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The thermal properties of polyphosphazenes synthesized by the anionically initiated polymerization of phosphoranimines

Michael L. White, Robert A. Montague and Krzysztof Matyjaszewski*
Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA

and Tadeusz Pakula
Max-Planck-Institut für Polymerforschung, 55021 Mainz, Germany
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The thermal properties of a number of polyphosphazene random and block copolymers synthesized by the anionic polymerization of phosphoranimines have been examined by differential scanning calorimetry and correlated with variable-temperature wide-angle X-ray scattering. These studies show the effect of structure, molecular weight, composition, side groups and thermal history on the thermal transitions of these materials. In addition, annealing studies were performed to estimate the degree of crystallinity and attempts were made to detect microphase separation by small-angle X-ray scattering.

(Keywords: polyphosphazenes; copolymers; thermal properties)

INTRODUCTION

Polyphosphazenes are an important class of polymers because of their unique combination of high-temperature stability and low-temperature flexibility. Low rotational barriers lead to very low glass transition temperatures. In fact, poly(diisopropoxyphosphazene) has one of the lowest known T_g values at −105°C[1]. Polyphosphazenes are thermally stable up to 300°C with alkoxy or aryloxy substituents and up to 350°C with alkyl or aryl substituents[2]. This combination of low-temperature flexibility and high-temperature stability is shared only with polysiloxanes and has led to applications that include high-performance seals, gaskets and O-rings[3]. Understanding the thermal properties of polyphosphazenes is therefore of considerable academic interest.

There are currently several methods for synthesizing polyphosphazenes. The classical way to produce these polymers is to thermally polymerize hexachlorocyclotriphosphazene by the ring-opening process at 250°C for 2–3 days. A wide variety of alkoxy-, aryloxy- and amino-substituted polymers can be produced by nucleophilic substitution on the resulting poly(dichlorophosphazene)[3]. This method was pioneered by Allcock in the mid-1960s[4] and was used for the commercial synthesis of polyphosphazenes. $Cl_3P{=}N{-}P(O)Cl_2$ has also been used to produce the dichloro precursor polymer[5]. Another route to polyphosphazenes involves the polymerization of phosphoranimines[6]. This method was used by Neilson to produce the first fully alkylated polyphosphazenes in 1980[7]. However, all of these methods require long polymerization times and high temperatures (typically 1–3 days at 200–250°C) to produce high polymer.

These limitations led to the exploration of new methods for the catalysis of phosphoranimines to accelerate the polymerization. A number of studies done by our group have shown that the use of a variety of anionic and nucleophilic catalysts can be used to fully convert alkoxy-substituted phosphoranimines in as little as 5 h at 100°C[8–10]. In the initial studies, tetra-n-butylammonium fluoride (TBAF) was used as an initiator for the polymerization of phosphoranimines because of the 'silylphilic' nature of the fluoride anion. Subsequent studies have shown that numerous fluorides, chlorides, amines, amides and alkoxides greatly enhance polymerization rates. Neilson has since shown that these types of catalysts are also effective for the polymerization of alkyl-substituted phosphoranimines[11].

Recent efforts in our group have concentrated on the preparation of polyphosphazene random[12] and block[13] copolymers by the simultaneous or sequential anionically initiated polymerization of phosphoranimines. In this way, it has been possible to prepare polyphosphazene copolymers with various combinations of alkoxyalkoxy and trifluoroethoxy groups and various block lengths (*Scheme 1*).

The thermal properties of polyphosphazenes are very interesting and have therefore been studied extensively. D.s.c.[14–17], X-ray scattering and electron diffraction[15,18–21], dynamic n.m.r.[22] and d.m.a.[23] have been used to explore the phase behaviour of polyphosphazenes. It is well known that poly(bis-2,2,2-trifluoroethoxyphosphazene) has three distinct thermal transitions. In addition to a T_g at −66°C, this polymer undergoes a transition to a hexagonal mesophase at

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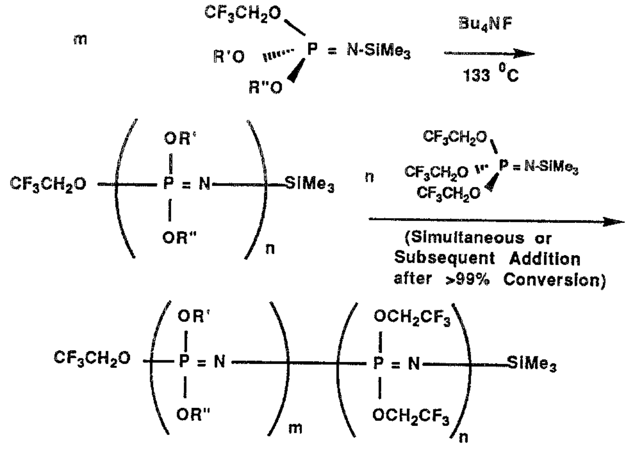
* To whom correspondence should be addressed



1a Random R' = $CH_3OCH_2CH_2$-; R'' = CF_3CH_2O-
1b Random R' = $CH_3OCH_2CH_2OCH_2CH_2$-; R'' = CF_3CH_2O-
1c Random R', R'' = $CH_3OCH_2CH_2$-
1d Random R', R'' = $CH_3OCH_2CH_2OCH_2CH_2$-
2a Block R' = $CH_3OCH_2CH_2$-; R'' = CF_3CH_2O-
2b Block R' = $CH_3OCH_2CH_2OCH_2CH_2$-; R'' = CF_3CH_2O-
2c Block R', R''= $CH_3OCH_2CH_2OCH_2CH_2$-

Scheme 1

$T(1) = 66$–90°C and then becomes isotropic at $T_i \approx 240$°C[14]. The precise temperatures are very dependent upon thermal history and molecular weight[13,14,24]. As cast from solution, this polymer forms spherulitic and conical fan-like morphologies, which have a monoclinic crystal structure[25,26]. After the temperature is raised above $T(1)$, the spherulitic structures are maintained but the crystal structure changes to the hexagonal mesophase (δ). The spherulitic structures are destroyed above T_i and, upon cooling, rod-like batonnets are formed in the δ phase. This structure is maintained below $T(1)$, where an extended-chain, orthorhombic crystal structure forms. Similar mesophase behaviour has been observed in poly(diphenoxyphosphazene) and other symmetrical poly(diaryloxyphosphazenes) with substituents on the benzene ring[27,28], poly(diarylphosphazenes)[29,30], as well as in some poly(dialkoxyphosphazenes)[31]. Additionally, we have recently shown that the random[12] and block[13] copolymers with mixed trifluoroethoxy and alkoxyalkoxy substituents exhibit thermal behaviour similar to poly(bistrifluoroethoxyphosphazene). Although some initial thermal characterization data were reported with the synthetic results, it was necessary to perform a detailed study to understand the effects of composition, molecular architecture and thermal history on the phase behaviour of these copolymers. In addition, since it is possible to control the molecular weight of polyphosphazenes using the anionically initiated polymerization of phosphoranimines[9,10,22], it is also possible to systematically investigate the effect of molecular weight on the thermal properties of such materials.

