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Thermal behaviour 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 T_g, $T(1)$ and T_m and the relative change in these temperatures with heating, cooling and time of annealing. 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 behaviour of these flexible liquid crystal-forming macromolecules which have considerable potential technologically.

(Keywords: differential scanning calorimetry; thermal properties; specific heat; enthalpy of transition; crystallinity; mesophases; morphology)

INTRODUCTION

The thermal and physical properties of polyphosphazenes have received much attention in recent years[1-4]. Much of the interest centres around their mesomorphic nature as it relates to morphology and chemical constitution[5-8]. Dynamic mechanical[9], n.m.r.[10], i.r. and Raman spectroscopy[11], calorimetric (d.s.c.) 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 among 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. In any event, these materials[19-21] 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, T_g, mesophase transition, $T(1)$, and melting temperature, T_m, in typical polyphosphazene samples. A study of time effects in relation to observed phase transformations, assessed qualitatively and quantitatively by d.s.c., has been instrumental in providing a clearer picture of the underlying factors associated with T_g, and the two first order transitions, $T(1)$ and T_m, as well as the magnitude of the corresponding parametrical changes and their interrelationships with structure in polyphosphazenes.

EXPERIMENTAL

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 ($\bar{M} \geqslant 10^5$), and broad molecular weight (*MW*) distribution (often $\bar{M}_w/\bar{M}_n \geqslant 10$). Samples 2(a) and 2(b) obtained by solution polymerization[23] were of narrower *MW* distribution ($M_w/M_n < 3.0$). All polymers were precipitated from solution and dried before use.

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 also effected in the calorimeter. The PBFP specimens were held at selected temperatures up to 30 min duration before scanning. For each curve a new sample was used so that a standard reference condition

Table 1 Description of homopolymer* specimens with material sources

	Sample (No./type)	Substituents	Source
1	Poly[bistrifluoroethoxyphosphazene] (PBFP)	CF_3CH_2O	AMMRC (No. 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 (No. 75)
5	Poly[bis-p-methylphenoxyphosphazene] (PBMPP)	p-CH_3-C_6H_4-	AMMRC (No. 229)
6	Poly[bis-p-methylphenoxyphosphazene] (PBMPP)	p-CH_3-C_6H_4-	BRL-1009-7 AMMRC

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

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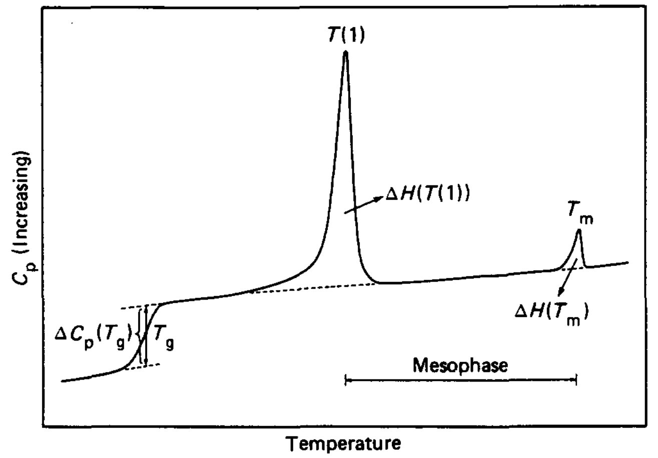

Figure 1 General schematic of thermal behaviour for polyphosphazene homopolymers. In this figure, T_g* is the glass transition temperature (taken as the mid-point of the slope of the C_p–T curve: $\Delta C_p(T_g)$ = specific heat change at T_g; $T(1)$ = thermotropic transition temperature; $\Delta H(T(1))$ = enthalpy change at $T(1)$; T_m = melting point; $\Delta H(T_m)$ = enthalpy change at T_m (*Richardson's method of T_g determination based upon enthalpy change (ref. 25) was also employed for some determinations. The results obtained by both methods were self consistent (within ±2 K) for polyphosphazenes. Consequently, the simpler mid-point technique once it was substantiated, was adopted for these polymers)

was ensured. Various thermal treatments were used to study T_g, $T(1)$ and T_m transitions.

For T_g measurements, liquid nitrogen or dry ice/alcohol coolant was used (depending on the temperature range).

The d.s.c. 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 d.s.c. instrument was calibrated according to recommended procedures[24].

