Thermal Degradation of Polyphosphazene Homopolymers and Copolymers Prepared by the Anionic Polymerization of Phosphoranimines

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THERMAL DEGRADATION OF POLYPHOSPHAZENE HOMOPOLYMERS AND COPOLYMERS PREPARED BY THE ANIONIC POLYMERIZATION OF PHOSPHORANIMINES

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ABSTRACT

The thermal degradation of poly(bis-trifluoroethoxyphosphazene), as well as random and block copolymers bearing trifluoroethoxy and alkoxyalkoxy groups synthesized by the anionically initiated polymerization of phosphoranimines, has been investigated by TGA. These studies indicate that the thermal stability of the copolymers decreases with incorporation of alkoxyalkoxy groups. There is no direct correlation between the calculated activation energies of decomposition. This has been attributed to entropy differences. Molecular weight vs conversion plots indicate that depolymerization occurs by chain end initiation followed by complete unzipping to cyclic trimer. This is in contrast to polymers prepared by the ring-opening method. This difference has been attributed to a defect-free structure. The primary product of the decomposition of these polymers is the corresponding cyclic trimer.

INTRODUCTION

The thermal properties of polyphosphazenes are significant due the fact that many past and potential applications result from the unique combination of low temperature flexibility and high thermal stability that many of these polymers display [1]. The importance of the latter property has led to numerous studies on the thermal degradation of polyphosphazenes. Since the initial, pioneering optimization of the process involving the ring-opening polymerization of hexachlorocyclotriphosphazene by Allcock et al. in the mid-1960s, a vast number of polyphosphazenes have been prepared by the nucleophilic substitution of the resultant poly(dichlorophosphazene) with various alkoxides, aryloxides, and amines [1, 2]. Not surprisingly, some of the initial studies on the thermal depolymerization of poly(2,2,2-trifluoroethoxyphosphazene) (PBFP) were also performed by the Allcock group [3]. It was suggested that PBFP depolymerizes to hexatrifluoroethoxycyclotriphosphazene and the analogous cyclic tetramer at temperatures above 150°C by a two-step process involving chain scission at weak points in the backbone followed by rapid depropagation to cyclic oligomers. This was determined by GPC studies at various times and analysis of the decomposition products by NMR and GC/MS. Other early studies were performed by MacCallum and Tanner [4] and by Valaitis and Kyker on the kinetics of the degradation of $-(CF_3CH_2O)_{0.64}(HF_2C(CF_2)_4)_{0.36}-$ $(P=N)_n--$ copolymer [5]. The long-chain fluoroalkoxy group was utilized commercially to disrupt the high degree of crystallinity observed in the PBFP homopolymer.

A more sophisticated kinetic analysis was later performed on PBFP by Zeldin et al. [6]. These authors compared the molecular weight vs depolymerization time curve (determined by GPC) to theoretical estimates and noted a maximum in the decomposition rate at 40%. They determined that the reaction order is 0.8 and calculated the activation energies of the process by the method developed previously by MacCallum to propose that PBFP depolymerizes by random chain scission followed by partial unzipping with a small contribution from chain end initiation.

Magill et al. also studied the isothermal and dynamic thermal degradation kinetics of PBFP [7] but on the basis of their data fitted to the equation developed by Boyd [8] and reanalysis of Zeldin's data. Magill concluded that initiation occurs at the chain ends followed by depolymerization and then chain transfer with some chain scission at weak points in the backbone. He also speculated that differences in the samples might also have led to the apparently different results.

More recently, the thermal degradation of PBFP was studied by Papkov and coworkers [9]. These authors noted a significant decrease in themal stability proportional to the number of phosphoramide defects in the backbone which are formed by the hydrolysis of P—Cl bonds for polymers formed by the ring-opening process. Based on their kinetic analysis, they proposed a two-stage initiation occurs whereby the backbone first rearranges from a dialkoxyphosphazene repeating unit to a phosphoramide by the shift of a trifluoroethyl moiety to the nitrogen, followed by chain scission at the resultant weak points in the backbone. Supporting evidence included ESCA and titration with iodine and sodium thiosulfate, a process sensitive to phosphoramides, at short decomposition times which showed an increase in the number of phosphoramide groups present in the system. Although such rearrangements are common in the case of alkoxy-substituted phosphazenes [10], they had not been previously noted for trifluoroethoxy substituents.

Recently, we reported the synthesis of PBFP [11], other polyphosphazenes [12, 13], and polyphosphazene random copolymers [14] by the anionically initiated polymerization of phosphoranimines using anionic initiators such as tetra-*n*-butylammonium fluoride and numerous other alkoxides, aryloxides, amines, and amides. Using this process, it is possible to control the molecular weight, polydispersities are generally narrower than those obtained by other methods, and polymerization times and temperatures are decreased from 2–3 days at 200–250°C, reported for the uncatalyzed ring-opening polymerization [2] and phosphoranimine polymerization [15, 16] processes, to a few hours at 100°C. Additionally, it is possible to access new molecular architectures such as polyphosphazene AB block copolymers which had not been previously reported [17].