EXPERIMENTAL

A Seiko 5200 or a Mettler TA4000 DSC with two 10 K $\min^{-1}$ heating and 20 K $\min^{-1}$ cooling cycles were used for d.s.c. measurements. Unless otherwise noted, the data for the second heating cycle are given in an attempt to eliminate thermal history differences. Results obtained from the two instruments were found to be comparable. Calibration of the instrument was done using Sn and In standards. The sample (10–15 mg) was typically placed in a sealed aluminium pan and duplicate runs were performed on many of the samples to ensure repeatability. The thermal properties are summarized in *Table 1*. The maximum enthalpy peak is given in the case of samples that exhibit multiple transitions near $T(1)$. These samples are marked with an asterisk. This phenomenon will be detailed in the 'Results and discussion' section. WAXS was performed on a Siemens D-500 Refractometer with a 0.3° slit using a 1.541 Å Cu Kα X-ray source with a graphite monochromator and a scintillation counter detector using a step size of 0.04° in the range $2 \leq 2\theta \leq 32$° and a data collection time of 4 s. WAXS samples were approximately 1 mm thick and were melt cast into a copper boat. The SAXS data were generated using a Kratky compact camera equipped with a one-dimensional position-sensitive detector. G.p.c. data were collected using a Waters 510 HPLC pump fitted with 100 Å, 1000 Å and Linear Ultrastyragel columns in series with a Waters model 450 u.v. detector and a model 410 refractive index detector and analysed vs. polystyrene standards. Polystyrene standards varying between $M_n = 760$ and 2 300 000 were purchased from Waters. A 0.1% solution of $(n\text{-}C_4H_9)_4NBr$ in tetrahydrofuran (THF) was used as a carrier solvent to prevent tailing of the chromatograms as described by Neilson[7]. ^1H n.m.r. spectra were generated on an IBM FTNMR 300 MHz instrument vs. a tetramethylsilane (TMS) standard. Compositions were determined by ^1H n.m.r. and elemental analysis on samples that were precipitated from THF solution with $CHCl_3$ and then vacuum dried overnight. Each method provides comparable results[10,13,14]. Elemental analysis was performed by M/M Laboratories in Indianapolis, Indiana. Compositions are given as $\Phi_m = m/(n+m)$, where m and n are shown in *Scheme 1* and Φ_m is the fraction of the repeating units bearing alkoxyalkoxy side groups. The synthesis of the poly(bis-2,2,2-trifluoroethoxyphosphazene)[8] (PBFP) and the random[12] and block[13] copolymers has been reported elsewhere.

RESULTS AND DISCUSSION

The effect of molecular weight on the thermal properties of PBFP

In an effort to study the effect of molecular weight on $T(1)$ and T_i, PBFP samples of several different molecular weights were analysed by d.s.c. The results of these studies are shown as Flory–Fox plots in *Figure 1*. These data indicate that the samples utilized in this study, which were prepared by the anionically initiated polymerization of phosphoranimines, are in the molecular-weight regime in which the thermal properties are influenced by end-group effects.

The effect of composition and molecular architecture on the thermal properties of polyphosphazene copolymers

Backbone molecular architecture also has a tremendous impact on the thermal properties of polyphosphazenes. Block copolymers have higher transition temperatures at a given composition than the corresponding random copolymers. The effect of composition on $T(1)$, T_i and the ΔH of $T(1)$ is shown in *Figure 2* for

Table 1 Polyphosphazene compositions, molecular weights and thermal properties (polymerization time 13 h unless noted)

Sample	Type	Φ_m[a]	M_n ($\times 10^{-3}$)	M_w/M_n	$T(1)$[b] (K)	ΔH (J g^{-1})	T_i[c] (K)
1	PBFP	0	18	1.39	338	43	–
2	PBFP	0	34	1.88	343	36	454
3	PBFP	0	34	1.71	347	39	454
4	PBFP	0	37.5	1.49	347	39	474
5	PBFP	0	69.2	2.14	353	40	478
6	PBFP	0	79	1.54	356	45	480
7	PBFP	0	81.5	1.87	353	40	482
8	PBFP	0	99	1.46	356	47	483
9	PBFP	0	116.3	1.50	355	42	482
10	PBFP	0	175	1.67	355	45	495
11	PBFP	0	187	1.66	356	43	496
12	1a	0.019	37.7	2.34	342	35	466
13	1a	0.053	59.6	1.59	338	33	460
14	1a	0.101	43.9	1.41	331	23	435
15	1a	0.166	44.9	1.55	327	5	–
16	1a	0.028	53.2	1.78	344	41	463
17	1a	0.053	40.1	1.92	335	36	444
18	1a	0.126	41.1	1.60	316	13	434
19	1a	0.035	20.3	1.38	334	33	444
20	1a	0.069	20.1	1.36	329	27	429
21	1a	0.096	18.1	1.38	323	23	427
22	1a	0.111	16.7	1.31	319	22	–
23	1a	0.161	13.9	1.41	311	16	–
24	1a	0.202	30.6	1.77	N/A	N/A	–
25	1b	0.013	17.3	1.40	341	38	439
26	1b	0.026	17.5	1.45	341	37	428
27	1b	0.051	18.7	1.61	332	28	–
28	1b	0.118	9.2	1.71	321*	12	–
29	1c	0.017	16.5	1.39	338*	36	439
30	1c	0.024	12.8	1.38	337*	27	–
31	1c	0.066	9.7	1.36	337*	21	–
32	1c	0.102	8.0	1.35	326*	22	–
33	1d	0.007	28.1	1.58	337	28	435
34	1d	0.024	25.3	1.44	340*	22	–
35	1d	0.027	44.0	1.39	340*	22	–
36	1d	0.038	29.4	1.37	337*	14	–
37	1d	0.088	16.6	1.30	319*	5	–
38	2a	0.028	41.2	1.54	347	40	466
39	2a	0.043	43.0	1.52	346	37	456
40	2a	0.113	36.2	1.51	348	32	446
41	2a	0.197	35.1	1.44	344	21	438
42	2a	0.294	24.8	1.44	340	22	–
43	2a	0.036	49.6	1.57	352	43	463
44	2a	0.046	32.7	1.62	346	34	453
45	2a	0.136	34.3	1.43	341	28	434
46	2a	0.187	29.7	1.38	342	22	–
47	2a[d]	0.047	127.4	1.36	353	46	484
48	2a[d]	0.080	73.4	1.56	341	39	456
49	2a[d]	0.126	49.1	1.57	339	27	–
50	2a[d]	0.134	46.4	1.34	320	22	–
51	2a[d]	0.026	47.7	1.76	351	36	474
52	2a[d]	0.042	54.7	1.50	339	35	447
53	2a[d]	0.113	57.7	1.36	332	25	433
54	2a[d]	0.134	44.1	1.39	330	24	–
55	2a[d]	0.175	67.7	1.36	326	21	–
56	2b[e]	0.037	9.5	1.28	344*	33	436
57	2b[e]	0.055	8.8	1.76	338*	29	–
58	2b[e]	0.091	10.4	1.42	337*	21	–
59	2b	0.012	22.7	1.67	344	40	448
60	2b	0.019	21.1	1.54	340	36	439
61	2b	0.053	22.7	1.56	339*	32	433
62	2b	0.089	22.6	1.58	344*	24	420
63	2c	0.019	13.5	1.32	337	35	437
64	2c	0.033	10.0	1.17	323	25	–