RESULTS AND DISCUSSIONS

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 d.s.c. sample holder at the desired temperatures for 30 min, 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' preceding 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 (curves 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 at about 349 K (*Figure 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

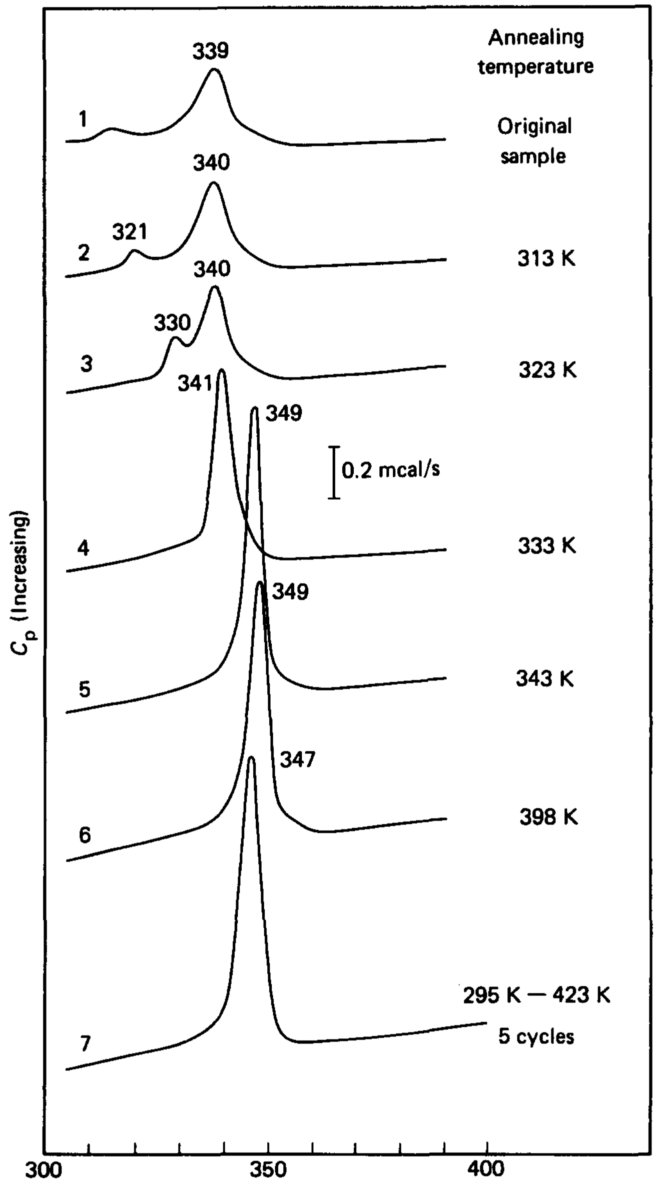

Figure 2 D.s.c. curves showing the effect of annealing on the $T(1)$ transition for PBFP samples (designated as sample 1 in *Table 1*). Samples were annealed for 30 min at the temperatures indicated before scanning in the calorimeter. Each heating curve represents a new specimen taken from the same source. The heating rate was 10 K/min

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* 'Curve' and 'run' are used interchangeably

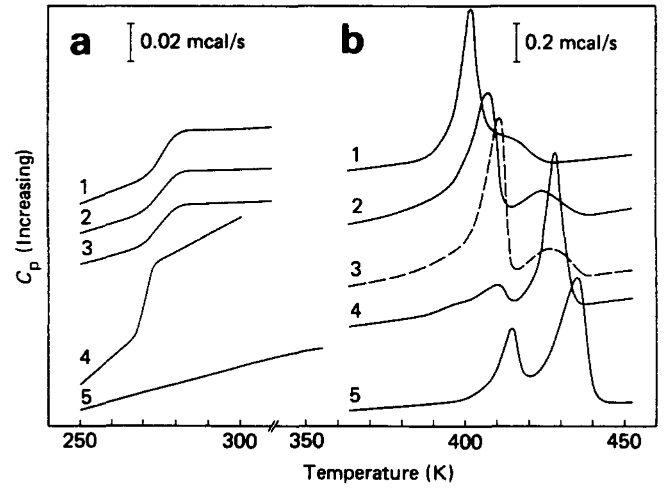

Figure 3 D.s.c. curves for PBPP (sample 3) following a heating sequence depicted in *Table 2*. The T_g transitions are shown in part (a) and the $T(1)$ transition are illustrated in part (b), respectively. Heating rate is 10 K/min. *Table 2* contains the measured T_g, $\Delta C_p(T_g)$, $\Delta H(T(1))$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