As recognized above, although several groups have studied the thermal decomposition of PBFP, the samples examined to date have been prepared by the ring-opening process. Since polyphosphazenes prepared from phosphoranimines do not have P—Cl bonds, they should initially be completely free of phosphoramide defects, and thus it is of interest to compare the kinetics of decomposition of the PBFP synthesized by this technique to past studies. Additionally, it was of interest to investigate the effect of a random or blocky polyphosphazene copolymer structure and to examine the consequence of varying the composition and the length of the alkoxyalkoxy side groups on the thermal stability of such materials.

THEORY

In general, three different methods are used to determine the activation energy for the decomposition process (E_d). This value is usually interpreted to be an average energy for all of the many complex and often competing degradation processes which occur during the thermal decomposition of polymers. The first involves the use of an Arrhenius-type method developed by Madorsky [18] in which the extrapolated initial isothermal rate of weight loss (k_d) is related to the activation energy by the relation

$$E_d = -2.3R[d(\log k_d)/d(1/T)] \tag{1}$$

This method was used by the groups of Valaitis [5], Zeldin [6], and Magill [7] to calculate E_d.

A second route involves TGA with variable heating rates (β) as used by Flynn and Wall [19] in which E_d can be determined by the relation

$$\frac{dC}{dT} = \frac{A}{\beta}(1 - C)^n \exp\left[-\frac{E_d}{RT}\right] \tag{2}$$

where the fractional weight loss $C[=(W_0 - W)/W_0]$, W is the sample weight at a given time, W_0 is the initial sample weight, A is the frequency factor, and n is the decomposition reaction order. This equation was used by Magill [7] to estimate E_d values for PBFP by integrating and measuring the temperature at which a constant fractional weight loss is obtained and then using the relation

$$E_d \approx -4.35\left(\frac{d \log \beta}{d(1/T)}\right) \tag{3}$$

Zeldin also used the method of Flynn and Wall to determine E_d [6].

The third route, which was first applied to PBFP by Zeldin [6] and was also used by Magill [7] to determine E_d, is the relation developed by Reich [20] in which the following equation is used:

$$\frac{S_1}{S_2} = \left(\frac{W_{1,c}}{W_{2,c}} \right)^n \left[\frac{1 - (W_{1,c}/W_{0,c})^{1-n}}{1 - (W_{2,c}/W_{0,c})^{1-n}} \right] \tag{4}$$

where $W_{i,c} = (W - W_r)/W_0$, W_r = the weight of the inactive material remaining, and $S_i = dW_i/d(1/T)$. The reaction order (n) can be determined by measuring S_1/S_2 at different weight fractions. E_d and A can then be obtained from the relations

$$\frac{E_d}{R} = \left[\frac{S_i(1-n)}{W_i^n(W_{0,c} - W_i^{1-n})} \right] \tag{5}$$

and

$$\log A = \log\left[\frac{\beta S_i}{C^n T^2} \right] + \frac{E_d}{2.303RT} \tag{6}$$

The entropy of activation for the decomposition can then be calculated by the Arrhenius–Eyring equation

$$\Delta S^{\ddagger} = 4.576 \log(A/T) - 49.21 \tag{7}$$

All of these methods will be used to investigate the mechanism of the thermal decomposition of polyphosphazenes synthesized by the anionically initiated polymerization of phosphoranimines.
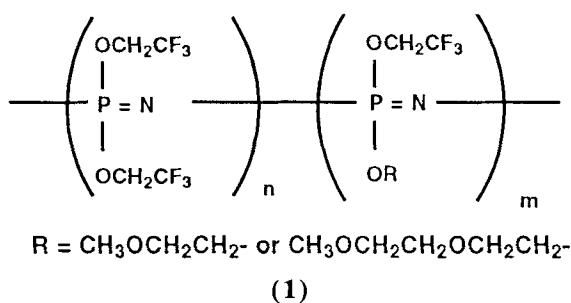
EXPERIMENTAL

Measurements

TGA was performed on a Seiko 300 TGA/DTA and analyzed on a 5040 disk station at various heating rates. Samples were typically 2.5–4.5 mg and run in open pans in air or under Ar or N_2 at a 180 mL/min flow rate. Duplicate samples were run to ensure repeatability. Decomposition product analysis was done either in vacuum-sealed glass ampules immersed in a temperature-controlled sand bath or by placing round-bottom flasks connected by a U-tube with an attached shutoff valve to a vacuum source with one flask placed in a sand bath and the other in a Dewar filled with liquid nitrogen. A 0.3 mmHg vacuum was pulled on the apparatus before placing the flask containing the polymer sample into a sand bath heated to the appropriate temperature. NMR spectra were recorded on an IBM NR-300 FT-NMR 300 MHz instrument versus TMS and 85% H_3PO_4 standards for ^1H and ^{31}P, respectively. GPC 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 UV detector and a 410 refractive index detector and analyzed vs polystyrene standards, varying between M_n = 760 to 2,300,000 (Waters). Toluene was used as a low molecular weight standard. A 0.1% solution of (n-C_4H_9)$_4$NBr in THF was used as a carrier solvent to prevent tailing of the chromatograms as described by Neilson

[21]. Elemental analysis was performed by M/M Laboratories in Indianapolis, Indiana.