[a] Φ_m = fraction of the repeating units bearing alkoxyalkoxy side groups
[b] The asterisks (*) indicate multiple transitions near $T(1)$
[c] Dashes indicate that T_i was too weak to determine by d.s.c.
[d] Polymerization time 33 h
[e] Polymerization time 5 h

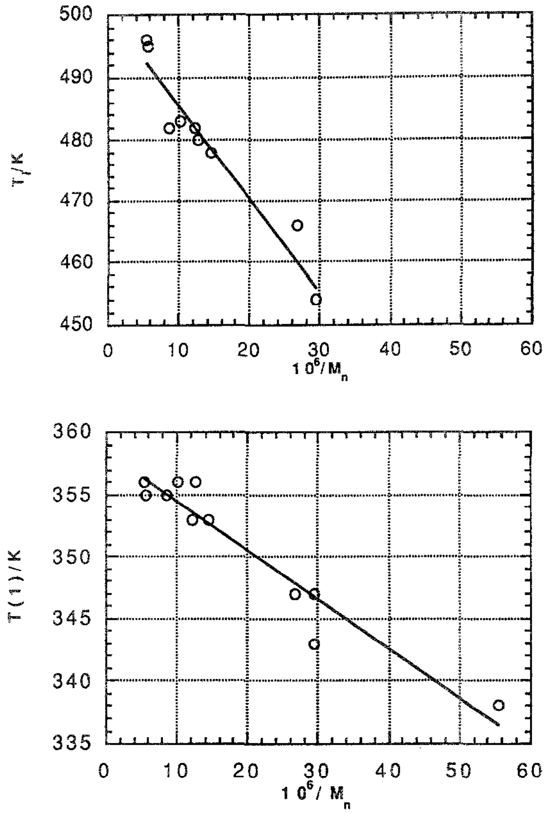


Figure 1 The effect of molecular weight on the $T(1)$ and T_i of PBFP

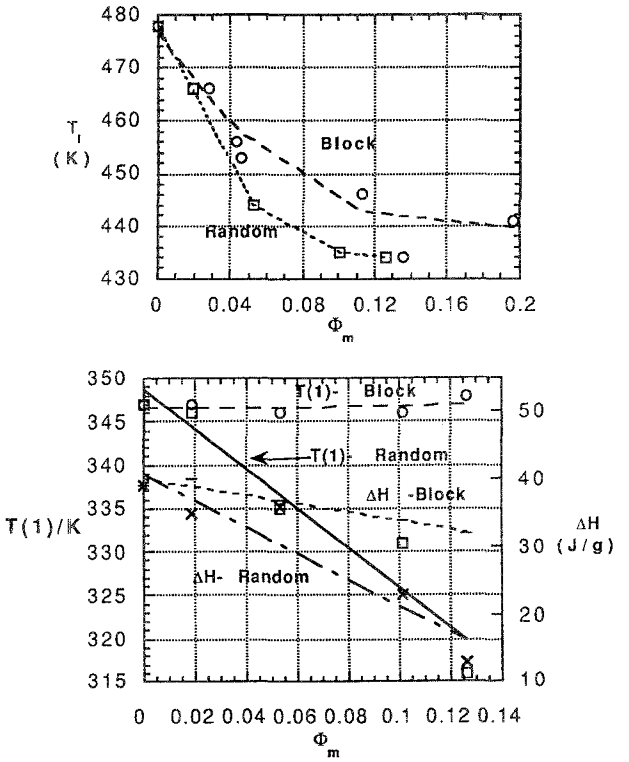


Figure 2 The effect of composition and molecular architecture on the $T(1)$, T_i and ΔH of the $T(1)$ for polymers **1a** and **2a**: (○) block, 13 h polymerization time; (□) random

samples of comparable molecular weights ($M_n = 36\,000 \pm 6000$).

Figure 2 shows a clear dependence of $T(1)$ on both the composition and the molecular architecture. In the case of the random copolymers, the $T(1)$ and the ΔH of that

Table 2 The effect of addition order on block copolymer properties

First monomer	Amount of **4** reacted (%)	$\Phi_m{}^a$	Yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n	$T(1)$ (K)
4	5	4.7	87.6	127.4	1.36	353
4	10	8.0	95.7	73.4	1.56	341
4	15	12.6	88.4	49.1	1.52	339
4	22	13.4	51.7	46.4	1.34	321
3	11	1.2	95.5	47.6	1.76	340
3	21	2.4	82.4	54.8	1.50	339
3	45	5.6	ND	57.7	1.36	340

[a] Φ_m is the percentage of repeating units bearing a 2-methoxyethoxy unit as shown in *Scheme 1*

transition decrease dramatically with the incorporation of alkoxyalkoxy groups into the backbone. The block copolymers have a $T(1)$ transition temperature that is relatively unaffected by the composition in this range. As previously noted, the molecular weight also affects $T(1)$. For instance, $T(1) = 311$ K for the $M_w = 21\,900$ sample 23 with 16.1% 2-methoxyethoxytrifluoroethoxyphosphazene repeating units ($\Phi_m = 0.161$) and $T(1) = 327$ K for the $M_w = 69\,700$ sample 15 of similar composition ($\Phi_m = 0.166$). This change is consistent with the aforementioned molecular-weight effects in PBFP. Sample 13 has a 50% higher molecular weight than sample 17, but the $T(1)$ is only 3 K higher. Many other analogous examples are present in *Table 1.*

