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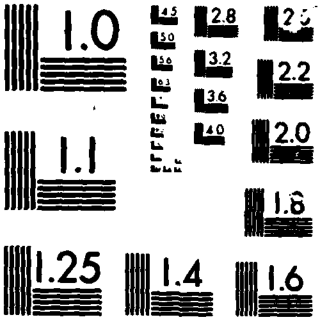

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THERMAL BEHAVIOR OF POLYPHOSPHAZENES
IN RELATION TO STRUCTURE

by

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Thermal Behavior Of Polyphosphazenes In Relation To Structure

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Differential scanning calorimetry has been employed to characterize polyphosphazene homopolymers. Thermal analysis provided a qualitative and quantitative description of the magnitude of the enthalpies of transition at Tg, T(1) and Tm and the relative change in these temperatures with heating, cooling and time of annealing, too. Aryloxy and alkoxy homopolymers were investigated. Changes in morphology and crystallinity were correlated with thermodynamic parameters to provide a basic understanding of mesophase formation and the conditions which influence the behavior of these flexible liquid crystal-forming macromolecules which have considerable potential technologically.

KEY WORDS: DSC thermal properties, specific heat, enthalpy of transition, crystallinity, mesophases, morphology.

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Differential scanning calorimetry has been employed to characterize polyphosphazene homopolymers. Thermal analysis provided a qualitative and quantitative description of the magnitude of the enthalpies of transition at Tg, T(1) and Tm and the relative change in these temperatures with heating, cooling and time of annealing, too. Aryloxy and alkoxy homopolymers were investigated. Changes in morphology and crystallinity were correlated with thermodynamic parameters to provide a basic understanding of mesophase formation and the conditions which influence the behavior of these flexible liquid crystal-forming macromolecules which have considerable potential technologically.

Key words: DSC thermal properties, specific heat, enthalpy of transition, crystallinity, mesophases, morphology.

THERMAL BEHAVIOR OF POLYPHOSPHAZENES IN RELATION TO STRUCTURE

INTRODUCTION

The thermal and physical properties of polyphosphazenes have received much attention in recent years.(1-4) Much of the interest centers around their mesomorphic nature as it relates to morphology and chemical constitution.(5-8) Dynamic mechanical,(9) nmr,(10) i.r. and Raman spectroscopy,(11) calorimetric (DSC) analysis,(2,6) birefringence,(3,12) optical and SEM microscopy,(13) x-ray analysis (wide(5,14) and small angle(15)), electron microscopy(16) feature among many of the techniques employed to investigate morphology-structure relationships in these interesting polymeric materials. Crystallization from the melt and solution feature amongst these studies. However, the broad high-molecular weight distributions associated with synthesis(7,17,18) by melt polymerization have been overcome to a degree by using solution polymerization techniques where distributions are narrower, but still not free of complications. Anyhow, these materials(19,20,21) have proved to be interesting technologically and challenging, particularly from the viewpoint of their transitional and structural changes involved with aryloxy and alkoxy homopolymers. In this regard, the present article presents an overall interpretation of the changes in morphology and in thermal physical properties associated with the glass transition, Tg, mesophase transition, T(1), and melting temperature, Tm, in typical polyphosphazene samples. A study of time effects in relation to observed phase transformations, assessed qualitatively and quantitatively by

DSC, has been instrumental in providing a clearer picture of the underlying factors associated with Tg, and the two first order transitions, T(1) and Tm, as well as the magnitude of the corresponding parametrical changes and their interrelationships with structure in polyphosphazenes.

EXPERIMENTAL

A. MATERIALS

The polymers used in this work were obtained from several sources listed in Table 1. Most polyphosphazene samples were melt polymerized,(22) of high average molecular weight ($\bar{M} \geq 10^5$), and they had broad M.W. distribution (often $\bar{M}_W/\bar{M}_N \geq 10$). However, samples 2(a) and 2(b) were obtained by solution polymerization(23) and were therefore of narrower M.W. distribution ($M_W/M_N <$ 3.0).

B. DIFFERENTIAL SCANNING CALORIMETRY

A Perkin-Elmer DSC2 calorimeter with a scanning auto zero was used to measure the thermal properties of polyphosphazene samples as a function of temperature in the range of T_g, T(1), and T_m, respectively. Annealing experiments were carried out in situ in the DSC apparatus where the specimens were held at desired temperatures for up to 30 minutes duration before scanning. The effects of thermal history on thermal transition behavior were investigated by scanning the same samples as many as 7 cycles sometimes. The kinetics of recrystallization were also studied for PBFP specimens by cooling the melts from above T_m to below T(1), using various cooling rates specified in the text. For T_g measurements, liquid nitrogen or dry ice/alcohol coolant was used (depending on the temperature range).

The DSC output was digitized and stored in the IBM PC computer for subsequent data analysis. Thermal transitions, such as the glass transition, the thermotropic T(1) transition, and the final melting point, T_m, and their associated thermal property changes are illustrated schematically in Figure 1. All the heating rates used in this study are 10 K/min; cooling rates were varied as required. In other investigations various heating and cooling rates have been reported.(2,5) The DSC instrument was calibrated according to recommended procedures (24).

RESULTS AND DISCUSSIONS

A. ANNEALING

Annealing experiments conducted at temperatures in the vicinity of T(1) were made using PBFP samples (designated as specimen 1 in Table 1). Samples were kept in the DSC sample holder at the desired temperatures for 30 minutes, then cooled down to room temperature and reheated. The heating curves* of these annealed PBFP samples are shown in Figure 2.

The heating curve for the original, unannealed sample (curve 1) shows a single peak with a small "bump" preceeding the T(1) peak. This bump develops into a small peak and tends to move to a higher temperature while the position of the main peak remains unchanged as the annealing temperature is increased (curve 2 and 3). At an annealing temperature of 333 K, both peaks seem to merge and appear as a single peak (curve 4). A significant shift in the T(1) temperature does not occur until the annealing temperature is raised higher than the T(1) temperature of the original sample (339 K). The increase in the magnitude of T(1) by thermal analysis seems to be abrupt about 349 K (Figure

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*"Curve" and "run" are used interchangeably.

2). Annealing at temperatures above this value and as high as 398 K (curve 6) show no further change in peak position. Other work (15) particularly using SAXS substantiates a jump in crystallite size whenever the T(1) region is traversed. Curve 7 represents the heating curve for a PBFP specimen which had previously undergone 5 heating-cooling cycles between 295 K and 423 K prior to this recorded scan. In this example, the T(1) peak is just as sharp as it is in curve 6, but the T(1) temperature is 2 K lower.

It has been well established that in crystalline homopolymers, the molecules can reorganize themselves upon annealing through partial melting and subsequent recrystallization. The development of the small peak and the T(1) increase, plus the improvement in sharpness of T(1) peaks are indeed a clear manifestation of structural reorganization in this thermotropic polyphosphazene. The ease with which morphological reorganization occurs depends upon the mobility of polymer chains in the condensed state. Along these lines the marked increase in T(1) temperature on the curve 5 is then due to the fact that the sample was annealed at a temperature higher than the thermotropic T(1) transition and the mobility of PBFP molecules is suddenly enhanced.

A conceptual difference, however, exists here for PBFP specimens and most of other polyphosphazene polymers which exhibit a thermotropic T(1) transition. The crystalline structure in PBFP samples can be improved by annealing the sample at a temperature above this first-order transition. A conventional polymer would have become completely disordered and molten at its first-order transition, T_m.

Studies using electron microscopy and x-ray diffraction techniques have revealed that when PBFP crystals are heated through the T(1) transition, a structural change occurs.(5) This transformation involves the formation of a chain extended morphology from a lamellar or chain folded state, and the change is irreversible after heating and then cooling the specimen from above T(1). Thus, reorganizational behavior below T(1) is somewhat analogous to structural behavior observed in conventional polymers, where the smaller or less stable crystals "melt" and then recrystallize from crystal "remanents" which most probably act as the seeds for this transformation process. For PBFP samples annealed above T(1), the results indicate that new structures are being created and controlled by thermodynamics which "push" the transformation towards it lowest free energy state. Above T(1) the 2-D chain-extended crystals still maintain some of the structural integrity, which pre-existed in the original 3-D state below the T(1) transition. Here this structure is more closely packed by some 6%, which is the overall volume change at T(1) itself(3). Relaxation of PBFP chains occurring at T(1), is believed by some authors,(10) to be a dynamic equilibrium which is enhanced by alignment in the chain direction. At the same time as the crystal modification changes from α orthorhombic to δ pseudohexagonal there is a substantial change (increase) in the entropy of the polymer derived from the side group disordering which occurs upon traversing this transition(5,12,13,15). Since most polyphosphazenes exhibit two first-order transitions (T(1) and T_m), the kinetics of the reorganizational processes which take place in the vicinity of T(1) and T_m, respectively, are important in so far as an understanding of the thermal behavior of these polymers is concerned. This topic will be discussed later in this article. However, it is appropriate now to address another aspect of chain mobility.