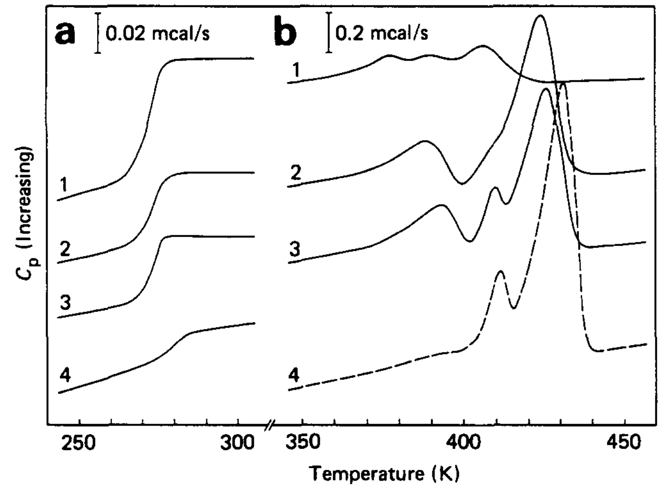

Figure 4 D.s.c. curves for PBPP (sample 4) following the heating sequence shown in *Table 2*; part (a) lists the T_g transitions and part (b) shows the $T(1)$ values. The measured values of T_g, $\Delta C_p(T_g)$), $\Delta H(T(1))$ are tabulated. The heating rate is 10 K/min

$T(1)$ peaks are indeed a clear manifestation of structural reorganization in this thermotropic polyphospazene. 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 other polyphosphazene polymers which exhibit a thermotropic $T(1)$ transition. The organization within PBFP samples can be improved by annealing the sample at a temperature above this first-order transition. A conventional polymer becomes completely disordered above its first-order transition, T_m.

Whenever PBFP crystals are heated through the $T(1)$ transition, a structural change occurs[5]. This transformation gives rise to a chain extended morphology, from a lamellar or chain folded state. This change is irreversible morphologically since the specimen does not return to a chain folded state. Thus, reorganizational behaviour below $T(1)$ is somewhat analogous to structural behaviour observed in conventional polymers, where the smaller or less stable crystals 'melt' and then recrystallize from crystal 'remnents' 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 its lowest free energy state. Above $T(1)$ the 2-D chain-extended form still maintains some degree of structural integrity. Note that the volume change on passing through $T(1)$ is some 6%[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 behaviour 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.

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, $\Delta C_p(T_g)$ 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

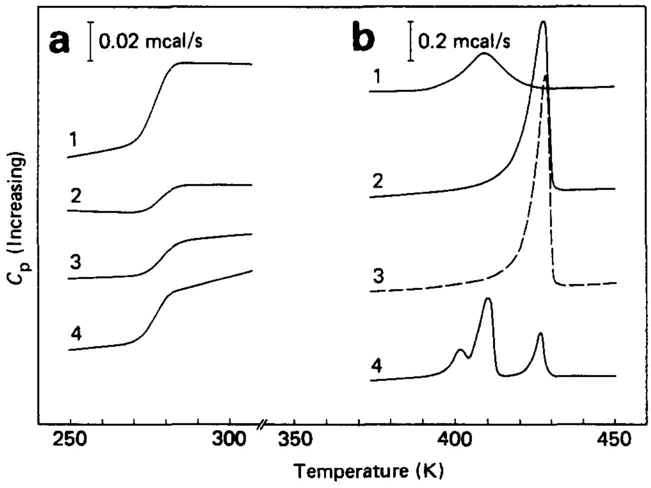

Figure 5 D.s.c. curves for PBMPP (sample 5) according to the heating sequence designated in *Table 2* at 10 K/min heating rate. Part (a) indicates T_g temperatures and part (b) lists $T(1)$ transition temperatures, measured values of T_g, $\Delta C_p(T_g)$, $\Delta H(T(1))$ are listed in *Table 2*

T_g temperature *per se* 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 PBMPP 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 suspected, it is accompanied by a change in the $T(1)$ peaks. This aspect of the work will be discussed later.

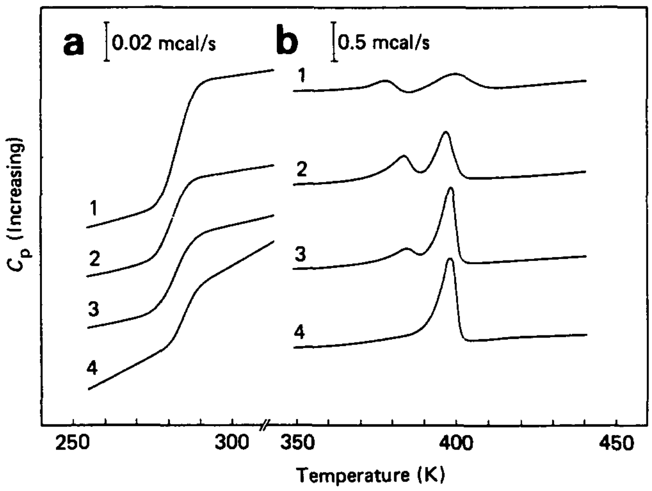

Figure 6 D.s.c. curves for PBMPP (sample 6) following the heating sequence listed in *Table 2* at 10 K/min. The measure values of T_g, $\Delta C_p(T_g)$, $\Delta HT(1)$) are tabulated