Unlike $T(1)$, T_i is affected by composition in the case of both the random and the block copolymers. An increasing concentration of alkoxyalkoxy groups dramatically lowers and broadens the T_i in the case of both the random and block copolymers. This broadening may be attributed to increasing disorder imparted by the presence of the disrupting alkoxyalkoxy side groups. T_i values determined by optical birefringence measurements correspond to the high end of the endothermic peak observed by d.s.c.[32]. For instance, homopolymer sample 9 has a peak d.s.c. T_i of 210°C and an optically determined value of 230°C. ΔH values for T_i are of the order of $1-4\ \mathrm{J\,g^{-1}}$ and are dependent upon Φ_m. The values of T_i obtained for the PBFP samples vary between 3.2 and $5.4\ \mathrm{J\,g^{-1}}$, depending upon the molecular weight and the thermal history of the sample. Comparable samples are in agreement with the literature[14].

T_g values also shift slightly with molecular weight and composition and are of the order of −60 to −54°C for the copolymers. The T_g values are difficult to determine by d.s.c. for the PBFP homopolymer and the low-Φ_m copolymers due to high degrees of crystallinity. The ΔC_p of the T_g increases with increasing Φ_m.

It has been proposed that only chain segments with relatively long runs of bistrifluoroethoxy units can form the hexagonal mesophase[13], as should be the case for the block copolymers. The transition temperature decreases as the concentration of 2-methoxyethoxy-bearing repeating units increases.

It has been noted that longer polymerization times lead to higher molecular weights, but lower $T(1)$ transition temperatures at a given composition. This effect has been previously discussed, and may be attributed either to a randomization by nucleophilic attack of the alkoxide by-product of the polymerization on the backbone or to macrocondensation, which would lead to a multiblock structure[13]. This effect is responsible for the deviation between $X_{n,\mathrm{PBFP}}$ and X_n by s.e.c. The same type of analysis can be used to investigate the effect of polymerization time on $T(1)$. Sample 49 (33 h polymerization time after the subsequent addition, $\Phi_m = 0.126$, $M_n = 46\,400$, $M_w/M_n = 1.34$) would have a calculated X_n of 56 as opposed to the 190 estimated by s.e.c.

The effect of the order of monomer addition

In an effort to study the effect of the order in which the materials are added during block copolymerization, a series of block copolymers were made by polymerizing tris-2,2,2-trifluoroethoxy-*N*-trimethylsilylphosphoranimine (**3**) from 2-methoxyethoxy-bis-2,2,2-trifluoroethoxy-*N*-trimethylsilylphosphoranimine (**4**) and also **4** from **3**. The samples were polymerized for 43 ± 1 h after making the subsequent addition of monomer. The M_n before addition of **3** was 16 000 as determined by s.e.c. Similarly, the M_n was 25 800 before the addition of **4**. The properties of the resulting materials are shown in *Table 2*.

It can be noted that far fewer 2-methoxyethoxy groups are incorporated into the copolymer when the polymerization is conducted from the products of the polymerization of **3** compared to those in which **4** is polymerized first. This may be attributed to a greater tendency for **4** to homopolymerize due to its relatively weaker N–Si bond. This effect has been previously described and is also believed to be responsible for the lower molecular weights that result from chain transfer to monomer[10]. This homopolymer is then lost in the purification step. Since it has been hypothesized that the thermal properties are determined by the length of the bis(trifluoroethoxy)phosphazene segments that are undisrupted by alkoxyalkoxy groups[13] and the chain length with these moieties is the same in the samples that start from **3**, the thermal properties are basically unaffected by the short segments of repeating units bearing 2-methoxyethoxy groups on one end of the polymer chain.

The effect of thermal history

The $T(1)$ temperatures attained upon cooling are considerably lower than on the heating cycle. Typical data are compiled in *Table 3*. $\Delta H(T(1)_{\mathrm{cooling}})$ values are similar. The transition temperature is somewhat dependent upon the cooling rate for the samples studied. For instance, block copolymer 49 had a peak value of $T(1) = 316.4$ K ($\Delta H = 25.8\ \mathrm{J\,g^{-1}}$) at a $5\ \mathrm{K\,min^{-1}}$ cooling rate and 313.3 K at $40\ \mathrm{K\,min^{-1}}$ ($\Delta H = 25.0\ \mathrm{J\,g^{-1}}$).

Table 3 A comparison of heating and cooling $T(1)$ values

Sample	$T(1)$ 2nd heating (K)	$T(1)$ 2nd cooling (K)
16	344	324
17	335	316
18	316	285
49	331	301

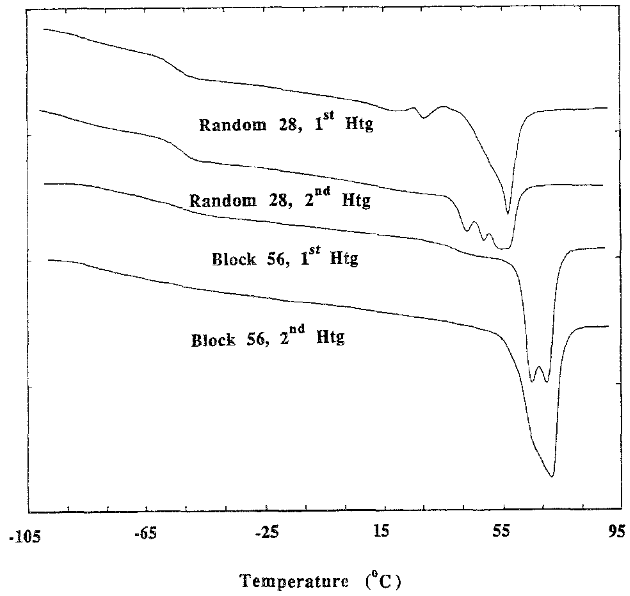


Figure 3 D.s.c. traces of polymers 56 and 28, which show multiple thermal transitions on the first and/or second heating cycles

Intermediate cooling rates show intermediate $T(1)$ and ΔH values. Additional experiments were also performed in which samples were heated above T_i and then cooled and heated at various rates. Random copolymer sample 17 had a $T(1)$ of 42°C on cooling at 20°C min^{-1} and 63°C after subsequently heating at 10°C min^{-1} in comparison to 43°C and 63°C, respectively, at 0.1°C min^{-1}. Block copolymer sample 45 had a $T(1)$ of 67°C and 69°C on the second heating following a 20°C min^{-1} and 0.1°C min^{-1} cooling, respectively. As the cooling rate increases, the $T(1)$ peak broadens, but the transition from the mesophase to the orthorhombic crystalline phase is apparently fast enough on the d.s.c. timescale that kinetic effects are not significant for the copolymers of types **1a** and **2a** in the composition and molecular-weight ranges studied.