Materials

Poly(bis-2,2,2-trifluoroethoxyphosphazene) (PBFP) was prepared by the anionically initiated polymerization of tris-2,2,2-trifluoroethoxy-*N*-trimethylsilylphosphoranimine in the presence of 1 mol% tetra-*n*-butylammonium fluoride at 133°C as previously described [11]. The synthesis of the phosphoranimine monomers via the Staudinger reaction [22] between azidotrimethylsilane and the suitably substituted phosphite was also previously reported [12]. The random copolymers were made by the simultaneous polymerization of $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P=N-Si(CH_3)_3$ or $(CH_3OCH_2CH_2OCH_2CH_2O)(CF_3CH_2O)_2P=N-Si(CH_3)_3$ and $(CF_3CH_2O)_3P=N-Si(CH_3)_3$ [14]. Block copolymers were synthesized by the polymerization of the former phosphoranimine followed by the subsequent addition of the latter after conversion of the first [17]. Purification of all polymers was performed by dissolving the polymers in THF and then precipitating with chloroform. After filtration and washing with excess chloroform, the samples were vacuum dried for a minimum of 13 hours. No evidence of residual solvent was noticeable by ^{1}H NMR, DSC or TGA. The compositions were determined by ^{1}H NMR on the purified polymer and correlated with elemental analysis as previously described [14, 17]. The basic characterization data for these samples are given in Table 1. In addition to PBFP, the polymers used for this study are of the form

$$
-\left(\begin{array}{c} OCH_2CF_3 \\ | \\ P = N \\ | \\ OCH_2CF_3 \end{array}\right)_n\left(\begin{array}{c} OCH_2CF_3 \\ | \\ P = N \\ | \\ OR \end{array}\right)_m -
$$

$$R = CH_3OCH_2CH_2- \text{ or } CH_3OCH_2CH_2OCH_2CH_2-$$

(1)

The fraction of repeating units bearing one 2-methoxyethoxy (Series A) or 2-(2-methoxyethoxy)ethoxy group (Series B) and one trifluoroethoxy group on phosphorus will henceforth be referred to as "Φ_m," where $\Phi_m = m/(m + n)$.

Hexa(trifluoroethoxy)cyclotriphosphazene was synthesized by adding 2.97 g (0.129 mol) Na and 9.4 mL (0.14 mol) CF_3CH_2OH (purchased from Aldrich) to 50 mL THF under Ar in a flame-dried, round-bottom flask. The THF was dried by distillation from sodium/benzophenone, and the CF_3CH_2OH was distilled under vacuum prior to use. After the alkoxide was formed, 5.98 g of vacuum dried hexachlorocyclotriphosphazene (Nippon Soda Co., 0.017 mol) was added to the reaction vessel and the solution was refluxed for 16 hours. The product was purified by precipitation from deionized water and filtration. The product was dissolved in acetone, reprecipitated from DI water, and then dried for 4 hours under a 1 mmHg vacuum at 100°C. Yield: 6.66 g (53%); ^{1}H NMR: δ ($CD_3C(O)CD_3$) 4.62 ppm

TABLE 1.   Characterization Data[a]

Sample	Type	Φ_m	M_n	M_w	T_d
1	PBFP	0	18	25	299
2	PBFP	0	34	64	313
3	PBFP	0	69	148	342
4	PBFP	0	79	122	347
5	PBFP	0	99	145	347
6	PBFP	0	175	293	346
7	Homo A[b]	0	26	48	266
8	Random A	0.028	53	95	325
9	Random A	0.053	40	77	320
10	Random A	0.126	41	66	311
11	Random A	0.202	30	54	292
12	Random A	0.035	20	28	303
13	Random A	0.069	20	27	295
14	Random A	0.096	18	25	290
15	Random A	0.111	17	20	287
16	Random A	0.161	17	22	285
17	Block A	0.047	127	173	322
18	Block A	0.080	73	115	311
19	Block A	0.126	49	77	299
20	Block A	0.134	46	62	297
21	Random B	0.013	17	24	309
22	Random B	0.026	18	25	305
23	Random B	0.051	19	30	294
24	Block B	0.012	23	38	312
25	Block B	0.019	21	32	305
26	Block B	0.053	23	35	278
27	Block B	0.089	22	36	274
28	Rev Bl A[c]	0.012	48	84	306
29	Rev Bl A[c]	0.024	55	83	304
30	Rev Bl A[c]	0.054	58	78	306

[a]"Φ_m" is the fraction of repeating units bearing one 2-methoxyethoxy group (Series A) or 2-(2-methoxyethoxy)ethoxy group (Series B). "T_d" is the temperature at which the sample reaches 10% weight loss in air at 10°C/min.

[b]The polymer synthesized from $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P=N-SiMe_3$.

[c]Block in $(CF_3CH_2O)_3P=N-SiMe_3$ which was polymerized first.