The specific heat change at T_g, $\Delta C_p(T_g)$, decreased upon heating–cooling cycles through $T(1)$. For all polymer specimens (with the exception of PBPP, sample 3), a marked decrease in $\Delta C_p(T_g)$ 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

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* Not necessarily fully extended. Note especially that sample 3(a) (PBPP) did not exhibit either a T_g or a noticeable $\Delta C_p(T_g)$ as indicated by run 5 in *Table 2* and in *Figure 3*. This behaviour 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 equations (1) and (2))

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)	$\Delta C_p(T_g)$ (cal/g/K)	$T(1)$ (K)	$\Delta H(T(1))$ (cal/g)	Remarks
			Sample 3 (PBPP)			
1	original	276	0.015 (1)[a]	401	5.80 (1)	heated through $T(1)$
2	20	276	0.014 (0.93)	407, 424	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[b]
4	5	270	0.018 (1.2)	410, 428	5.25 (0.9)	—
			Sample 3(a) (PBPP)[c]			
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[b]
4	160	275	less than 0.004 ($\leq$0.1)	411, 431	7.3 (2.8)	—
			Sample 5 (PBMPP)			
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[d]
4	10	275	0.025 (0.63)	402, 411, 427	4.1 (1.52)	—
			Sample 6 (PBMPP)			
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[d]
4	160	285	0.020 (0.49)	399	6.4 (3.05)	—

* All heating rates were 10 K/min

[a] The values in parentheses indicate the relative changes using the starting material as the basis

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

[c] Original sample heated to 573 K, quenched to 200 K before run no. 5

[d] For PBMPP polymers, T_D is reported as 580 K and its T_m is stated to be 613 K [ref. 2]

run through $T(1)$. Subsequent heating–cooling cycles simply perfect 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 $\tan\delta$ values in crystalline polyphosphazenes, 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%).

$T(1)$ transition and enthalpy change at $T(1)$, $\Delta H(T(1))$

$T(1)$ transition results obtained upon heating–cooling treatments are shown in part (b) of *Figures 3–6*. *Table 2* lists peak temperatures and $\Delta H(T(1))$ 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 *MW* distribution and (ii) to the crystallization conditions which these samples have experienced. Neither slow heating rates not sample evacuation changed this situation overnight. 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 PBMPP sample 6. 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 on occasion. 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, $\Delta H(T(1))$ increases significantly also, sometimes reaching a value three times as large as is found for the original material (see *Table 2*). Relatively, the biggest increase in $\Delta H(T(1))$ 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 $\Delta H(T(1))$ value which is also significantly lowered.

Crystalline perfection and crystallinity

An unanswered question, frequently raised concerns the mechanisms that contribute to the large increases in the $T(1)$ and $\Delta H(T(1))$ values, respectively. These may affect crystalline perfection, as well as crystallinity. The magnitude of the $\Delta C_p(T_g)$ and the $\Delta H(T(1))$ 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 $\Delta H(T(1))$ are proportional to the amounts of amorphous and crystalline phases respectively, then one can estimate approximately the sample crystallinity.

One can relate $\Delta C_p(T_g)$ and $\Delta H(T(1))$ 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 constants* 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 determined. 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 times 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 $\Delta H(T(1))$ 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 occur 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 $\Delta H(T(1))$ upon cyclic heating, possessed a relatively higher crystallinity in its initial state before scanning†, as its $\Delta H(T(1))$ 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).

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 transformation 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

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* K_1 is a function of T_g and K_2 is a function of $T(1)$, hence Equation (3) does not imply that $\Delta C_p(T_g)$ and $\Delta H[T(1)]$ are proportional for all degrees of crystallinity, but it is still useful here

† May be due to prior heating of sample above $T(1)$

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)	$\Delta H(T(1))$ (cal/g)	T_m (K)	$\Delta H(T_m)$ (K)	Remarks
	Sample 2(a) (PBFP)					
1	as received	351	5.1 (1)[a]	513	1.02 (1)	heated up to 540 K[b]
2	(a) c.r.[c] = 160 through T_m (b) c.r. = 1.25 through $T(1)$	357	7.2 (1.41)	515	0.92 (0.9)	heated up to 540 K[b]
3	(a) c.r. = 160 through T_m (b) held at 383 K for 1 h (c) c.r. = 1.25 through $T(1)$	356	7.0 (1.37)	515	0.94 (0.92)	heated up to 540 K[b]
	Sample 2(b) (PBFP)					
1	as received	351	5.1 (1)	513	0.94 (1)	heated up to 540 K[b]
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)	heated up to 540 K[b]
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)	heated up to 540 K[b]
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)	heated up to 540 K[b]
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)	heated up to 540 K[b]
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)	heated up to 540 K[b]
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)	heated up to 540 K[b]