As noted in *Table 1*, a number of the **1b**, **1c**, **1d**, **2b** and **2c** samples display multiple thermal transitions below $T(1)$. This phenomenon has been observed in the case of both the random and block copolymers with higher concentrations of alkoxyalkoxy side groups and is extremely dependent upon the thermal history of the sample. It is particularly prevalent in the samples bearing the longer 2-(2-methoxyethoxy)ethoxy substituents. Typical d.s.c. scans for the first and second heating are shown in *Figure 3* for a sample exhibiting multiple transitions near $T(1)$.

One possible explanation for these multiple endothermic transitions is that they are transforming from one crystalline form to another. This has been observed in the case of poly(diphenylphosphazene)[30] and analogous copolymers with phenyl-*o*-tolylphosphazene as well as in poly((bis-2,2,3,3,3-pentafluoropropoxy)phosphazene)[33]. However, these transitions are exothermic. Another more plausible explanation for the multiple transitions observed in these copolymers is partial melting behaviour, which can be attributed to a distribution of crystallite sizes that undergo phase transitions at slightly different temperatures. This behaviour has been observed by Magill in the case of the poly(bis-2,2,2-trifluoroethoxyphosphazene) precipitated from solution[14]. Two peaks were observed and studies showed that it is possible to anneal the samples above $T(1)$ such that the $T(1)$ transition temperature increases and the lower-temperature peak is eliminated. Similar behaviour has been noted for the polyphosphazene copolymers studied. For example, block copolymer 43 has $T(1) = 332$ K with a ΔH of 25 J g^{-1} on the first 10 K min^{-1} heating cycle (as precipitated from solution). Additionally, a small shoulder is observed at ca. 313 K. After heating the sample to 513 K ($> T_i$) and cooling at 20 K min^{-1}, the $T(1)$ increases to 341°C, the $\Delta H = 39$ J g^{-1} and the shoulder disappears. This corresponds to increased order in the samples, which go from a lamellar fan-like monoclinic structure as cast from solution to a more ordered orthorhombic rod-like batonnet structure when cooled from isotropization, as confirmed by optical and electron microscopy and X-ray and electron diffraction[33,35]. In the case of the block copolymers with 2-(2-methoxyethoxy)ethoxy groups, similar effects are noted, except that two peaks are resolved in lieu of a shoulder as cast from solution (see *Figure 3*). However, after heating above T_i and cooling at 20 K min^{-1}, the peaks converge into one. This dual transition may be more pronounced due to the difficulty in packing the bulky 2-(2-methoxyethoxy)ethoxy side groups upon fast crystallization from solution. However, when these samples are cooled rather slowly, there might be time for the bistrifluoroethoxy regions to associate into uniform phase-separated or partially phase-separated crystals. In the case of the random copolymers, however, the situation is much more complex in that the alkoxyalkoxy groups should be randomly distributed along the chain and therefore it might be thermodynamically favourable to pack into crystals of several different sizes depending upon the location of the disrupting groups. Thus, as precipitated from solution, broad $T(1)$ transitions are noted for some samples, which are resolved into two or more peaks upon slow cooling. The $T(1)$ transition in these samples is very dependent upon the thermal history of the samples and heating and cooling rates. This phenomenon is shown in *Figure 4*.

Annealing studies

Annealing studies were performed to determine the degree of crystallinity (X_c) using the method developed by Magill *et al.*[14]. This method assumes that the ΔC_p of the T_g and the ΔH of the $T(1)$ are linearly related to X_c by the relations:

$$\Delta C_p(T_g) = k_1(1 - X_c) \qquad (1)$$

and

$$\Delta H(T(1)) = k_2 X_c \qquad (2)$$

where k_1 and k_2 are constants. Although they recognize

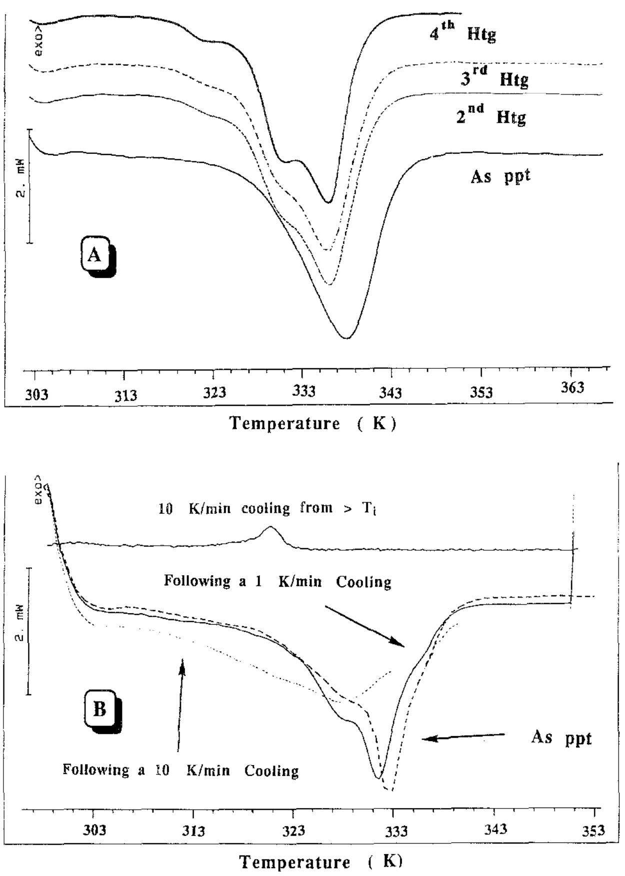


Figure 4 The effect of thermal history on the multiple transition phenomenon for random copolymers: (A) sample 28 for several 10 K min^{-1} heating and 20 K min^{-1} cooling cycles; (B) sample 56 at 10 K min^{-1} as precipitated, following a 10 K min^{-1} cooling from 473 to 298 K, and following a 1 K min^{-1} cooling from 353 to 298 K

that the assumption of linearity is not completely valid, the authors were able to show that this technique is useful for obtaining a rough estimate of the degree of crystallinity of the poly(bis-2,2,2-trifluoroethoxyphosphazene) homopolymer (PBFP). As discussed above, the polymers prepared by the anionic polymerization of phosphoranimines are believed to be highly linear. This is manifested by the observation that PBFP prepared by this route has an almost immeasurably small ΔC_p, indicating a very high degree of crystallinity as cast from solution. The block copolymers are also more crystalline that the analogous random copolymers, based on similar observations. The PBFP sample prepared by the ring-opening technique and studied by Magill has a chain-folded structure as cast from solution in which X_c was estimated at 0.34. X_c increased to 0.94 after heating above $T(1)$, followed by cooling to the orthorhombic phase.