(m); ^{31}P NMR: δ (CD$_3$C(O)CD$_3$) 22.3 ppm; GC/MS: (m/z) ($-$(CF$_3$CH$_2$)$_2$O): 548; mp = 174.

RESULTS AND DISCUSSION

The Effect of Composition, Structure, and Atmosphere on the Thermal Stability of Polyphosphazene Copolymers

Thermal decomposition studies were conducted on the PBFP homopolymer and random copolymers as well as block copolymers with different compositions of trifluoroethoxy and 2-methoxyethoxy side groups using DSC at 10°C/min in air and under nitrogen. Additionally, several random copolymers of several different molecular weights with 2-(2-methoxyethoxy)ethoxy groups were investigated. The composition and molecular weight data obtained by GPC are shown in Table 1, and typical TGA curves are shown as Fig. 1.

The effects of composition and side-group structure on the thermal stability in air, where T_d is defined as the temperature at which the sample has lost 10% of its original weight at a 10°C/min heating rate, is shown in Fig. 2.

There are several observations that can be made from Fig. 2. First, the thermal stability of polyphosphazene copolymers is clearly affected by the side-group com-
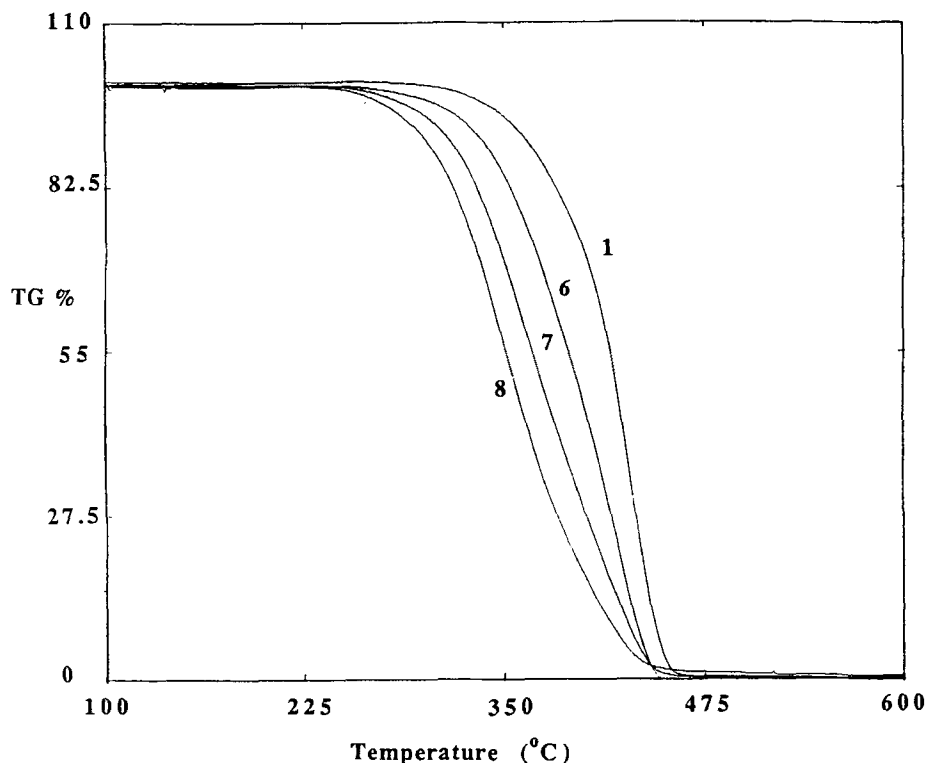

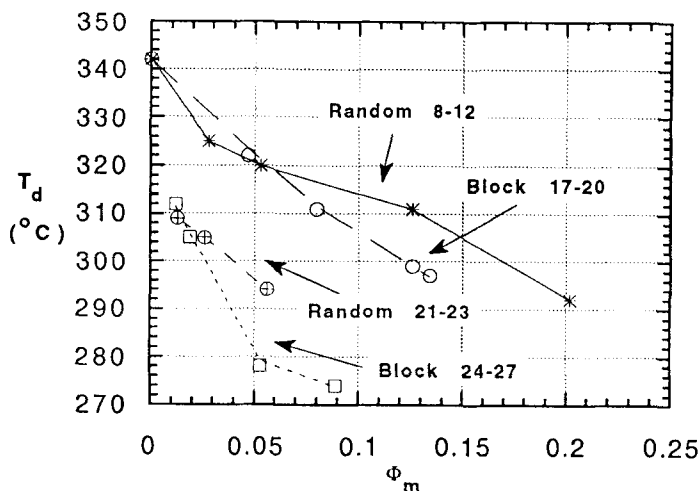FIG. 1. TGA curves for block copolymer Samples 17–20 and PBFP Sample 3.