[a] The values in parentheses indicate the relative changes using the starting material as a reference

[b] This temperature is well below the decomposition temperature of PBFP polymer, 630 K [ref. 2]

[c] c.r. denotes cooling rate, K/min

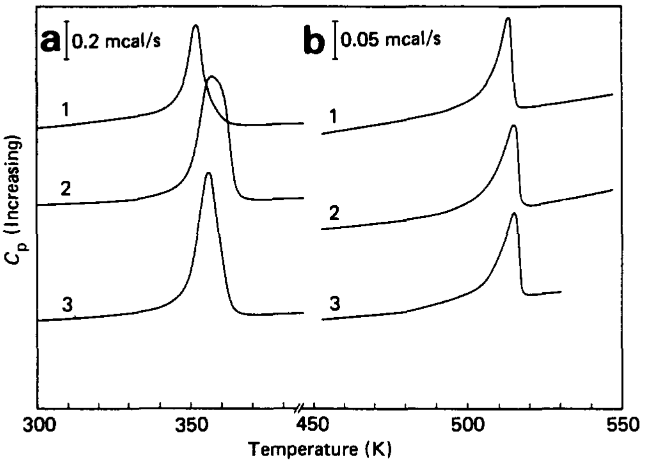

Figure 7 D.s.c. curves for PBFP homopolymer, sample 2(a), after a series of heat treatments shown in *Table 3*. The $T(1)$ transitions are shown in part (a) and T_m transition in part (b) for a heating rate of 10 K/min. Also tabulated are $T(1)$, $\Delta H(T(1))$, T_m and $\Delta H(T_m)$ values

down from above T_m to below $T(1)$ temperature. Since the kinetics of transformation 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 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 PBFP 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 extended chain γ-form which is also orthorhombic[5]. The PBFP $T(1)$ value of 357 K, is 6 K higher than is found for the starting material. This is still 6 K lower than the highest value (363 K) reported above. Recrystallization processes that lead to a more perfect structure are supported 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 (i) induced multiphase morphology or (ii) been responsible for the segregation of the shorter from the longer molecules in samples of large polydispersity. At present evidence from electron diffraction favours situation (i). 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 min before cooling it down again through $T(1)$. Now, not only did the $T(1)$ transition showed two peaks, but the final melting curve

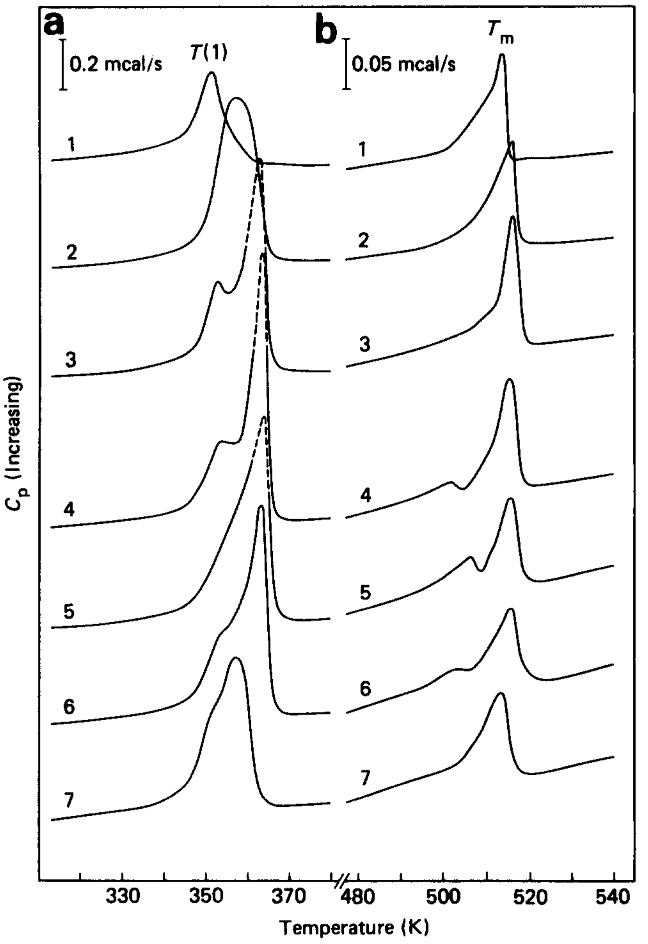

Figure 8 D.s.c. curves for PBFP, sample 2(b), after a series of heat treatments shown in *Table 3*. The $T(1)$ transitions are shown in part (a) and the T_m transitions in part (b) for a heating rate of 10 K/min. Values of $T(1)$, $\Delta H(T(1))$, T_m and $\Delta H(T_m)$ are given in *Table 3*