B. GLASS TRANSITION AND CHANGE OF SPECIFIC HEAT

Results of glass transition and the concomitant specific heat changes are shown as curves in part (a) of Figures 3 → 6 for samples 3 → 6. The T_g

temperature, ΔCp (Tg) value, and thermal history for specimens are listed in Table 2. Samples investigated were PBPP and PBMPP polymers. Each figure shows the heating curves for a polymer sample which underwent a series of heating and cooling treatments. Since some polyphenoxyphosphazenes PBPP and PPMPP polymers are reported (2) to decompose at temperatures not far below their respective melting points, the final high temperature heating runs were the last performed for each of the samples. Check runs were always made with fresh samples to establish whether or not deterioration had occurred.

Some general trends have been observed here. First, the T_g temperature <u>per se</u> remains virtually unaltered upon heating-cooling cycles through T(1) (but at temperatures still well below T_m), showing that the T_g is insensitive to cooling rates. Samples previously heated through their reported decomposition temperature, T_D, showed a decrease in the T_g temperature (see Table 2 and appropriate figures for PBPP sample 3 and PPMPP sample 5) when they were rerun through T(1). Noticeable decomposition seemed to occur in some of these samples presumably because of products formed which may act as plasticizers. On the other hand, for samples also heated to high temperatures (well above T(1)) but still below T_D (see Table 2 and appropriate figures for PBPP, sample 4 and PBMPP, sample 6), do show some increase in the value of T_g. Whenever decomposition is suscepted, it is accompanied by a change in the T(1) peaks. This aspect of the work will be discussed later.

The specific heat change at T_g, $\Delta Cp(T_g)$, decreased upon heating-cooling cycles through T(1). For all polymer specimens (with the exception of PBPP, sample 3), a marked decrease in $\Delta Cp(T_g)$ was found on the second heating run. The values in the parentheses indicate the relative changes with respect to the first heating run which is used as the reference basis. Convincingly, the structural transition from a lamellar or chain-folded morphology(5,12,15), to a chain-extended form*, crystallinity, occurs in these samples on their first heating run through T(1). Subsequent heating-cooling cycles simply perfects the crystalline order associated with the chain extended morphology. Other evidence from creep(3) and dynamic mechanical(9) (DM) measurements support the fact that crystallinity is enhanced whenever heating-cooling cycling takes place through $T_{(1)}$. For instance, the magnitude of DM tan δ values in crystalline polyphosphaszenes, decreased upon heat treatment. ΔC_p changes in like manner, but it is noted that $\Delta C_p(T_g)$ can be eliminated as the crystallinity tends to high values (probably above 90%).

C. T(1) TRANSITION AND ENTHALPY CHANGE AT T(1), ΔH(T(1)

T(1) transition results obtained upon heating-cooling treatments are shown in part (b) of Figures 3 - 6. Table 2 lists peak temperatures and ΔH(T(1) values, and thermal histories for samples 3 - 6. Note however, the difference in specific heat scale between part (a) and part (b) in each of these figures.

The results reveal that all the original materials (as precipitated from solution) have a wide range of crystallite size distribution, which was obtained from two sources: (i) probably caused by or is related to a broad M.W. distribution and (ii) to the crystallization conditons which these samples have experienced. Neither slow heating rates nor sample evacuation overnight changed this situation. Hence sample quality was unchanged by this treatment. PBPP sample 3 showed a peak with a right shoulder, whereas two distinct peaks were observed on the first heating curve of PPMPP sample 6.

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*Not necessarily fully extended. Note especially that sample 3(a) (PBPP) did not exhibit either a T_g nor a noticeable ΔC_p (T_g) as indicated by run 5 in Table 2 and in Figure 3. This behavior is consistent with other experimental work where it was noted(3,15) that specimens became friable or brittle in line with their much enhanced crystallinity (see p. 8, this article).

Other samples showed broad peaks in the initial heating runs. The right shoulder in Figure 3 grows into a small peak which also moves, along with the main peak, to a higher temperature as the sample is reheated sequentially. Three peaks were observed, sometimes. In samples with two or three peaks, the high temperature one always continues to grow at the expense of the low temperature peaks. While the T(1) transition shifted toward a higher temperature it was noted that its main peak also became sharper. The enthalpy change associated with the T(1) transition, ΔH(T(1)) increases significantly too, sometimes reaching a value three times as large as is found for the original material (see Table 2). Relatively, the biggest increase in ΔH(T(1)) was found on the second run. Signs of decomposition are noticeable in the last heating run of Figure 5, when sample 5 (PBMPP) was heated well above T_D and cooled again, to show three low peaks and a ΔH(T(1)) value which is also significantly lowered.

D. CRYSTALLINE PERFECTION AND CRYSTALLINITY

An unanswered question, frequently raised concerns the mechanisms that contribute to the large increases in the T(1) and ΔH(T(1)) values respectively. These may affect crystalline perfection, as well as crystallinity. The magnitude of the $\Delta Cp(T_g)$ and the ΔH(T(1)) values recorded in Table 2, suggest that both crystalline perfection and crystallinity probably improve simultaneously here, even in a cooperative manner. Based upon the assumption that $\Delta C_p(T_g)$ and ΔH(T(1)) are proportional to the amounts of amorphous and crystalline phases respectively, then one can estimate sample crystallinity.

One can relate $\Delta C_p(T_g)$ and ΔH(T(1)) using the following equations

$$\Delta C_p(T_g) = K_1 \ (1 - X_c) \qquad (1)$$

$$\Delta H(T(1)) = K_2 X_c \qquad (2)$$

$$\Delta C_p(T_g) = K_1 \left[1 - \frac{\Delta H(T(1))}{K_2}\right] \qquad (3)$$

where K_1 and K_2 are proportionality contants and X_c is the degree of crystallinity in the sample. Once K_1 and K_2 are obtained for a particular sample, heat treated in different ways, then X_c may be estimated. Taking sample 4, (PBPP) as an example, the starting material may consist initially of 34% crystalline and 66% amorphous phases. After cycling the sample 3 times through T(1), it now reaches about 93% crystallinity (i.e., just over 2.8 its original value; see Table 2) and about 7% amorphous phase (i.e., reduced by just under 10% in this step).

It is interesting that $\Delta C_p(T_g)$ of sample 3(a) is absent in run 5, Figure 3, thus implying that the crystallinity of this sample is probably close to 100%. Other polyphosphazene samples exhibiting similar properties have been investigated, too. Despite the fact that the T(1) transition is usually accompanied by changes in crystal modifications supported by x-ray measurements (5) which may alter ΔH(T(1)) values, rough estimations made here, based upon thermal methods, indicates that all the starting materials employed in this study are of relatively low crystallinity (<40%). On the first run through T(1) and in the subsequent heat treatments, thicker crystalline lamellae are formed facilitated by the substantial volume expansion (6%) through T(1) and by concomitant chain extension which occurs in the mesophase. Meantime, disordering and rearrangement of defects and side group motions occurs facilitating molecular chains extension and subsequent transformation into a higher crystalline state on cooling again. Of the polyphosphazenes investigated, PBPP sample 3, which exhibited the smallest increase in ΔH(T(1)) upon cyclic heating, possessed a relatively higher crystallinity in its initial state before scanning,* as its ΔH(T(1)) value (5.8 cal/g) is very much higher than 2.6 cal/g observed for the starting sample 4 (PBPP) obtained from a different source (even though this value subsequently increased to 7.3 cal/g later upon heating).

E. RECRYSTALLIZATION KINETIC PROCESSES IN PBFP POLYMERS

In the preliminary measurements, we have found that the T(1) value of sample 2(a) or sample 2(b) (which was a PBFP polymer from the same source, see Table 3) is 351 K and is hardly changed (increased less than 3 K) by annealing or cyclic heating specimens several times in the vicinity of T(1). When the sample was heated through T_m and then cooled down, again however, the T(1) transition shifted upon reheating to a temperature ranging from 357 K to 363 K. This actual value depended upon the cooling rates used before the test run. The T(1) temperature was found to be higher whenever a slower cooling rate was employed. These two observations indicate that the 3-D crystalline structure (present at room temperature in PBFP samples) may be controlled by two crystallization processes which occur in the vicinity of T_m and T(1), respectively, and alter sequentially as the sample in its molten state is cooled down from above T_m to below T(1) temperature. Since, the kinetics of recrystallization in these two regions is substantial, their relative importance was investigated. Earlier work(3,16) in this area also prompted a close evaluation of the problem. PBFP polymer was found to be a good candidate for this study since it was thermally stable even at temperatures

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*Probably due to its having been subjected to high temperature.

well above T_m (its T_D temperature is ~ 630 K(2) while T_m temperature was found to be 513 K, in this study).