FIG. 2.   The effect of composition on the decomposition temperature in air as determined by TGA (T_d = the temperature at which 10% weight loss occurs at a 10°C/min heating rate, and Φ_m = the fraction of the repeating units bearing an alkoxyalkoxy group).

position. There is a direct correlation between thermal stability and the concentration of alkoxyalkoxy side groups. Homopolymer 7, the polymer synthesized from $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}N{-}SiMe_3$, has a T_d of 266°C. It can also be noted that the polymers bearing the longer 2-(2-methoxyethoxy)ethoxy side groups are less thermally stable at a given composition than those with 2-methoxyethoxy groups. It can also be noted that at higher concentrations of repeating units bearing alkoxyalkoxy groups (m), the block copolymers are less thermally stable than the random copolymers. Due to the order of monomer addition, the segments bearing the alkoxyalkoxy groups are concentrated on the P-terminal end of the chain in these materials; this would seem support a process whereby the depolymerization reaction is initiated at the P-terminal end of the chain. Block copolymer Samples 28–30, which were synthesized by first polymerizing $(CF_3CH_2O)_3P{=}N{-}SiMe_3$ and thus would have the bis-trifluoroethoxy segment on the P-terminal end of the chain, exhibit values of T_d which are independent of the composition. This is additional supporting evidence that initiation occurs at the P-terminal end of the chain.

The Effect of Molecular Weight on the Thermal Stability

Molecular weight also has a considerable effect on the thermal stability of polyphosphazenes. Figure 3 shows a plot of M_n vs T_d for PBFP. The apparent leveling off in the T_d of PBFP is probably anomalous as the transition to the hexagonal mesophase ($T(1)$) and the isotropization temperature (T_i) slowly increase even above molecular weights of $M_n \approx 200,000$ [24].

Another interesting question that arises is related to the relative thermal stability of the polymers produced by the anionically initiated polymerization of phosphoranimines in comparison to those produced by the ring-opening route. Perhaps
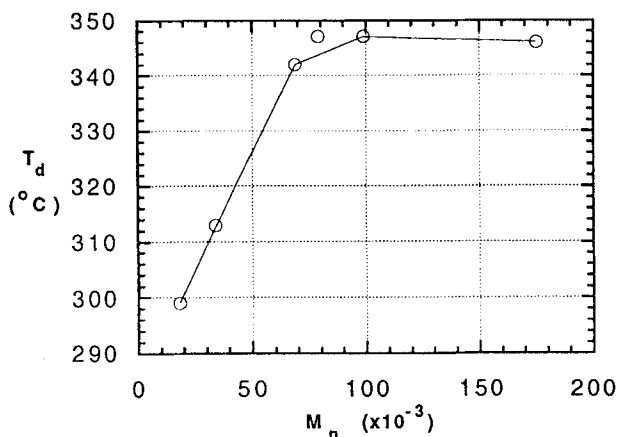
FIG. 3. The effect of M_n on T_d for PBFP Samples 1-6.

the most comparable PBFP samples are Sample 1 used in this study and the M_n = 80,000 sample used by Magill [7]. A 10% weight loss was obtained in comparable flow rates in N_2 at approximately 340°C whereas our sample reached a similar weight loss fraction at 366°C. Similar comparisons can be made with McCallum's data [4]. However, Zeldin's samples are somewhat more thermally stable [6]. Just as Papkov demonstrated that the presence of phosphoramide defects in the backbone dramatically impact thermal stability [9], these studies using the PBFP produced by the anionically initiated polymerization of phosphoranimines indicate the significant effect of molecular weight on the thermal stability as molecular weight control is possible by this method.

Isothermal kinetics have also been done at 322°C under argon. Figure 4 exhibits the natural log of the weight fraction remaining vs time for several PBFP sam-
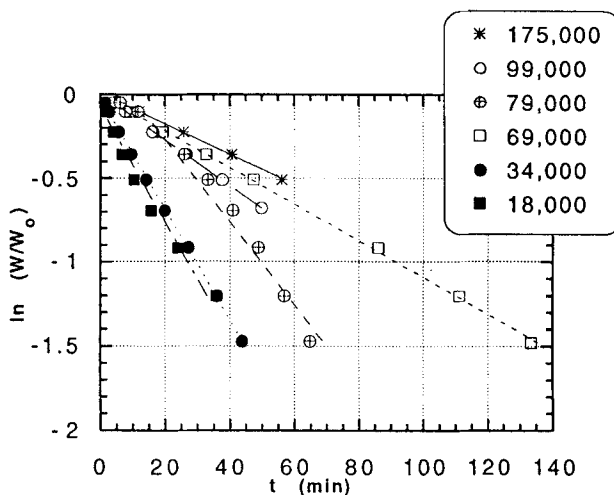

FIG. 4. Natural logarithm of the relative weight loss vs time for PBFP Samples 1-6.

ples. Based on these studies, the rate of decomposition is directly related to the molecular weight and thus to the end-group concentration. The rates calculated above are plotted vs inverse X_n (the degree of polymerization) for these PBFP samples in Fig. 5. The order of the depolymerization of PBFP is estimated to be 0.7 from the Fig. 5 plot. Although one might expect that the depolymerization would be first order in end group if the depolymerization were occurring solely at the chain ends, the fractional order may indicate a contribution of a random scission mechanism.

