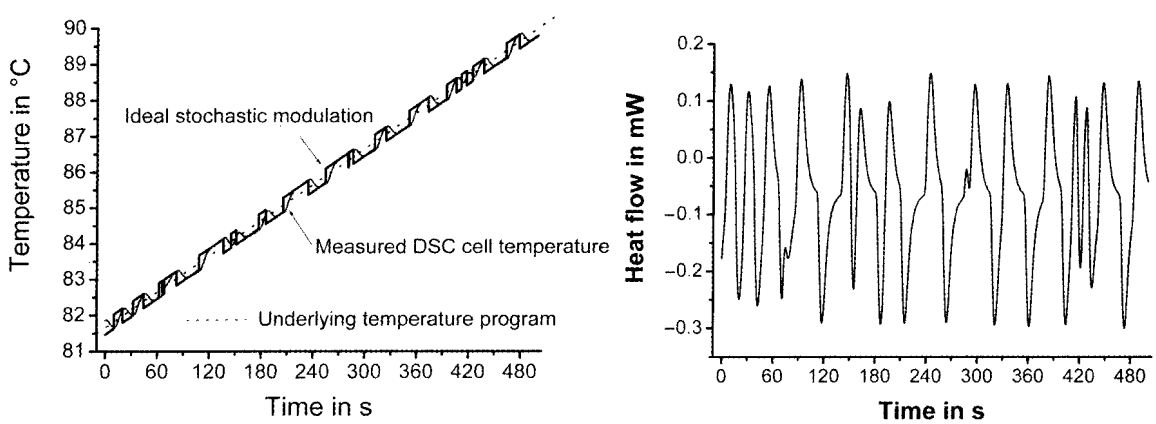

图 1.5 TOPEM™方法中炉体设定值的温度曲线(黑线)，炉体温度(红线)产生在平均值上下变动的加热速率。如右图所示，流向样品的热流也不规则变动。

Fig. 1.5. Temperature curve of the furnace set value (black line) in a TOPEM™ method in which the furnace temperature (red curve) generates a heating rate that fluctuates around a mean value. The heat flow to the sample also fluctuates irregularly as shown in the diagram on the right.

1.2 热重分析(TGA) Thermogravimetric Analysis

当样品被加热时，质量开始减少。失重可能产生于蒸发或有样品生成和逸出气体产物的化学反应。如果

When a sample is heated, it often begins to lose mass. This loss of mass can result from vaporization or from a chemical reaction in which gaseous products are formed and evolved from the

保护气氛不是惰性的，样品还能与气体反应。在某些情况下，样品质量也可能增加，例如在当生成产物是固体的氧化反应中。

在热重分析(TGA)中，测量样品质量的变化与温度或时间的函数关系。

TGA 提供关于样品性能及其成分的信息。如果样品分解产生于化学反应，则样品质量通常呈台阶状变化。台阶出现时的温度可表征该样品材料在所用气氛中的稳定性。

图 1.6 所示为典型的 TGA 曲线。通过分析单独质量台阶的温度和高度能确定材料的成分。

sample. If the purge gas atmosphere is not inert, the sample can also react with the gas. In some cases, the sample mass may also increase, e.g. in an oxidation reaction if the product formed is a solid.

In thermogravimetric analysis (TGA), the change in mass of a sample is measured as a function of temperature or time.

TGA provides information on the properties of the sample and its composition. If the sample decomposes as a result of a chemical reaction, the mass of the sample often changes in a stepwise fashion. The temperature at which the step occurs characterizes the stability of the sample material in the atmosphere used.

Figure 1.6 shows a typical TGA curve. The composition of a material can be determined by analyzing the temper-atures and the heights of the individual mass steps.