Figure 7 shows the heating curves for PBPP sample 2(a), where fast cooling rates through T_m were used. Here, T(1) increased by 6 K on the second heating run. Although only a cooling rate of 1.25 K/min through T(1) was used in these heating-cooling cycles, other runs using higher cooling rates through T(1) (not shown here) did not indicate a change in the T(1) temperature by more than 1 K as long as the cooling rate of 160 K/min through T_m is used. Annealing at a temperature about 20 K above T(1) (see curve 3 in Figure 7 and Table 3) simply sharpened the T(1) peak, but its position hardly moved. These curves indicated that fast cooling of the specimen through T_m resulted in broader crystallite size distribution and/or a more defective γ-form.(5) The PBFP T(1) value of 357 K, is 6K higher than is found for the starting material. This is still 6K lower than the highest value (363K) reported above. Recrystallization processes that lead to a more perfect structures are suppported in fact.

Starting from the curve 3 in Figure 8, the cooling rates were reversed so that a slow cooling rate of 1.25 K/min through T_m and a fast cooling rate of 160 K/min through T(1) were used (see Table 3, PBFP sample 2(b) for thermal histories). Afterwards a striking observation was found: the T(1) transition shows two peaks with the higher temperature peak appearing at 363 K. Presumably, the slow crystallization in the vicinity of T_m appears to have been responsible for the segregation of the shorter from the longer molecules. In order to investigate this effect further, the sample was now held at a temperature close to (or sometimes within) the T_m peak for 30 minutes before cooling it down again through T(1). Now, not only did the T(1) transition showed two peaks, but the final melting curve also split into two peaks. Furthermore, upon cooling this sample in the DSC, a T(1) doublet was formed too (not shown). The single T(1) peak of curve 5 is apparently a combination of two peaks as indicated by the corresponding T_m peaks. The last heating run (curve 7 in Figure 8) shows that whenever a sample is cooled rapidly (eg. > 40 K/min) through T_m the T(1) temperature is lowered as a consequence of morphological changes, regardless of the previous history of the PBFP material (which is thermally stable under these conditions).

Several important thermal phenomena in PBFP polymers have been revealed here.* To obtain a higher T(1) temperature (implying a larger crystalline structure exists) a slow cooling rate through T_m must be used. It seems that the first crystallization just below T_m predominantly controls the morphology of the 3-D crystal which later develops upon cooling below T(1). However, once imperfect 2-D crystals are formed from the molten state because of relatively fast cooling, subsequent annealing and heat cycling below T_m cannot eliminate the inherent structural imperfections (incomplete chain extention and various defects, presumably) within a practical time interval of heat treatment (several hours). A lower T(1) peak is a manifestation of this behavior (see, for example, Figure 7). Besides mesostate segregation is precluded as witnessed by the single T_m and T(1) peaks, regardless of the annealing or heat cycling experienced below T_m (Figure 7) in this study. Not only is the T(1) peak dependent on the 3D crystallite size, but the T_m peak still seems to be sensitive to the 2D crystallites in the chain direction as well as domain order/size (5,15). Both of these morphological changes are mutually related.

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*This topic will be further examined in the next section.

F. CORRELATIONS AMONG LAMELLAR THICKNESS, T(1), AND T_m

Other studies using synchrotron radiation (SAXS and WAXS modes) have observed,(15) in situ, an increase in lamellar thickness to levels in excess of 600 Å for PPMPP and other specimens. If the lamellar thickness represents some measure of chain extention, and this in turn substantially determines the T(1) temperature in polyphosphazene polymers; the analogy with the well-known melting point - lamellar thickness relationship(26) for conventional (3D) polymers may give some insights into the kinetic effects discussed above. For example:

$$T_m = T_m^o \left(1 - \frac{K}{\ell}\right) \qquad (4)$$

Where T_m is the observed melting temperature, T_m^o the thermodynamic melting point for the infinite chain, ℓ is the crystal thickness and K is a parameter (often constant)

Extending this methodology we can write for the polyphosphazenes:

$$T(1) = T(1)^o \left(1 - \frac{K'}{\langle \ell' \rangle}\right) \qquad (5)$$

for the 3D → 2D first order transition, where $\langle \ell' \rangle$ is some average crystallite size within the sample.

Thus, shifts which occur in T(1) temperature upon various crystallization conditions imply that the K′ value in equation (2) is a significant parameter. The melting point of PBFP samples only increased by 2K after the first heating run (see Table 3), and then remained at 515 K, virtually unchanged, regardless of subsequent heat treatment so that the analogues (4) and (5) do not apply to T_m. The highest values observed for T(1) (363 K) and

T_m (515 K) imply that some kind of equilibrium structure comprised of highly extended chains, exists under these recrystallization conditions. It has been noted previously that such samples are brittle,(3,9) highly crystalline,(5,13,27) and exhibit a high modulus.(3,9)

Another striking fact is that while ΔH(T(1)) values increase, ΔH(T_m) values are approximately the same (1.0 cal/g) within experimental error (± 0.05 cal/g). The reason for this fact deserves further study although it may appear that the T(1) transition which precedes the T_m transition on the first heating run may have increased the crystallinity in the newly formed, 2-D crystals to such an extent that small changes in ΔH(T_m) value upon heating-cooling cycles are undetectable using DSC measurements, because of limited accuracy here. This ΔH(T_m) change is further illustrated in Figure 9 where the first three curves in Figure 8 are replotted along with their enthalpy curves obtained by integrating the specific heat curves. The molten state was used as a reference level in this analysis. It can be seen that, below T(1), the specific heat for curve 1 is greater than that for either curve 2 or curve 3 which are approximately equal. Note that the three Cp-T curves correspond between T(1) and $T_{(m)}$ as well as above T_m. From the relative magnitude of the enthalpy curves, it is concluded that the state of the PBFP specimen is independent of its thermal histories above T(1) transition. Note, too, that dilatometric(3) and birefringence-temperature(12) changes are in accord with this observation. Below T(1), however, the magnitude of the enthalpy change is dependent upon heat treatment. Also note that enthalpy decreases as the 3-D crystalline structure in the PBFP specimen improves upon heating cycling.

G. CONCLUSIONS)

1. Polyphosphazenes exhibit a single glass temperature and two first order phase transitions with a large mesophase temperature interval between them.

2. As formed from solution, these polymers are of moderate (3D) crystallinity, but undergo chain extensions on being heated above their mesophase transition, T(1), where they exist as 2D structures until they are cooled to room temperature, when the crystallinity approaches very high levels, as substantiated by many physical property changes. Concomitantly, the value of the T(1) transition temperature is greatly increased and so is the enthalpy at T(1).

3. The glass transition temperature is almost <u>independent</u> of the level of crystallinity in these polyphosphazenes. The specific heat change at T_g depends upon crystallinity and becomes undetectable whenever the crystallinity is very high.

4. Upon heating some polyphosphazenes about $T_D \simeq T_m$ for prolonged periods noticeable degradation is induced and this influences the T(1) and T_g transitions.

5. The nature and magnitude of the T(1) and T_m transitions are not mutually exclusive, but depend upon processing conditions.

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TABLE CAPTIONS

Table 1.	Description of Homopolymer Specimens with Material Sources
Table 2.	Thermal Transition Data for Polyphosphazenes from Heating Curves Shown in Figures 3 through 6.
Table 3.	Thermal Transitions for PBFP Polymers Derived from Heating Curves Shown in Figures 7 and 8.

Table 1
Descriptions of Polymer* Specimens/Sources

	Sample (No./type)	Substituents	Source
1	Poly[bistrifluoroethoxyphosphazene] (PBFP)	CF_3CH_2O	AMMRC (#71D)
2(a) and 2(b)	Poly[bistrifluoroethoxyphosphazene] (PBFP)	CF_3CH_2O	T. Masuko
3 and 3(a)	Poly[bisphenoxyphosphazene] (PBPP)	C_6H_5O	AMMRC
4	Poly[bisphenoxyphosphazene] (PBPP)	C_6H_5O	AMMRC (#75)
5	Poly[bis-p-methylphenoxyphosphazene] (PBMPP)	$p-CH_3-C_6H_4-$	AMMRC (#229)
6	Poly[bis-p-methylphenoxyphosphazene] PBMPP)	$p-CH_3-C_6H_4-$	BRL-1009-7 AMMRC

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*Other solution polymerized polyphosphazenes prepared in our laboratory will be reported on later.