In order to obtain an estimate of the degree of crystallinity of one of the block copolymers from **2a** series (sample 45), independent samples were heated from 298 K to an annealing temperature below $T(1)$ at 10 K min^{-1} and then annealed for 30 min at 308, 318, 328 and 338 K, respectively. The samples were then cooled to 153 K at 20 K min^{-1} and then heated at 10 K min^{-1} to 523 K. The data from this second heating cycle were used to estimate X_c. The values for the sample after isotropization are also included. Repeatability was ensured by duplicate runs. By simultaneously solving

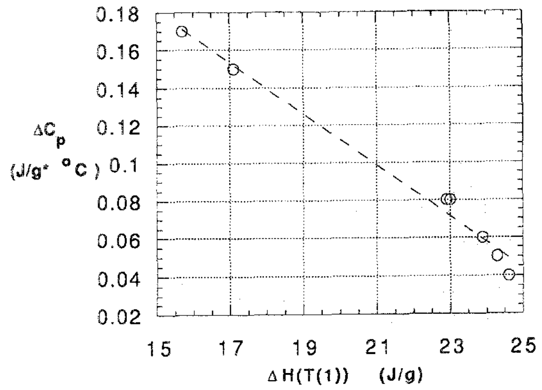


Figure 5 The determination of X_c for block copolymer sample 45

equations (1) and (2), k_1 can be obtained from the y intercept and $-k_1/k_2$ from the slope of the $\Delta C_p(T_g)$ vs. $\Delta H(T(1))$ plot (*Figure 5*).

From this plot, values of $k_1 = 0.385\,\mathrm{J\,g^{-1}}$ and $k_2 = 28.2\,\mathrm{J\,g^{-1}\,K^{-1}}$ can be determined. X_c is estimated at 0.66 for the sample as precipitated from solution and 0.87 after heating above $T(1)$ and then cooling using equation (2). Equation (1) gives 0.56 and 0.89, respectively, but the determinate error is higher due to the low values of ΔC_p. The correlation coefficient for the slope of this curve is 0.992, as determined by a least-squares fit of the data. This result would seem to indicate that the block copolymers synthesized by the anionic polymerization of phosphoranimines have a higher degree of crystallinity as precipitated than the PBFP prepared by the ring-opening method. This may be attributed to lower molecular weights, lower polydispersities and a more linear structure. Conversely, X_c is calculated to be lower for the block after cooling from above $T(1)$. This may be due to the presence of the alkoxyalkoxy-bearing repeating units concentrated on one end of the chain. Morphological studies have indicated that these segments may be excluded from the crystals in the case of the block copolymers[34]. This should result in a slightly lower degree of crystallinity. The fact that these blocks have an observable T_g in contrast to the homopolymer prepared in the same way is also an indicator that the values obtained for X_c are reasonable. The practically immeasurably small ΔC_p values for the PBFP homopolymer preclude similar analysis on that material.

Variable-temperature WAXS

WAXS samples were prepared by melting the sample into a 1 mm thick copper boat above the T_i of the sample. Data were gathered at 5 K increments in the region near $T(1)$ for block copolymer 46 (**2a** series—*Figure 6*) and random copolymer 18 (**1a** series—*Figure 7*). These samples have similar molecular weights and compositions but differ in their molecular architecture. Based on single-crystal X-ray diffraction studies on similar samples[35], block copolymer 46 should have a non-oriented, extended-chain orthorhombic crystalline structure at the beginning of the WAXS experiment since the sample was heated above T_i. Random copolymer 18 is known to have a monoclinic structure after cooling from above T_i.

There are several key differences between the variable-

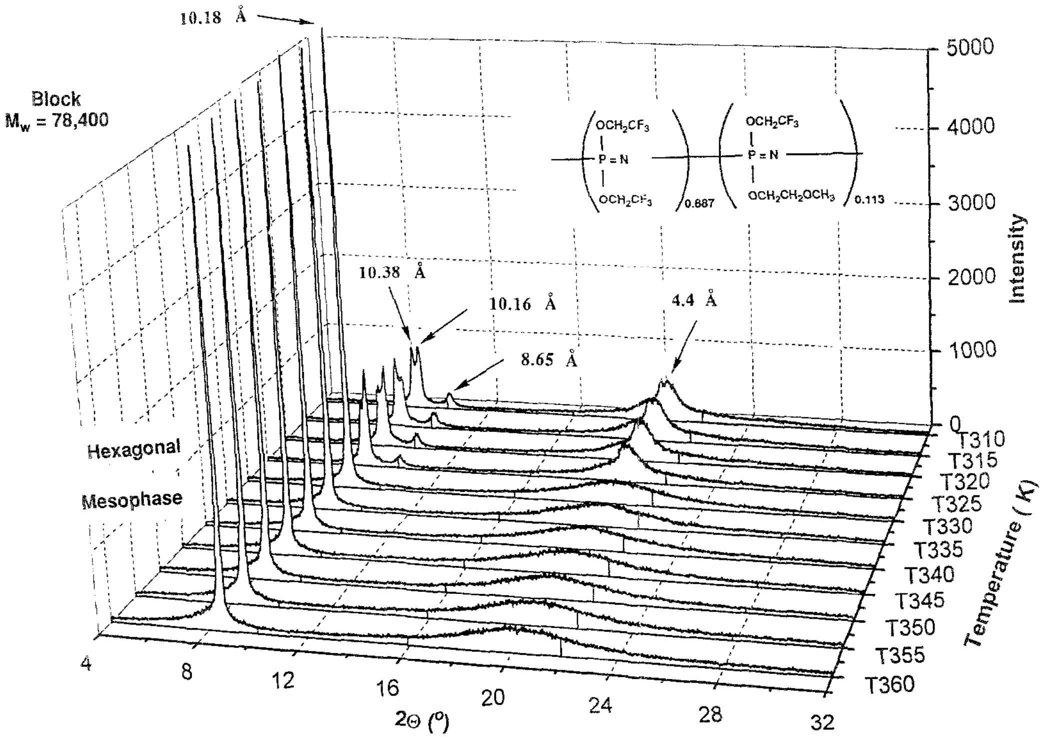


Figure 6 Variable-temperature WAXS data for block copolymer 46. The *d*-spacings are shown on the figure