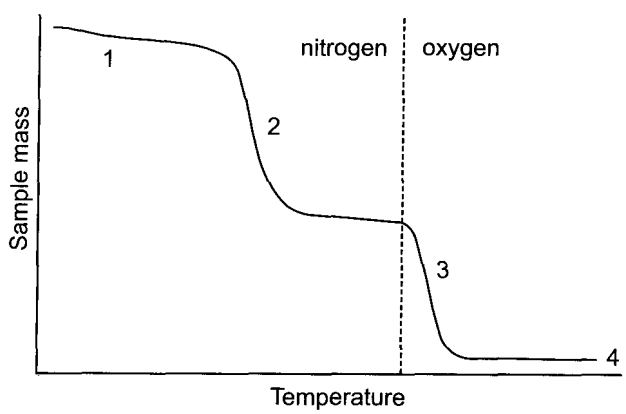

图 1.6　图示 TGA 曲线：1 由于挥发性成分蒸发导致的失重；2 在惰性气氛中的热解；3 当切换到氧化气氛后的碳黑燃烧；4 残留物。

Fig. 1.6　Schematic TGA curve: 1 loss of mass due to the vaporization of volatile components; 2 pyrolysis in an inert atmosphere; 3 combustion of carbon on switching from an inert to an oxidative atmosphere; 4 residue.

像水、残留溶剂或添加油这样的挥发性化合物在相对低的温度逸出。这样的化合物的排除取决于气体压力，在低压下(真空)，相应的失重台阶移到低温，就是说，蒸发加速。分析在惰性气氛中的热解反应能确定含量(从台阶高度)，甚至能确定材料的种类。

样品的碳黑或碳纤维含量可从切换到氧气气氛后的燃烧台阶的高度确定。残留填料、玻璃纤维和灰分由残留物台阶确定。测试曲线上由于浮力效应和气流速率而产生的小变

Volatile compounds such as water, residual solvents or added oils are evolved at relatively low temperatures. The elimination of such components depends on the gas pressure. At low pressures (vacuum), the corresponding mass loss step is shifted to lower temperatures, that is, vaporization is accelerated. The analysis of pyrolysis reactions in an inert atmosphere allows the content (from the step height) and possibly even the type of material to be determined.

The carbon black or carbon fiber content of a sample can be determined from the height of the combustion step after switching to an oxidative atmosphere. The residual filler, glass fiber or ash is determined from the residue. Small changes in the measurement curve due to buoyancy effects and gas flow rate can

化，可通过减去空白曲线得到修正。

TGA 测试常常用 TGA 曲线的一阶微分（称为 DTG 曲线）显示。于是，TGA 曲线上由质量损失所致的台阶在 DTG 曲线上以峰形呈现。DTG 曲线相当于样品质量变化的速率。

分解台阶的温度范围在一定程度上受到气体产物扩散出样品的容易性的影响。当使用反应性气体时，样品表面气体交换的效率是关键。可以使用合适的坩埚（例如，30μL 氧化铝坩埚这样的低壁高坩埚）和合适形状的样品（几个小颗粒或粉末）来降低测试时的扩散效应。

在 TGA 中，样品质量的变化被非常准确地测量。然而令人遗憾的是该技术不提供关于逸出气体分解产物性质的任何信息。不过用 TGA 与合适的气体分析器偶联（逸出气体分析 EGA），能分析这些产物。

be corrected by subtracting a blank curve.

TGA measurements are often displayed as the first derivative of the TGA curve, the so-called DTG curve. Steps due to loss of mass in the TGA curve then appear as peaks in the DTG curve. The DTG curve corresponds to the rate of change of sample mass.

The temperature range of the decomposition steps is influenced to a certain extent by the ease with which the gaseous products are able to diffuse out of the sample. When reactive atmospheres are used, the efficiency of gas exchange at the surface of the sample is crucial. The effects of diffusion on the measurement can be reduced by using suitable crucibles (e. g. crucibles with low wall-heights such as the 30-μL alumina crucible) and by suitable sample geometry (several small pieces or powder).

In TGA , the change in mass of the sample is measured very accurately. Unfortunately, however, the technique does not provide any information about the nature of the gaseous decomposition products evolved. The products can however be analyzed by coupling the TGA to a suitable gas analyzer (evolved gas analysis, EGA).

1.3 热机械分析(TMA) Thermomechanical analysis

热机械分析测试样品在加热时的尺寸变化，在该技术中，连续测量带一定力且放置于样品表面的探头位置或位移与温度或时间的函数关系。图 1.7 所示为典型的 TMA 曲线。事实上探头施加的压力和样品的硬度决定了 TMA 实验是膨胀还是穿透测试。

在热膨胀测试中，探头在样品表面仅施加低压力。样品在整个相应的温度范围内被线性加热。线性热膨胀系数（CTE）直接从测试曲线计算。

在穿透实验中，探头施加大得多的压力。当对样品加热时，可直接测得样品的软化温度，材料在玻璃化温度处或熔融时软化。

Thermomechanical analysis measures the dimensional changes of a sample as it is heated. In this technique, the position or displacement of a probe resting on the surface of the sample with a certain force is continuously measured as a function of temperature or time. Figure 1.7 shows a typical TMA curve. The pressure exerted by the probe and the hardness of the sample determine whether the TMA experiment is in fact an expansion or a penetration measurement.