Table 2
Thermal Transition Data of Polyphosphazenes Derived from Heating Curves# Shown in Figures 3 - 6

Run No.	Cooling Rate Between Runs K/min	T_g K	$\Delta Cp(T_g)$ cal/g°K	T(1), K	ΔH(T(1)) cal/g	Remarks
				Sample 3 (PBPP)		
1	original	276	0.015 (1.)*	401	5.80 (1.)	heated through T(1)
2	20	276	0.014 (0.93)	407,414	7.26 (1.25)	heated through T(1)
3	5	276	0.012 (0.8)	410,426	7.70 (1.33)	heated up to 675 K##
4	5	270	0.018 (1.2)	410,428	5.25 (0.9)	--
				Sample 3(a) (PBPP)**		
5	10	not observed		416,436	8.36 (1.44)	heated through T(1)
				Sample 4 (PBPP)		
1	original	272	0.040 (1.)	405	2.6 (1.)	heated through T(1)
2	160	272	0.024 (0.6)	389,424	6.0 (2.31)	heated through T(1)
3	1.25	273	0.022 (0.55)	393,410,426	6.3 (2.42)	heated up to 623 K##
4	160	275	less than 0.004 ($\leq$ 0.1)	411,431	7.3 (2.8)	--
				Sample 5 (PPMPP)		
1	original	278	0.040 (1.)	411	2.7 (1.)	heated through T(1)
2	20	278	0.016 (0.4)	429	6.8 (2.52)	heated through T(1)
3	5	278	0.015 (0.38)	430	7.2 (2.67)	heated up to 670 K$^{\Delta}$
4	10	275	0.025 (0.63)	402,411,427	4.1 (1.52)	--
				Sample 6 (PPMPP)		
1	original	283	0.041 (1.)	379,400	2.1 (1.)	heated through T(1)
2	20	282	0.028 (0.68)	384,398	5.7 (2.71)	heated through T(1)
3	20	283	0.027 (0.66)	385,399	6.3 (3.0)	heated up to 600 K$^{\Delta}$
4	160	285	0.020 (0.49)	399	6.4 (3.05)	--

\# All heating rates were 10K/min.

* The values in parentheses indicate the relative changes using the starting material as the basis.

\#\# Decomposition temperature (T_D) of PBPP polymers is ~ 650K, while the T_m temperature is ~ 663K [2].

** Original sample heated to 573K, quenched to 200K before run #5.

Δ For PPMPP polymers, T_D is reported as ~ 580K and its T_m is stated to be ~ 613K [2].

Table 3
Thermal Transition Data for PBFP Polymers Derived from Heating Curves Shown in Figures 7 and 8

Run No.	Cooling rates between runs, K/min	T(1), K	ΔH(T(1)) cal/g	T_m,K	ΔH(T_m), K	Remarks
			Sample 2(a) (PBFP)			
1	as received	351	5.1 (1.)[x]	513	1.02 (1.)	heated up to 540 K[#]
2	a. c.r‡ = 160 through T_m b. c.r = 1.25 through T(1)	357	7.2 (1.41)	515	0.92 (0.9)	"
3	a. c.r = 160 through T_m b. held at 383 K for 1 hr c. c.r = 1.25 through T(1)	356	7.0 (1.37)	515	0.94 (0.92)	"
			Sample 2(b) (PBFP)			
1	as received	351	5.1 (1.)	513	0.94 (1.)	"
2	a. c.r = 160 through T_m b. c.r = 1.25 through T(1)	357	7.4 (1.45)	515	0.94 (1.)	"
3	a. c.r = 1.25 through T_m b. c.r = 160 through T(1)	353,363	7.5 (1.47)	515	0.96 (1.02)	"
4	a. c.r = 1.25 through T_m b. held at 499 K for 30 min c. c.r = 160 through T(1)	353,363	7.8 (1.53)	515	0.98 (1.04)	"
5	a. c.r. = 1.25 through T_m b. held at 507 K for 30 min c. c.r = 160 through T(1)	363	8.2 (1.61)	506,515	0.94 (1.0)	"
6	a. c.r = 1.25 through T_m b. held at 510 K for 30 min c. c.r = 160 through T(1)	363	8.0 (1.57)	515	0.97 (1.03)	"
7	a. c.r = 160 through T_m b. held at 383 K for 30 min c. c.r = 160 through T(1)	358	7.1 (1.39)	514	0.99 (1.05)	"

X The values in parentheses indicate the relative changes using the starting material as a reference.
This temperature is well below the decomposition temperature of PBFP polymer, 630 K [2].
‡c.r. denotes cooling rate, K/min.

Figure Legends

Figure 1. General schematic of thermal behavior for polyphosphazene homopolymers. In this figure, T_g* is the glass transition temperature (taken as the mid-point of the slope of the C_p-T curve)

$\Delta C_p(Tg)$ = specific heat change at T_g

T(1) = thermotropic transition temperature

$\Delta H(T(1))$ = enthalpy change at T(1)

T_m = melting point

$\Delta H(T_m)$ = enthalpy change at T_m.

Figure 2. DSC curves showing the effect of annealing on the T(1) transition for PBFP samples (designated as Sample 1 in Table 1). Samples were annealed for 30 minutes at the temperatures indicated before scanning in the calorimetry. Each heating curve represents a specimen from the same source. The heating rate was 10 K/min.

Figure 3. DSC curves for PBPP (sample 3) following a heating sequence depicted in Table 2. The T_g transitions are shown in part (a) and the T(1) transition are illustrated in part (b), respectively. Heating rate is 10 K/min. Table 2 contains the measured T_g, $\Delta C_p(Tg)$, $\Delta H(T(1))$ values and thermal histories. Run 5 refers to sample 3(a).

Figure 4. DSC curves for PBPP (sample 4) following the heating sequence shown in Table 2; part (a) lists the T_g transitions and part (b) shows the T(1) values. The measured values of T_g, $\Delta C_p(Tg)$, $\Delta H(T(1))$ are tabulated. The heating rate is 10 K/min.

Figure 5. DSC curves for PBmPP (sample 5) according to the heating sequence designated in Table 2 at 10 K/min heating rate. Part (a) indicates T_g temperatures and Part (b) lists T(1) transition temperatures, measured values of T_g, $\Delta C_p(Tg)$, $\Delta H(T(1))$ are listed in this table.

Figure 6. DSC curves for PBmPP (sample 6) following the heating sequence listed in Table 2 at 10 K/min. The measure values of T_g, $\Delta C_p(Tg)$, [$\Delta HT(1))$ are tabulated.

---

*Richardson's method of T_g determination based upon enthalpy change (25) was also employed for some determinations. The results obtained by both methods were self consistent (within ± 2 K) for polyphosaszenes. Consequently, the simpler mid-point technique once it was substantiated, was adopted for these polymers.

Figure Legends (Continued)

Figure 7. DSC curves for PBFP homopolymer, sample 2(a), after a series of heat treatments shown in Table 3. The T(1) transitions are shown in part (a) and T_m transition in part (b) for a heating rate of 10 K/min. Also tabulated are T(1), ΔH(T(1)), T_m and ΔH(T_m) values.

Figure 8. DSC curves for PBFP, sample 2(b), after a series of heat treatments shown in Table 3. The T(1) transitions are shown in part (a) and the T_m transitions in part (b) for a heating rate of 10 K/min. Values of T(1), ΔH(T(1)), T_m and ΔH(Tm) are given in Table 3.

Figure 9. DSC curves for PBFP sample 2(b) for:

(a) Specific heat vs. temperature for the first three curves of T(1) and T_m, replotted from Figure 8.

(b) Corresponding enthalpy curves from Figure 9(a).