also split into two peaks. Furthermore, upon cooling this sample in the DSC instrument, a $T(1)$ doublet was formed (see *Figure 13*). 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 (e.g. >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 extension and various defects, presumably) within a practical time interval of heat testment (several hours). A lower $T(1)$ peak is a manifestation of this behaviour (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 3-D crystallite size, but the T_m peak still seems to be sensitive to the 2-D crystallites in the chain direction as well as domain order/size[5,15]. Both of these morphological changes are mutually related.

Transitional changes upon cooling. It is interesting to examine the transitional changes in polyphosphazenes on cooling. For instance, when PBFP (2a) is melted at 540 K, the cooling curve recorded at 5°/min following heating run 3 (*Table 3*) is shown in *Figure 10*. Here, at high sensitivity, the sample transforms from the molten state to mesophase (δ-form) at peak temperature 500 K. This corresponds to 15 K subcooling approximately. Further cooling produces a sharp $T(1)$ (2-D $\rightarrow$ 3-D phase change) at 335 K.

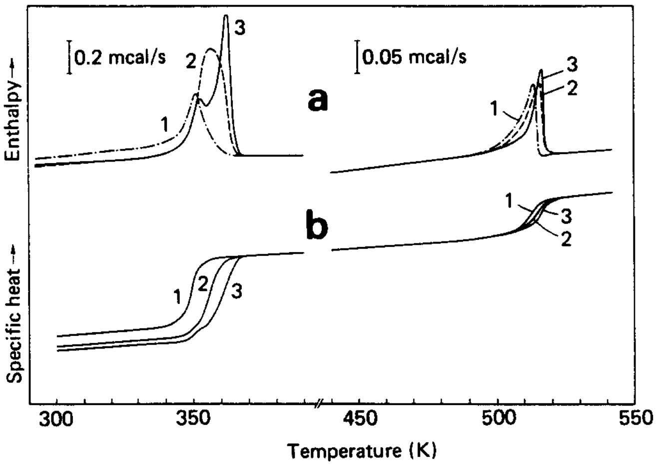

Figure 9 D.s.c. curves for PBFP sample 2(b) for: (a) Specific heat *versus* temperature for the first three curves of $T(1)$ and T_m, replotted from *Figure 8*. (b) Corresponding enthalpy curves from *Figure 9(a)*

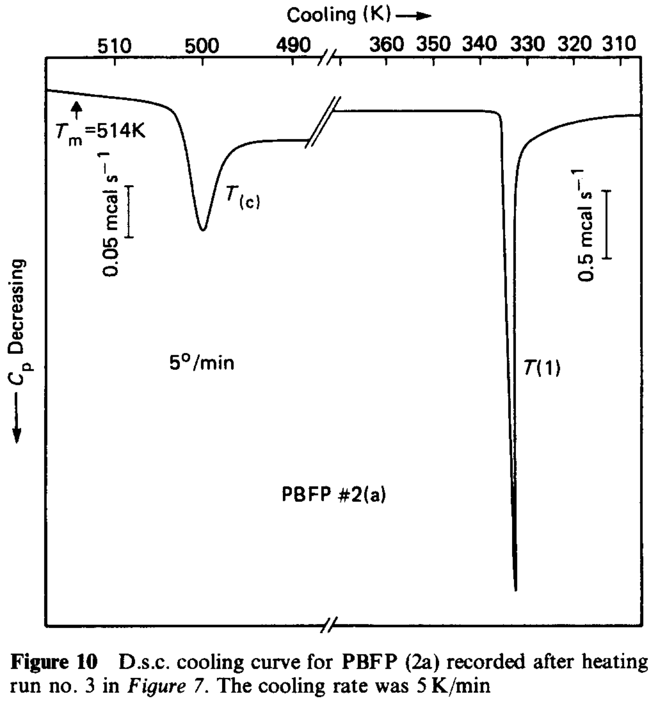

Figure 10 D.s.c. cooling curve for PBFP (2a) recorded after heating run no. 3 in *Figure 7*. The cooling rate was 5 K/min

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* This topic will be further examined in the next section