Residual Mass

Another notable phenomenon is that the amount of residual mass after depolymerization (W_r) is also dependent upon Φ_m as shown in Fig. 6. This may be attributed to crosslinking occurring by transetherification or transesterification reactions through the ether side groups. Although this behavior has not been seen in the case of PBFP, such reactions are well known for poly(diphenoxyphosphazene) and lead to increased W_r [7]. The homopolymer produced from $(CH_3OCH_2CH_2O)$-$(CF_3CH_2O)_2P{=}N{-}SiMe_3$ has a W_r of 22% under similar conditions.

The Effect of Atmosphere

Another phenomenon is that the polymers are somewhat more stable when decomposed under an inert atmosphere than they are in air (Fig. 7). Valaitis and Kyker reported a large difference in the thermal stability of their copolymer. Based on their data, it takes 50 minutes to reach 10% weight loss at 325°C in air but over 200 minutes in an N_2 atmosphere [5]. This may indicate that oxidative processes contribute to some of the thermal degradation processes.
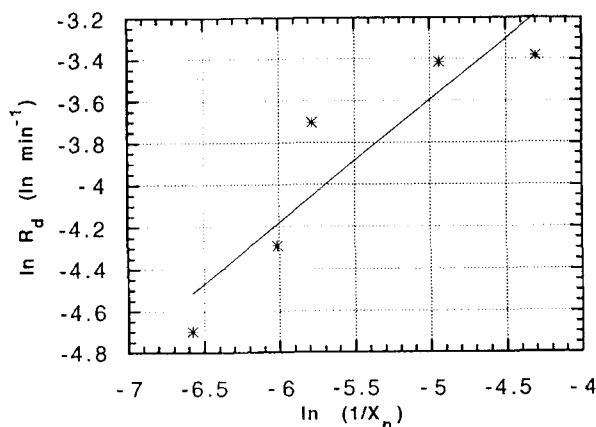

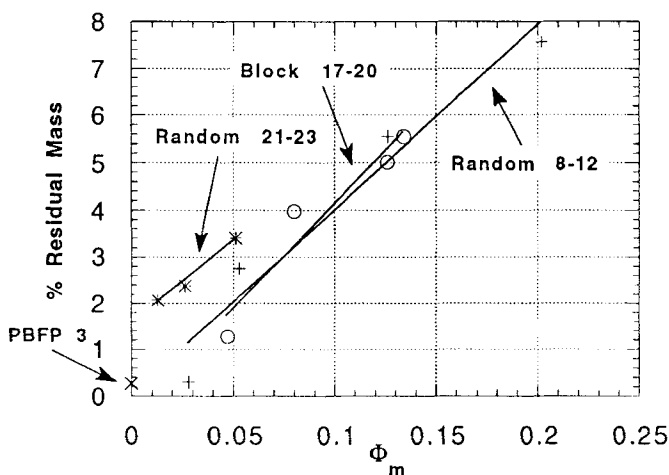FIG. 5.   The rate of decomposition vs the inverse degree of polymerization for PBFP Samples 1, 2, and 4–6.

FIG. 6. The residual mass after heating to 550°C at 10°C/min in air TGA (Φ_m = the fraction of the repeating units bearing an alkoxyalkoxy group).

Products of Decomposition

The decomposition products were studied by sealing various polymer samples in glass tubes under vacuum and then degrading them at 400°C in a sand bath for various times. The primary decomposition product of the PBFP homopolymer produced by the anionically initiated polymerization of phosphoranimines (Sample 1) is the corresponding cyclic trimer. This is similar to the results reported by other
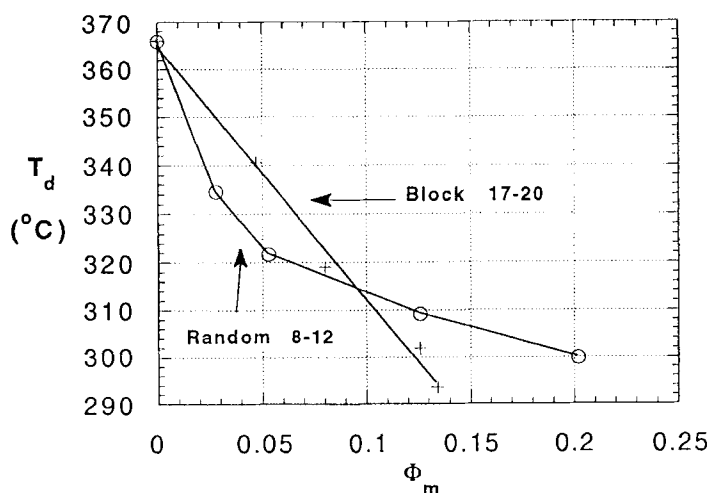
FIG. 7. The effect of composition on the decomposition temperature in nitrogen (T_d = the temperature at which 10% weight loss occurs at a 10°C/min heating rate, and Φ_m = the fraction of the repeating units bearing an alkoxyalkoxy group).

authors for PBFP synthesized by the ring-opening method [3, 6, 7]. The initial product of the decomposition of the PBFP homopolymer is identical to that from the trimer produced from hexachlorocyclotriphosphazene by ^{31}P NMR [$\delta(d$-acetone) = 22.3 ppm] and GC/MS (m/z = 549). The M and M + 1 peaks are not observed in these samples, but the breakdown patterns of the decomposition product are identical to the pattern of the synthetically produced cyclic trimer. A small amount of what is probably cyclic tetramer (^{31}P δ = 3.4 ppm) is also detected. At longer times, the trimer then decomposes to a number of products which were not identified. The decomposition products of the copolymers are also a mixture of cyclic trimers and tetramers as deduced from the trends in chemical shifts in ^{31}P NMR.