In the thermal expansion measurement, the probe exerts only a low pressure on the surface of the sample. The sample is heated linearly over the temperature range of interest. The linear coefficient of thermal expansion (CTE) is calculated directly from the measurement curve.

In a penetration experiment, the probe exerts a much greater pressure. The softening temperature can be directly measured when the sample is heated. Materials soften at the glass transition temperature or on melting.

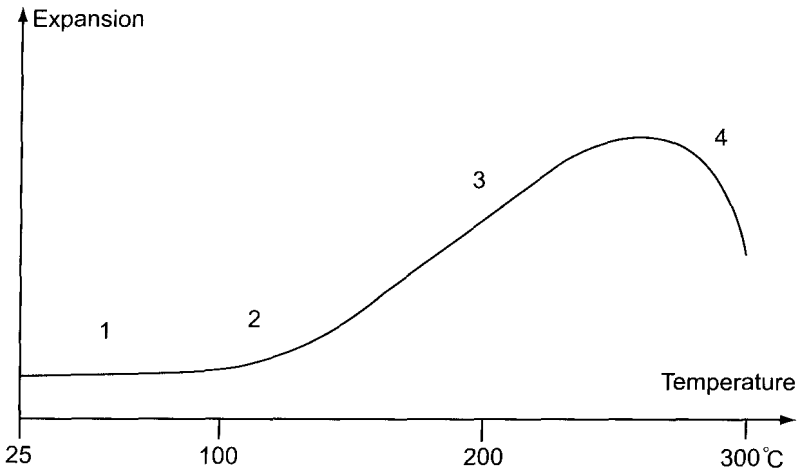

图 1.7　在低压缩应力下聚合物的图示 TMA 曲线：
1 低于玻璃化转变的膨胀；2 玻璃化转变(斜率变化)；3 玻璃化转变以上的膨胀；4 塑性形变

Fig. 1.7　Schematic TMA curve of a polymer under low compressive stress: 1 expansion below the glass transition; 2 glass transition (change of slope); 3 expansion above the glass transition; 4 plastic deformation

如果对样品施加周期性变化的力，样品尺寸也周期性变化。该测试模式称为动态负载 TMA，DLTMA，提供关于聚合物的粘弹行为的信息。从振幅和样品厚度能估算出样品的弹性模量(杨氏模量)。

使用弯曲附件，用此技术还能测量硬样品的弯曲行为。

可用专门的样品支架测量纤维和薄膜的尺寸变化。一个独特的应用是测量材料在溶剂中的溶胀行为。为此，样品放入一个小容器内，加入相应的溶剂，于是，在恒温下连续测量由于溶剂吸收导致的样品厚度随时间的变化。

If a periodically changing force is applied to the sample, the sample dimensions also change periodically. This measurement mode is called dynamic load TMA, DLTMA, and provides information on the viscoelastic behavior of polymers. The elastic modulus (Young'. s modulus) of the sample can be estimated from the amplitude and the sample thickness.

It is also possible to measure the bending behavior of hard samples with this technique using a bending accessory.

Special sample holders are available that allow the dimensional changes of fibers and films to be measured. A particular application is the measurement of the swelling behavior of materials in solvents. To do this, a sample is placed in a small container and the solvent of interest is added. The change in thickness of the sample due to solvent absorption is then contin-uously measured isothermally as a function of time.

1.4　动态热机械分析(DMA)　Dynamic Mechanical Analysis

在动态热机械分析中，测定动态模量与温度、频率和振幅之间的函数关系。

施加于样品的周期性(通常为正弦)变化的力在样品中产生周期性的应力。样品对该应力作出反应，仪器测量相应的形变行为，由应力和形变测定机械模量 M。无论测量剪

In dynamic mechanical analysis, a mechanical modulus is determined as a function of temperature, frequency and amplitude.