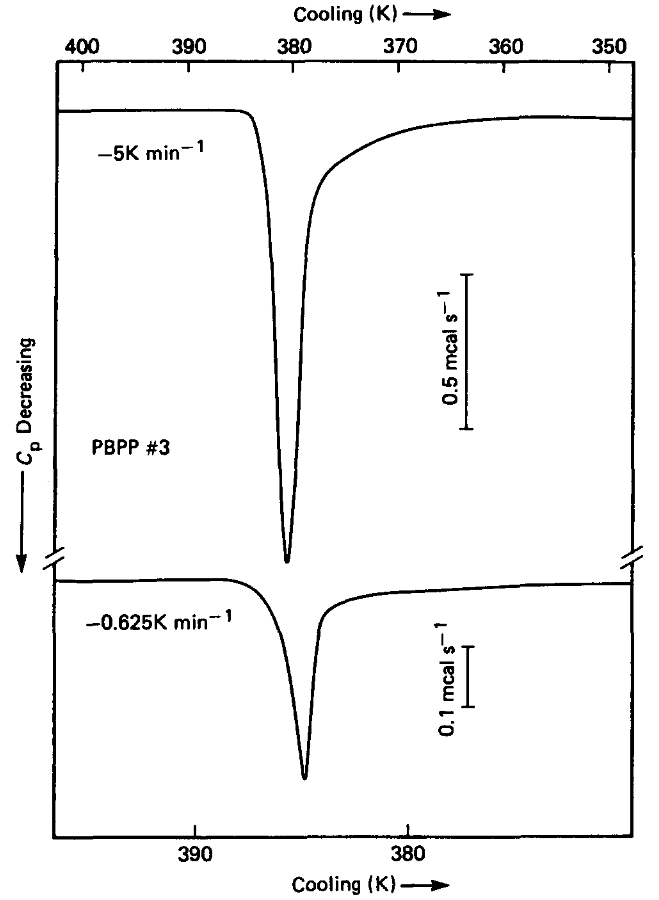

Figure 11 D.s.c. cooling curve for PBPP (3) at 5 K/min and (b) 0.625 K/min, respectively. Curves were recorded each time after heating run no. 1 in *Figure 3*

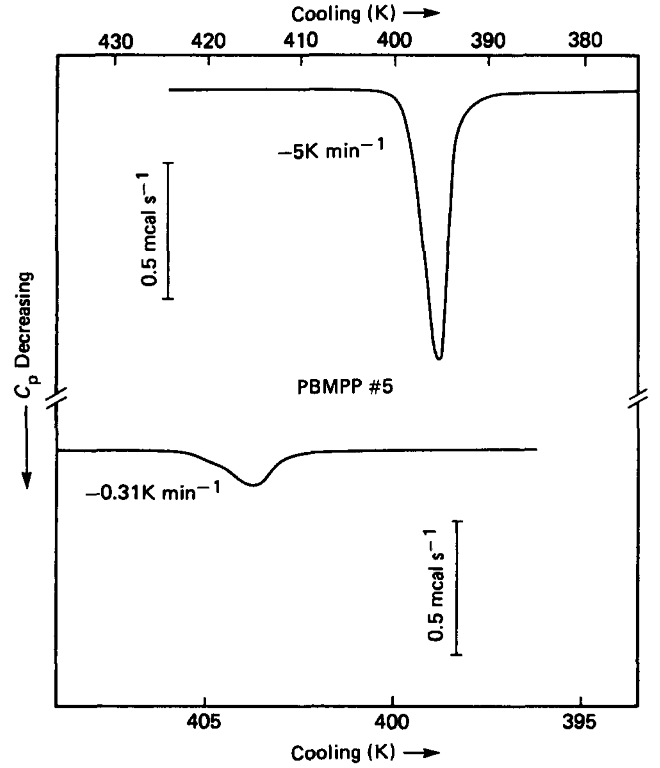

Figure 12 D.s.c. cooling curves for PBMPP (5) at (a) 5 K/min and (b) 0.31 K/min respectively. Curves were recorded after heating run no. 2 in *Figure 5*