THERMAL BEHAVIOR OF POLYPHOSPHAZENES IN RELATION TO STRUCTURE

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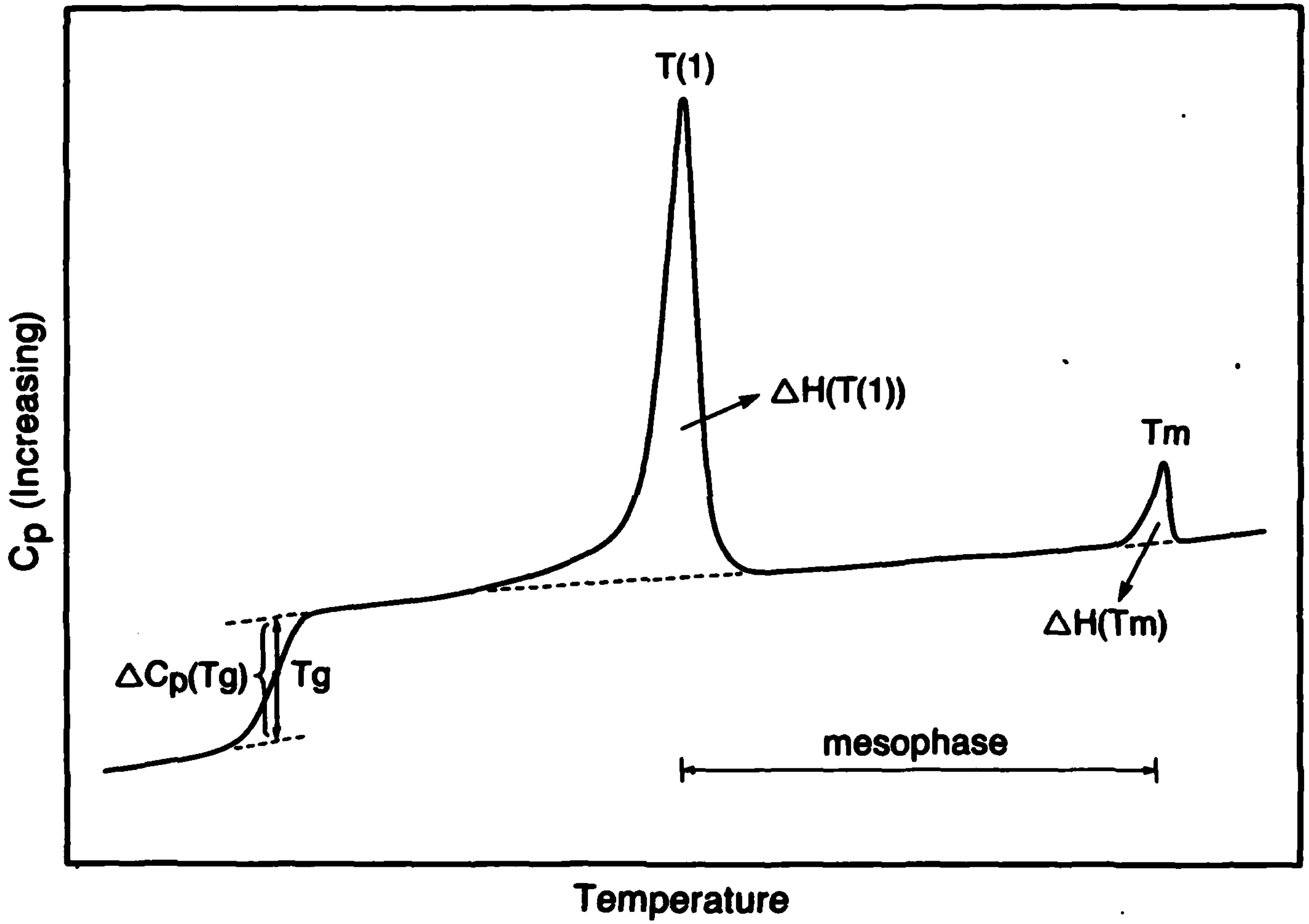
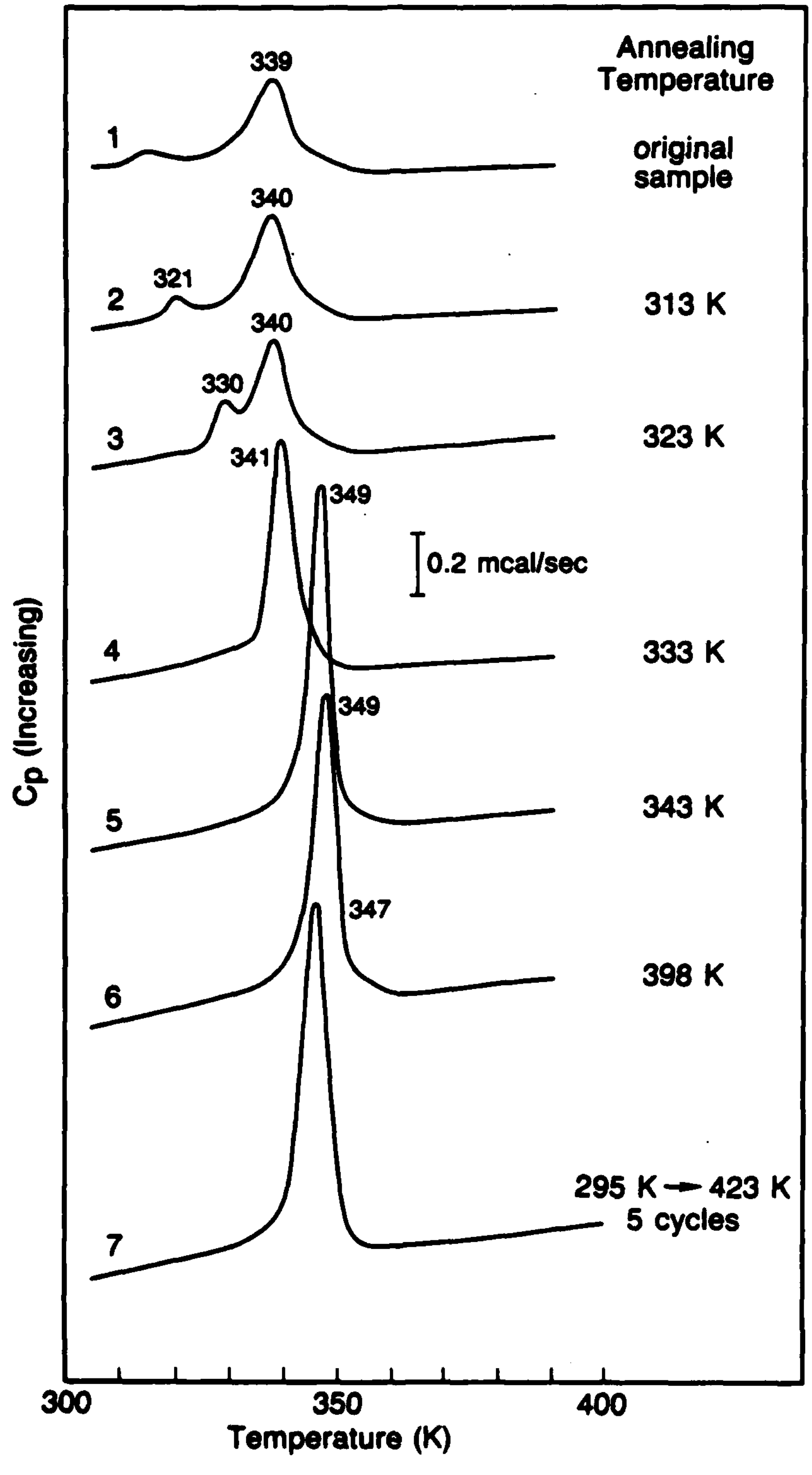


Figure 1. General schematic of thermal behavior for polyphosphazene homopolymers. In this figure, T_g* is the glass transition temperature (taken as the mid-point of the slope of the C_p-T curve)



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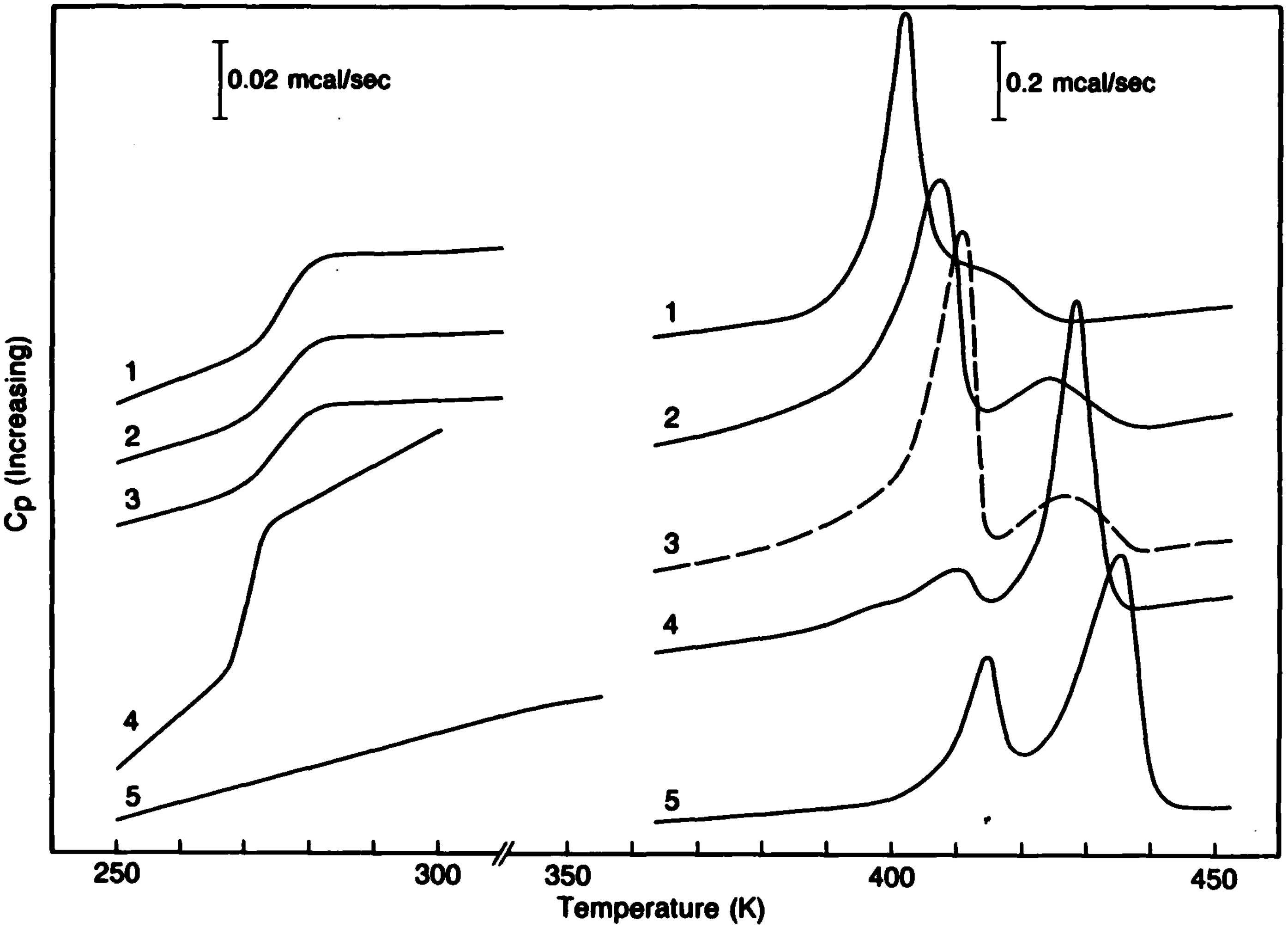