Molecular Weight vs Fractional Weight Loss

The molecular weight at various stages of decomposition was studied by removing the sample from the TGA at various times during the isothermal decomposition of the samples at 325°C and running a GPC. Other authors have shown that the molecular weight of the PBFP produced by the ring-opening process decreases rapidly with fractional weight loss, indicating a partial unzipping process [3, 6, 7]. Figure 8 exhibits the weight loss vs fractional conversion for the PBFP, and a random and a block copolymer of the same composition (Samples 10 and 19) prepared by the ring-opening route and plotted from Magill's data taken from Reference 7. It can be observed that the molecular weights remain constant for the PBFP homopolymer made by the anionic polymerization of phosphoranimines throughout the decomposition process. This is in sharp contrast to the literature results for the samples prepared by the ring-opening routes [3, 6, 7]. Although, as mentioned above, there have been different mechanistic interpretations of the data, all authors indicate a partial unzipping mechanism for polymers synthesized by the latter process. Papkov [9], as well as most other authors [3, 6], proposes that initiation of the decomposition process occurs at weak points in the polyphospha-
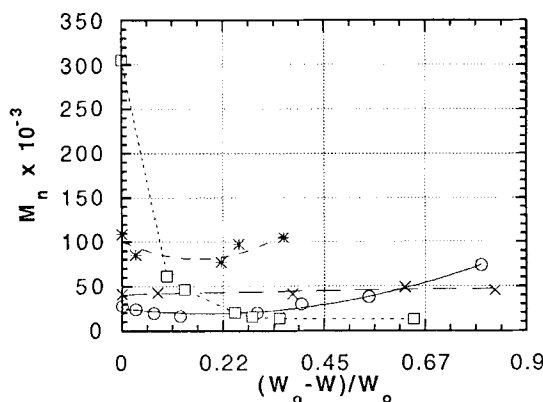

FIG. 8.   The molecular weight vs weight loss fraction behavior for PBFP from Reference 7 ($\square$), PBFP Sample 1 ($\times$), random copolymer 10 ($\bigcirc$), and block copolymer 19 ($*$).

zenes backbone, apparently at phosphoramide defects which result from P—Cl. Magill's interpretation [7] can also be explained by chain-end initiation followed by chain transfer at these defective units. The well-known presence of branching sites could also be weak points. The unknown nature of the end groups, however, makes it impossible to determine the precise decomposition mechanism.

The M_n vs conversion curve observed for Sample 1 indicates that the decomposition process involves initiation at the chain end followed by complete unzipping [22]. Polymers produced by the anionically initiated polymerization are thought to have very linear structures [24] and should be completely free of phosphoramide defects as synthesized. This defect-free structure is almost certainly responsible for the differences observed in the PBFP prepared by the two mechanisms. In addition, the end groups have been characterized by NMR and are known to be $(RO)_3P=N-$ on the P terminal end and trimethylsilyl on the N terminal end [17] although the latter is probably hydrolyzed to a phosphate end group during workup in a process analogous to the hydrolysis of the phosphoranimine monomer [25].

Figure 8 also shows that the molecular weights of both copolymers decrease slightly at first but then slowly increase vs fractional conversion. Coupled with the fraction of residual mass after decomposition, this can be explained by crosslinking of the ether side groups by transesterification or transetherification as mentioned above and as previously shown in the case of poly(diphenoxyphosphazene).

Activation Energies for the Decomposition Process

The activation energies were calculated for the PBFP homopolymer, a random and a block copolymer of the same composition (Samples 10 and 19, $\Phi_m = 0.126$) and similar molecular weights and another block copolymer (Sample 18, $\Phi_m = 0.080$) by varying the scan rates per the method of Flynn and Wall [19]. The Arrhenius-like plots of log β vs $1/T$ for various W/W_0 values are shown in Fig. 9.
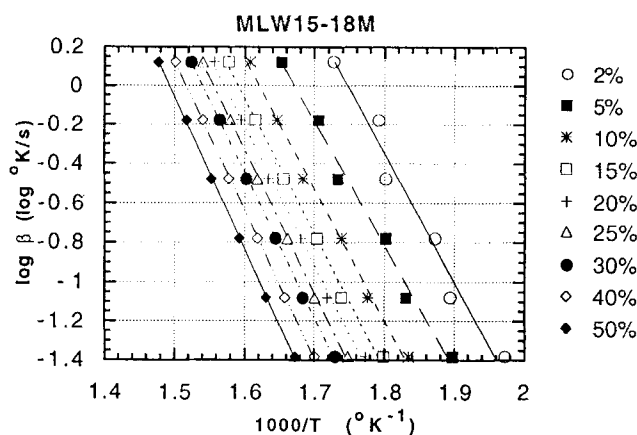

FIG. 9. Arrhenius plots at various degrees of decomposition for block copolymer Sample 9 at various weight fractions calculated by the scan rate variation method of Flynn and Wall.