A periodically changing force (usually sinusoidal) appliedto the sample creates a periodic stress in the sample. The sample reacts to this stress and the instrument measures the corresponding deformation behavior. The mechanical modulus, M, is determined from the stress and deformation. Depending on the

切模量 G（施加剪切应力）还是杨氏模量 E（拉伸或弯曲），均取决于所加应力的类型。

样品不总是对周期性变化的应力作出瞬间响应——依赖于样品的粘弹性而发生一定时间的滞后。这是产生施加应力和形变之间相位移的原因。将相位移考虑进去，动态测得的模量用实数部分 M′和虚数部分 M″来描述。实数部分（储能模量）描述与周期性应力同相的样品响应，它是样品（可逆的）弹性的量度。虚数部分（损耗模量）描述相位移为 90°的响应部分，它是转化为热（因而不可逆地损失了）的机械能量的量度。相位移的正切 tan δ 还被称作损耗因子，是材料阻尼性能的量度。模量和 tan δ 依赖于温度和测试频率。在室温下，橡胶的典型储能模量在 0.1MPa 至 10MPa 之间。

图 1.8 中的曲线显示了无定形和半结晶聚合物的储能和损耗模量与温度函数关系的典型行为。

type of stress applied, either the shear modulus, G (with shear stress) or the Young's modulus, E (with stretching or bending) is measured.

The sample does not always immediately react to the periodically changing stress-a certain time delay occurs that depends on the viscoelastic properties of the sample. This is the cause of the phase shift between the applied stress and the deformation. To take this phase shift into account, the dynamically measured modulus is described by a real part M′ and an imaginary part M″. The real part (storage modulus) describes the response of the sample in phase with the periodic stress. It is a measure of the (reversible) elasticity of the sample. The imaginary part (loss modulus) describes the component of the response that is phase-shifted by 90 °. This is a measure of mechanical energy converted to heat (and therefore irreversibly lost). The tangent of the phase shift, tanδ, is also known as the loss factor and is a measure of the damping behavior of the material. The modulus and tan δ depend on the temperature and the measuring frequency. At room temperature, rubbery materials show typical storage modulus values between 0.1 MPa and 10 MPa.

The curves in Figure 1.8 show the typical behavior of the storage and loss modulus of an amorphous and a semicrystalline polymer as a function of temperature.

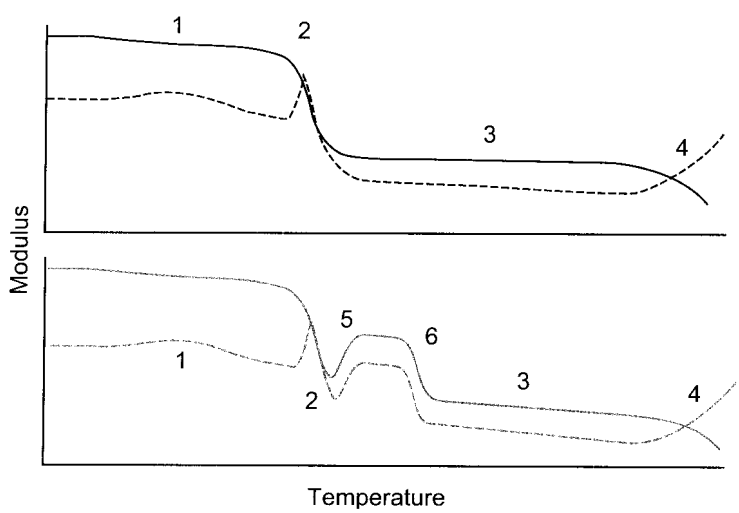

图 1.8　无定形聚合物（蓝色）和淬火冷却的部分结晶聚合物（红色）的储能模量 M′（实线）和损耗模量 M″（虚线）与温度的函数关系的典型曲线：1 次级松弛；2 主松弛；3 橡胶态（高弹态）；4 粘性流动；5 冷结晶；6 熔融。

Fig. 1.8　Typical curves of the storage component (continuous line) and the loss component (dashed line) of the modulus as a function of the temperature for an amorphous polymer (blue) and a shock-cooled partially crystalline polymer (red): 1 secondary relaxation; 2 main relaxation; 3 rubbery plateau; 4 viscous flow; 5 cold crystallization; 6 melting

在低温时，材料处于玻璃态，模量相对高（约 2GPa）。在该状态下常常

At low temperatures the material is in a glassy state. The modulus is relatively high (about 2GPa). In this state, a

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