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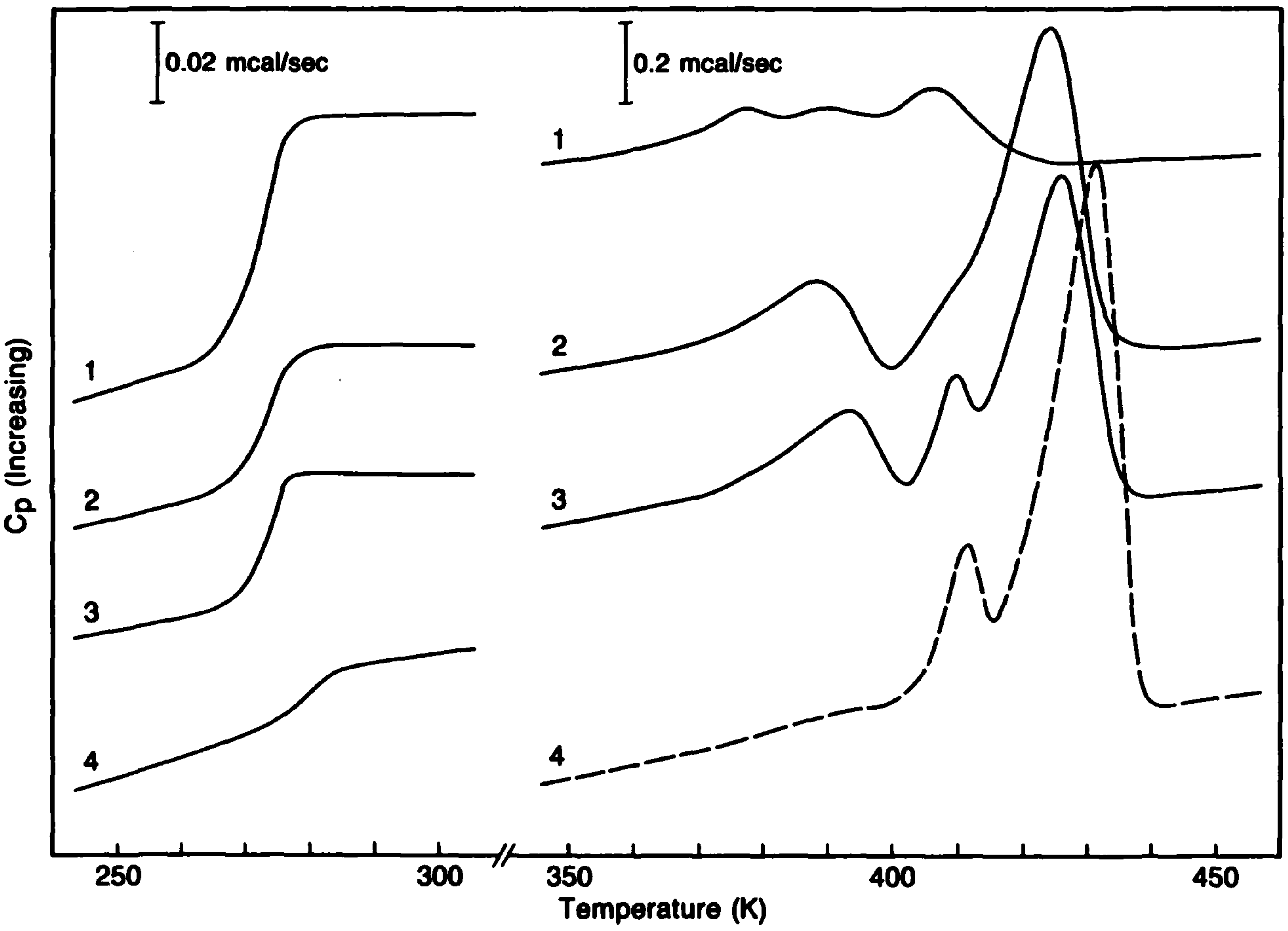


Figure 4. DSC curves for PBPP (sample 4) following the heating sequence shown in Table 2; part (a) lists the T_g transitions and part (b) shows the T(1) values. The measured values of T_g, $\Delta C_p(Tg)$, $\Delta H(T(1))$ are tabulated. The heating rate is 10 K/min.

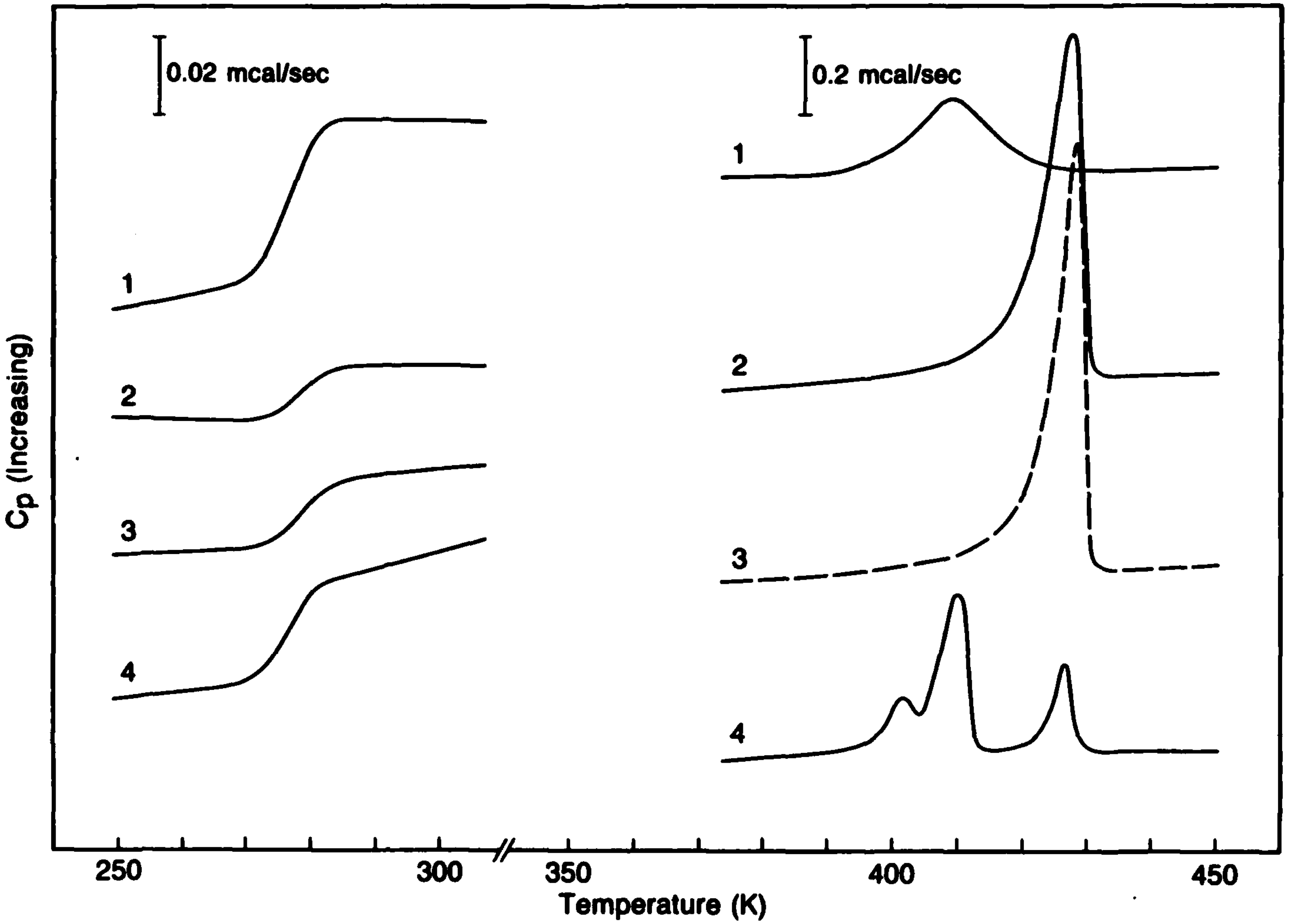


Figure 5. DSC curves for PBmPP (sample 5) according to the heating sequence designated in Table 2 at 10 K/min heating rate. Part (a) indicates T_g temperatures and Part (b) lists T(1) transition temperatures, measured values of T_g, $\Delta C_p(Tg)$, $\Delta H(T(1))$ are listed in this table.