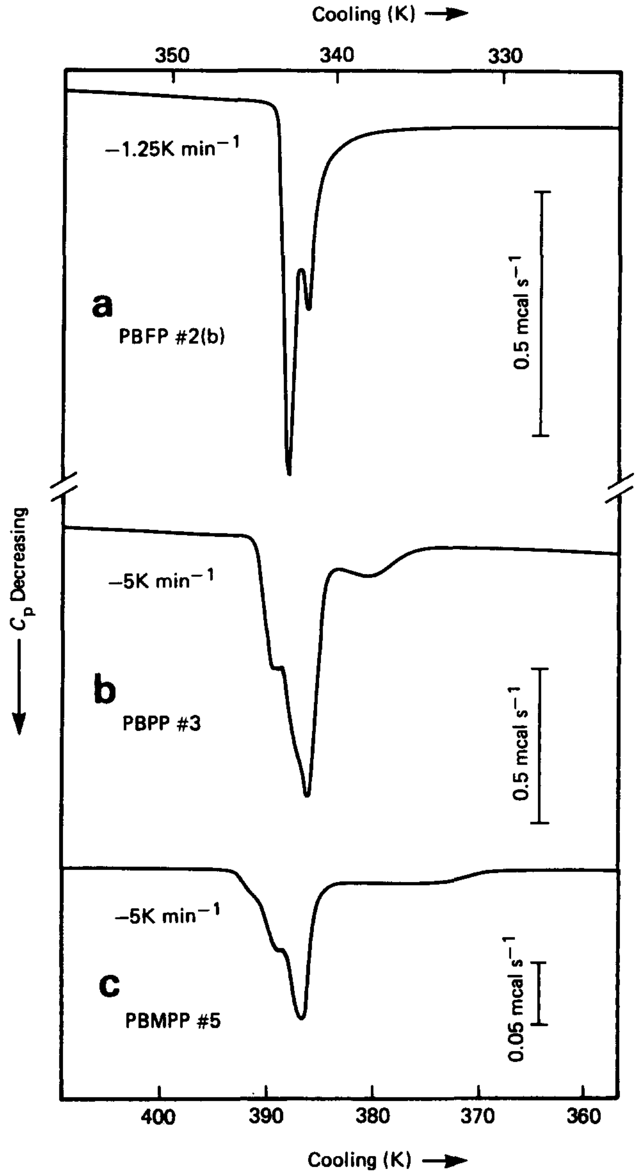

Figure 13 Cooling curves for (a) PBFP (2(b)) (b) PBPP (3) and (c) PBMPP (5) samples. Rates are specified in the Figure

Similar experiments conducted on PBPP (sample 3), *Figure 11*, and PBMPP (sample 5), *Figure 12*, indicate corresponding changes but at much higher degrees of subcooling* (presumably because of the greater chain stiffness in these materials). Also recorded in these preliminary measurements is the dependence of transformational changes upon cooling rate(s).

Under certain conditions, transition doublets and multi-cooling peaks are found for all three polyphosphazenes. For example, see *Figure 13* where multiple peaks in these polymers are represented. Note that curve (a) in *Figure 13* was recorded after run 7, *Figure 8* where doublets were observed in previous heating runs (see runs 5 and 6, *Figure 8*). In *Figure 13* curves (b) and (c) represent cooling curves obtained after the polymers were heated above ~670 K. Literature evidence[2] indicates that these samples may have been above their respective decomposition temperature. However, more work is needed with the fractionated materials in order to establish if depolymerization has taken place.

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* Suffice it to indicate at this point that there is a thermal history dependence which needs to be elucidated in more detail

Kinetics of isothermal crystallization have been examined by X-ray[15] and now by d.s.c.[16] with similar results. More detailed analyses are in progress.

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 PBMPP and other specimens. If the lamellar thickness represents some measure of chain extension, 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 (3-D) polymers may give some insights into the kinetic effects discussed above. For example:

$$T_m = T_m^\circ\left(1-\frac{K}{l}\right) \tag{4}$$

Where T_m is the observed melting temperature, T_m° 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:

$$T(1) = T(1)^\circ\left(1-\frac{K'}{\langle l'\rangle}\right) \tag{5}$$

for the 3-D → 2-D first order transition, where $\langle l'\rangle$ is some average crystallite dimension characteristic of the sample and K' is a parameter signifying the interface morphology.

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 2 K 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 (1) and (2) 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 comprising 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].

Note that $\Delta H(T(1))$ values increase, while $\Delta H(T_m)$ values are approximately constant (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 order in the newly formed 2-D state to such an extent that small changes in $\Delta H(T_m)$ value upon heating-cooling cycles are difficult to measure using d.s.c. This $\Delta H(T_m)$ change is further illustrated in *Figure 9* where the first three curves in *Figure 8* are replotted along with the enthalpy curves obtained by integrating the specific heat curves. The molten state was used as a reference level in this analysis. Below $T(1)$, the specific heat for curve 1 is greater than that for either curve 2 or curve 3 which are approximately the same. Note that the three C_p–T curves coincide 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 treatment above T_m transition. Dilatometric[3] and birefringence temperature[12] measurements are in accord with this observation. Below $T(1)$, however, the magnitude of the enthalpy change is dependent upon heat treatment. Also note that the enthalpy of the 3-D crystalline structure in the PBFP specimen decreases upon cycling, indicating that crystalline order is enhanced.

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

(3) The glass transition temperature is almost *independent* 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) 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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