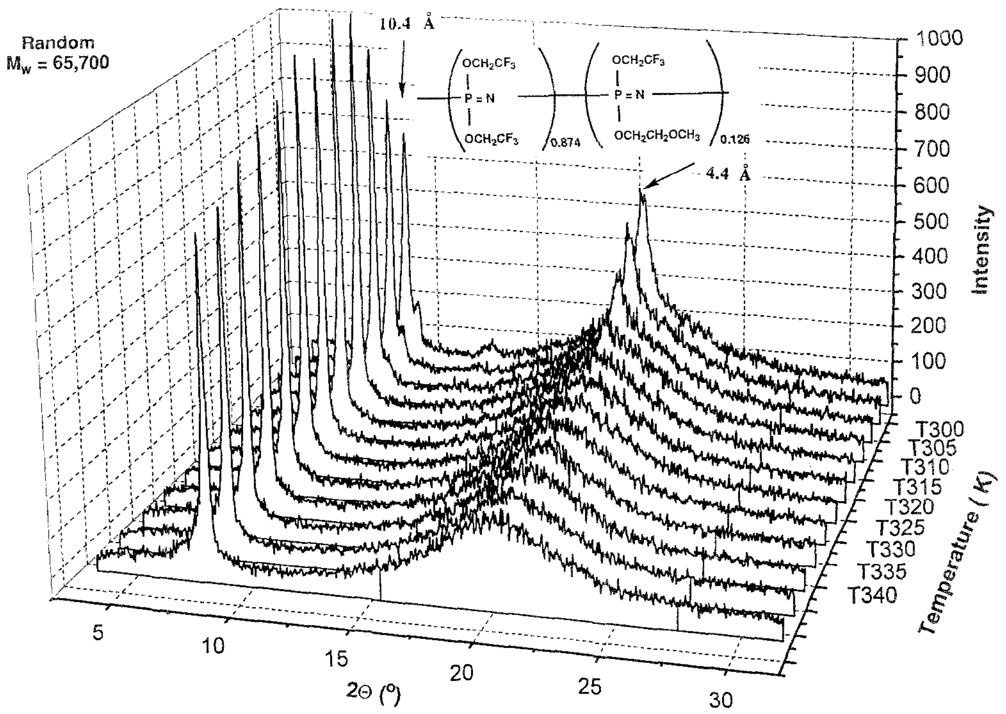


Figure 7 Variable-temperature WAXS data for random copolymer 18

temperature WAXS data for the block and random copolymers. The most striking difference is in the intensity of the reflection at $d \approx 10.2$ Å above $T(1)$ (the precise *d*-spacing is temperature-dependent owing to thermal expansion of the sample). This peak can be attributed to the (1 0 0) reflection and can be correlated with the interchain distance[26]. Assuming a hexagonal structure, this would correspond to an interchain distance of 12.0 Å. The block copolymer has a (1 0 0) reflection intensity of 5900 units after transforming into the hexagonal mesophase whereas the random copolymer has an intensity of 1075 for the same sample thickness. This suggests that the block copolymer has a more ordered mesophase structure. This is also supported by the observation that this reflection is somewhat broader for the random copolymer. This

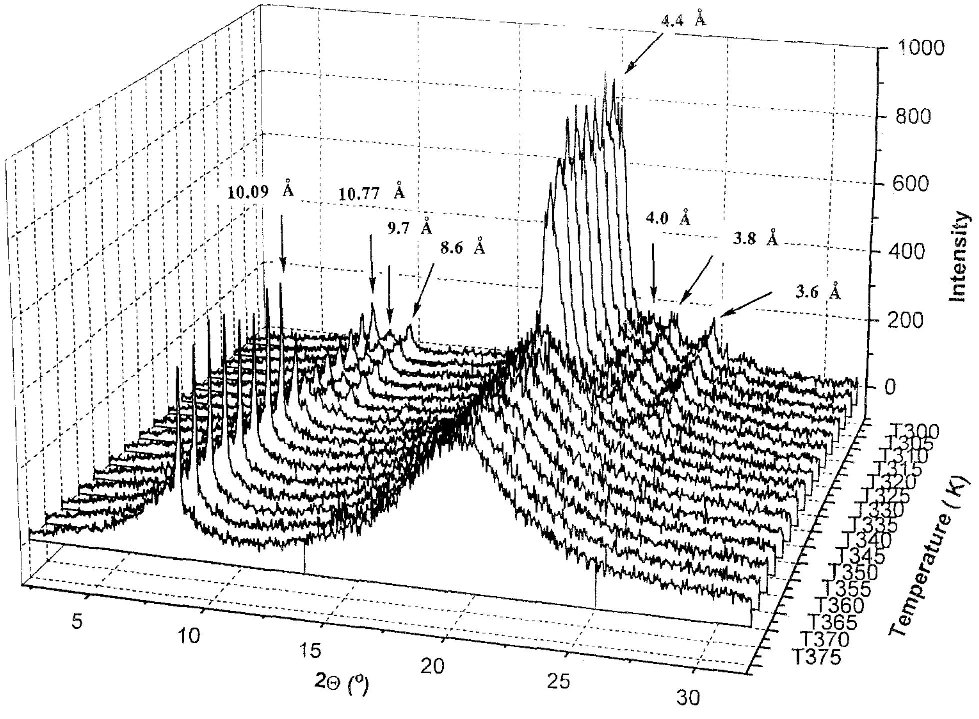


Figure 8 WAXS data for block copolymer 61 of the **2b** series

could be due to disordering of the backbone by randomly distributed alkoxyalkoxy moieties. The intensity ratio between the block copolymer orthorhombic (2 0 0) reflection (10.38 Å) to the mesophase (1 0 0) is 7.4 : 1 while the (1 0 0) peak increases by a factor of 1.4 in the random copolymer upon transforming into the mesophase. Random copolymer sample 17, which has a much lower proportion of 2-methoxyethoxy-bearing repeating units and is known to have an orthorhombic structure after heating above $T(1)$[35], exhibits an orthorhombic (2 0 0) to mesophase (1 0 0) intensity increase of a factor of 2.4 at about 340 K. This should be anticipated based on the fact that the length of the bistrifluoroethoxy runs that are available for alignment in the mesophase are longer for that copolymer. Such intensity increases were also shown in the case of the WAXS studies on poly(*p*-methylphenoxyphosphazene) by Magill and Rieckel[21], on PBFP by Desper *et al.*[35] and on bis-2,2,3,3-tetrafluoropropoxyphosphazene by Papkov[36]. In all cases, the transition temperature observed by WAXS is in good agreement with the d.s.c. data on the second heating cycle. In addition, it should be noted that there is a decrease in the intensity of the amorphous halo region at ca. 4.4 Å above $T(1)$ in all samples, which can be attributed to the onset of side-group motion above $T(1)$.