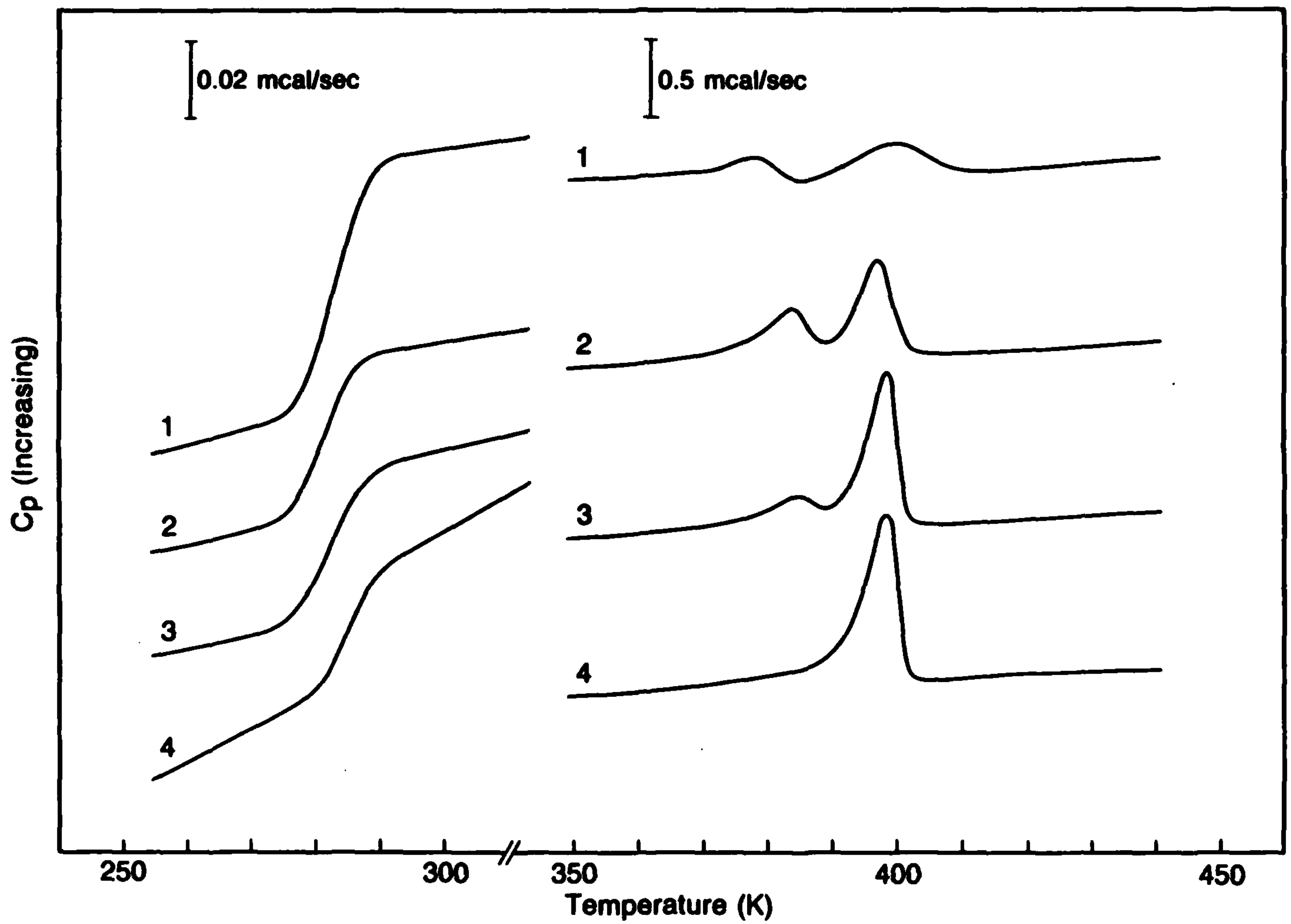


Figure 6. DSC curves for PBmPP (sample 6) following the heating sequence listed in Table 2 at 10 K/min. The measure values of T_g, $\Delta C_p(Tg)$, $\Delta HT(1))$ are tablulated.

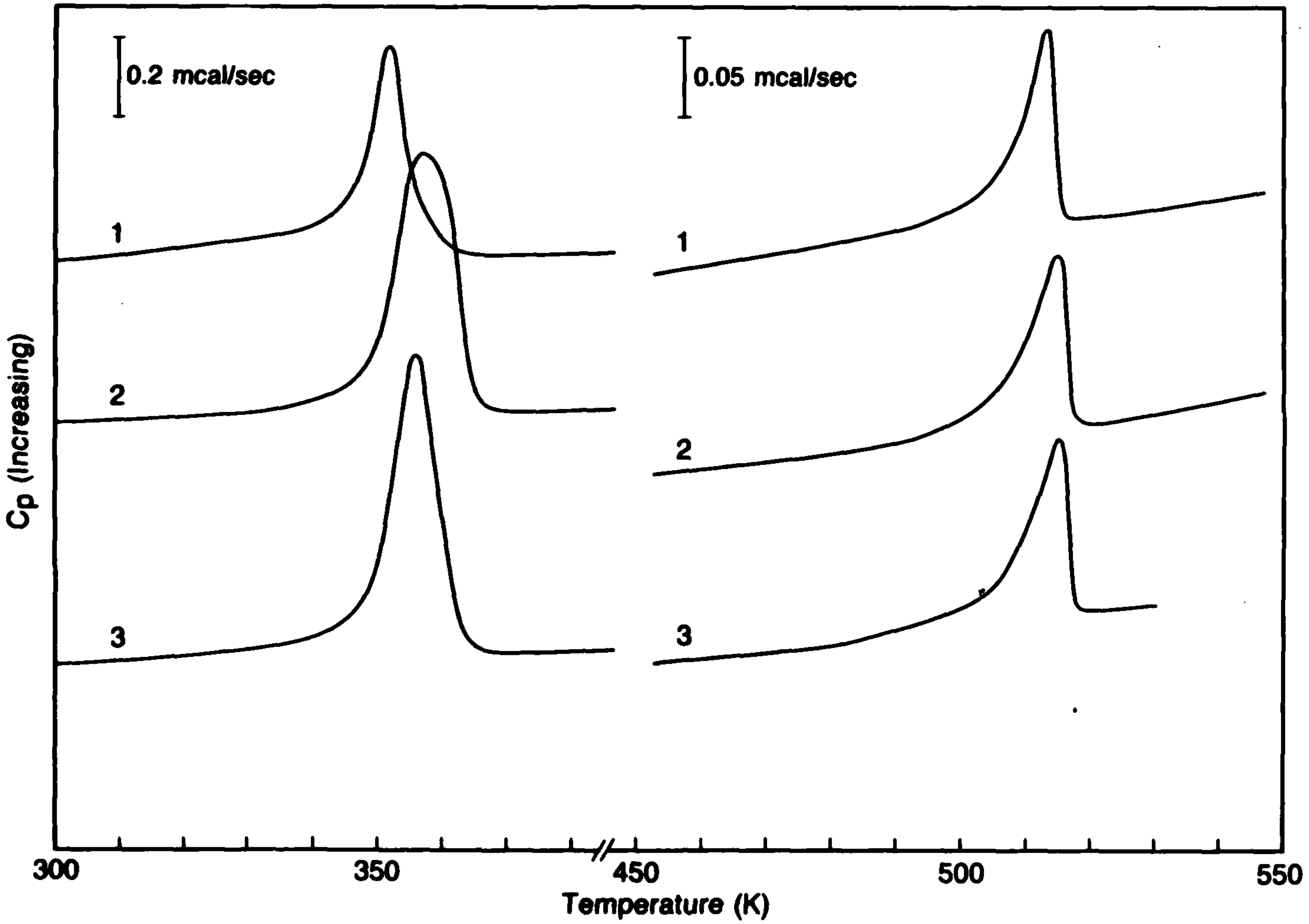


Figure 7. DSC curves for PBFP homopolymer, sample 2(a), after a series of heat treatments shown in Table 3. The T(1) transitions are shown in part (a) and T_m transition in part (b) for a heating rate of 10 K/min. Also tabulated are T(1), ΔHT(1), T_m and $\Delta H(T_m)$ values.

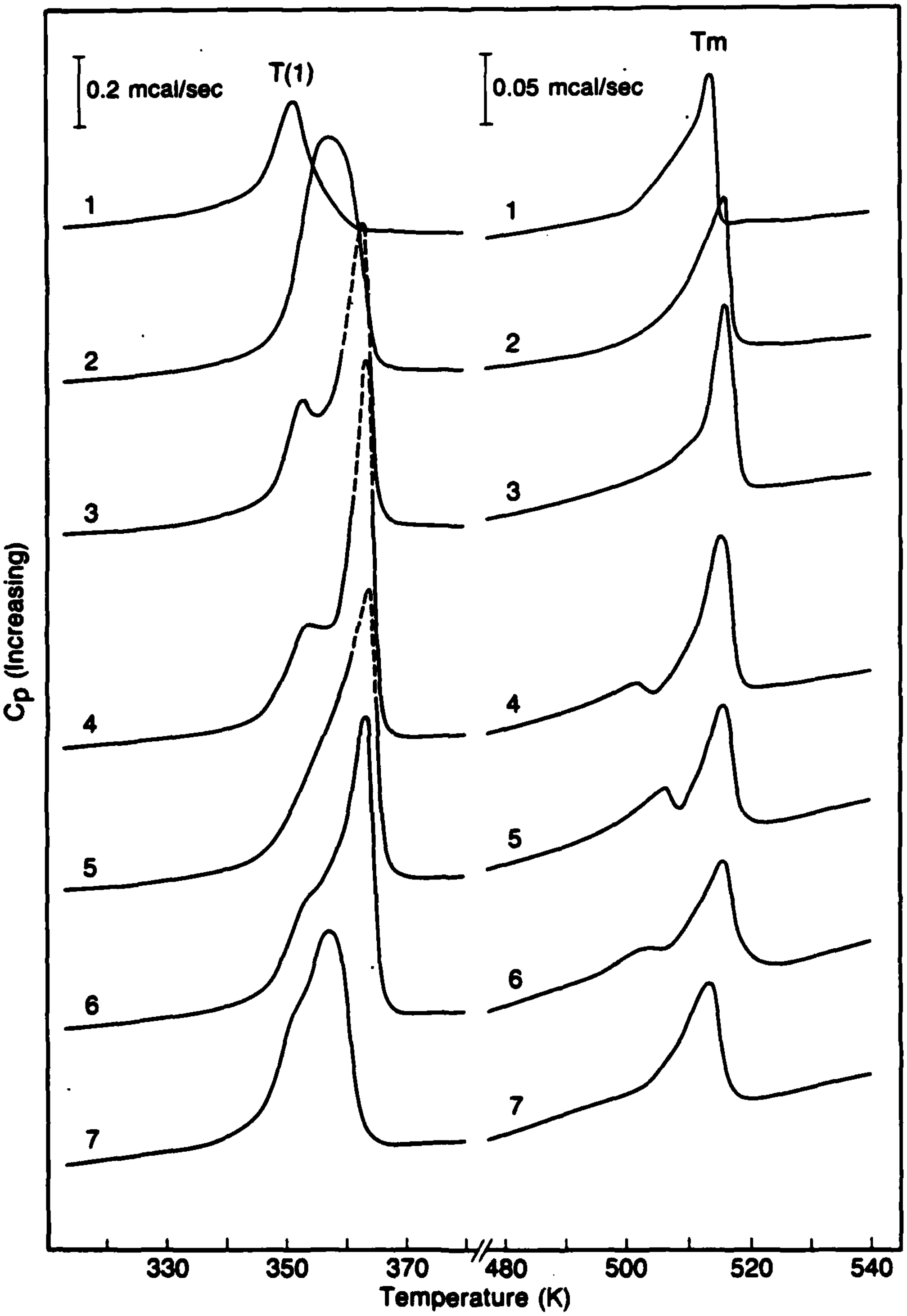
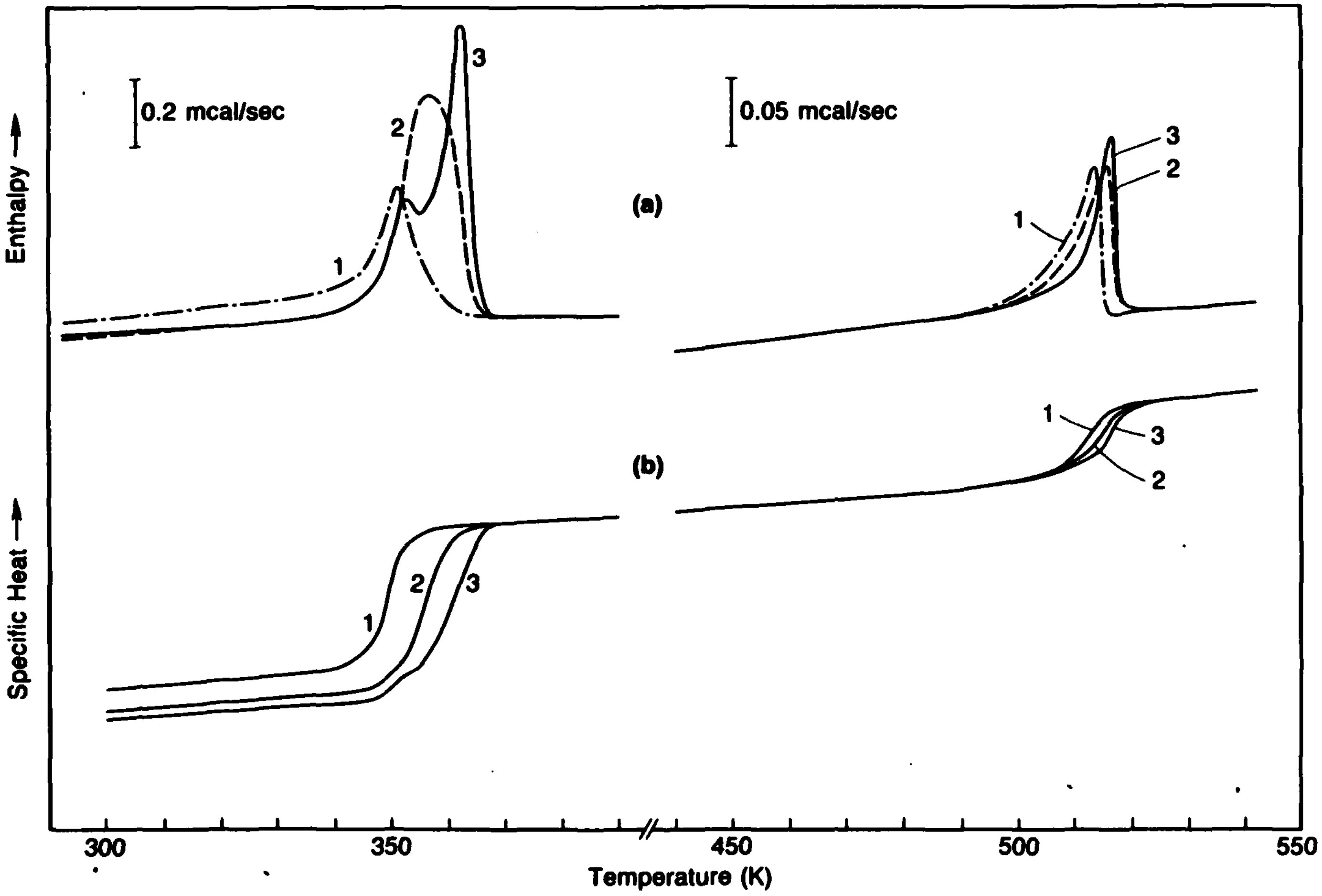


Figure 8. DSC curves for PBFP, sample 2(b), after a series of heat treatments shown in Table 3. The T(1) transitions are shown in part (a) and the $T(_m)$ transitions in part (b) for a heating rate of 10 K/min. Values of T(1), ΔH(T(1)) and ΔH(Tm) are given in Table 3.



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(a) Specific heat vs. temperature for the first three curves of T(1) and T_m, replotted from Figure 8.

(b) Corresponding enthalpy curves from Figure 9(a).

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