Another feature of the variable-temperature WAXS block-copolymer data is the existence of the reflection at 10.16 Å at the start of the experiment. This peak probably indicates the presence of mesophase, which is frozen into the orthorhombic structure after cooling from above T_i during sample preparation. The existence of an interspersed metastable mesophase has also been observed for the PBFP homopolymer[35] and in the case of polyphosphazene copolymers bearing aryl groups[37].

It was also of interest to investigate the effect of longer 2-(2-methoxyethoxy)ethoxy substituents on the WAXS behaviour of block copolymers in comparison to polymers of the **2a** series. The variable-temperature WAXS data for sample 61 can be seen in *Figure 8*. The structure of this copolymer after cooling above $T(1)$ has not been determined.

The intensity of the interchain distance peak is much lower and the peak is broader in the case of the block copolymer with the longer side groups. The intensity increases by a factor of 4 instead of 7.4 as for the block sample 46 mentioned above. This could be due to backbone disordering caused by the longer disrupting side-group length for this polymer. Additional studies with samples of comparable molecular weights and compositions are necessary to further elucidate the effect of side-group length.

Variable-temperature SAXS

Since the existence of microphase separation in polyphosphazene block copolymers could affect the mechanical properties of such materials, it was of interest to study one of these copolymers by SAXS to determine whether such a phenomenon is observed. Structural studies indicate that some sort of microphase separation might exist in polyphosphazene block copolymers due to the apparent exclusion of the alkoxyalkoxy moieties from the bistrifluoroethoxy domains[34]. Block copolymer sample 46 was chosen for this study because of the expectation that it was the most suitable sample due to a relatively low polydispersity index (1.38) and a relatively favourable composition (1 : 1 being ideal). The sample was studied as precipitated from solution. Variable-temperature WAXS for this sample shows a moderate 1.4-fold increase in intensity for the 10.4 Å interchain spacing reflection at $T(1)$. Significant changes were noted in the SAXS of this sample as the temperature was increased (see *Figure 9* and *Table 4*).

A periodicity of 20 nm is noted at room temperature.

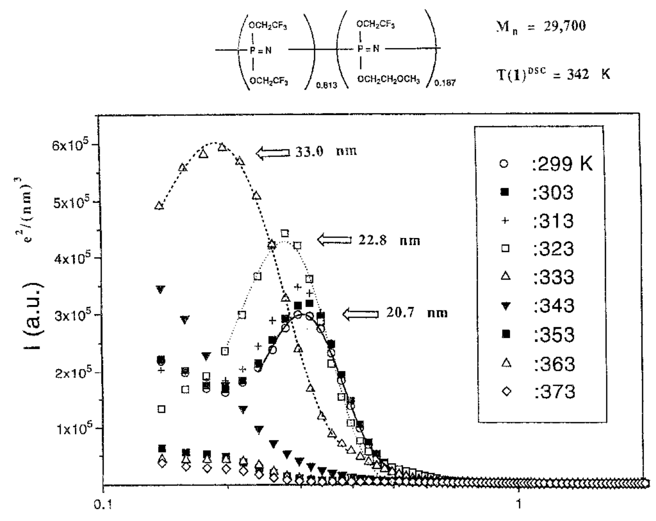


Figure 9 SAXS data for block copolymer 46

Table 4 SAXS data for block copolymer 46

T (°C)	Q (nm^{-1})	d (nm)
299	0.304	20.7
323	0.276	22.8
333	0.190	30.0

Assuming a planar *cis–trans* backbone conformation involving two repeating units, which is known for most polyphosphazenes[38] (including PBFP[26]), a fibre repeating period of 4.9 would yield a periodicity of about 82 repeating units. X_n is estimated to be 122 for this sample by s.e.c. It is known from end-group analysis[13], electron microscopy on shear-oriented samples[34] and unpublished light scattering results that s.e.c. is accurate to within about 15% for these polymers. This would indicate a partially chain-folded structure. Morphological studies also indicate that many of these polymers have about one fold per chain as precipitated from solution[34]. The onset of the $T(1)$ by d.s.c. is 320 K and takes the form of a shoulder observed on the first heating cycle ($T(1)_{\text{peak}} = 342$ K) and by 330 K the onset of the primary peak occurs. This corresponds with the SAXS data in which slight changes in the d-spacings, indicating an increase in the radius of gyration, are occurring at 323 K. This is probably related to the aforementioned partial 'melting' of the crystals containing shorter chain sequences. Significant changes are noted by 333 K. At temperatures above $T(1)$, a d-spacing of ca. 35 nm can be related to the periodicity of the extended parts of the chain. This corresponds to an X_n of approximately 124 and thus excellent agreement is obtained with the s.e.c. results. The intensity decreases significantly because the contrast between the crystalline and non-crystalline packing disappears. SAXS shifts at $T(1)$ were also noted by Magill in the case of poly(p-methlyphenoxyphosphazene)[21].

Since these changes correspond to the mesophase transition temperature, no evidence for microphase separation was found. It is unknown whether microphase separation does not occur, whether the Q shifts associated with the microphase transition temperature are obscured by the mesophase transition or whether this transition might be observed in the sub-ambient temperature region, which was not studied. Further investigation is required.

CONCLUSIONS

The thermal properties of a wide variety of polyphosphazene random and block copolymers have been studied by d.s.c. and WAXS. Very significant differences in the behaviour of the random and block copolymers have been noted. In addition, a sufficient variety of samples have been studied so that it is now possible to understand the relative contribution of molecular weight and composition on the mesophase transition temperature, $T(1)$. Additionally, $T(1)$ has been used to estimate the length of the PBFP segments contributing to the mesophase in polyphosphazene copolymers. Preliminary SAXS studies have failed to detect microphase separation in polyphosphazene block copolymers but have yielded some information about the transformation to the mesophase. Overall, these studies have yielded a significant piece of the puzzle, so that, in combination with the recently completed dynamic mechanical analysis, morphological studies, dielectric relaxation spectroscopy and thermal degradation kinetics, it will be possible to gain a thorough understanding of the properties of these polyphosphazene copolymers.

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