The slopes of the Flynn–Wall plots vary slightly with fractional conversion. This is common for many polymers [23] and may result from a change in the relative contribution of two or more decomposition processes as the temperature increases. This leads to slightly different values of activation energy. Plots of E_d at various fractional conversions can be observed in Fig. 10. The values of E_d obtained for the PBFP homopolymer is in reasonable agreement with the 26.6 kcal/mol reported by Magill et al. for the PBFP produced by the thermal ring-opening process. Although Magill noted a dependence upon conversion for the Reich method, a single value was reported for the dynamic TGA data calculated from the Flynn and Wall method. Activation energies in this range are usually considered to be consistent with a chain-end initiation mechanism [6, 17]. The activation energies at 10% decomposition as calculated by this method for Polymers 3, 8–12, and 17–20 are shown in Fig. 11.

Although Fig. 11 shows a clear dependence of the thermal stability on the composition, the activation energies calculated by the Magill modification to the Flynn and Wall method increase with the incorporation of alkoxyalkoxy groups while the overall thermal stability is decreased (Figs. 2 and 4). This would seem to indicate that the decrease in thermal stability is due to entropic factors. However, the E_d values of the random copolymers are clearly higher than for the blocks. This is probably not due to free volume effects which would lead to a decrease in E_d with Φ_m. Since the primary decomposition product is a trimer, the ring strain in the transition state may be the factor responsible for these trends.

In an effort to determine the reliability of this data, E_d for Sample 8 was also calculated from the isothermal weight loss data. Typical isothermal weight loss curves are shown in Fig. 12.

The initial rate constant of depropagation (k_d) was determined from initial slopes of the fractional weight loss vs time curves and an Arrhenius plot was con-
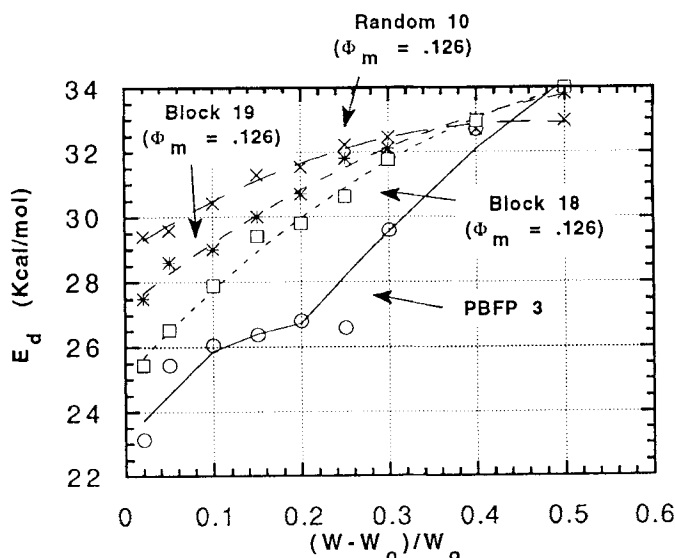

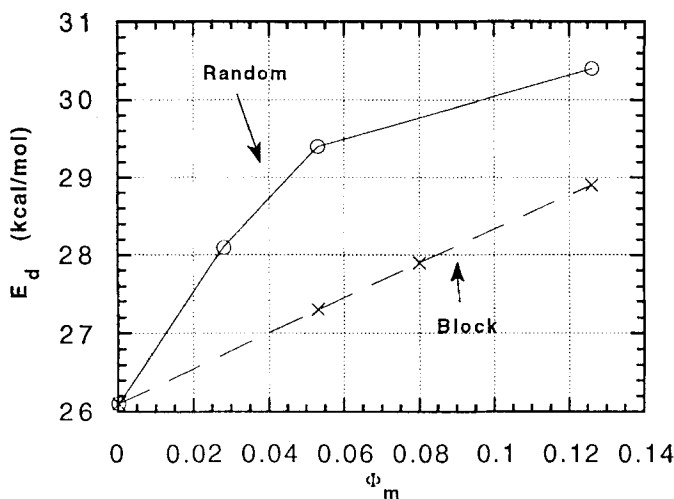FIG. 10.   Calculated E_d values at various decomposition conversions.

FIG. 11. The activation energy of decomposition for polyphosphazenes 3, 8–12, and 17–20.

structed as shown in Fig. 13. The activation energy for block copolymer 19 determined from this plot is $E_d = 31.1$ kcal/mol. Since the extrapolated value of activation energy using the Flynn–Wall method was 26.5 kcal/mol, fairly good agreement was obtained between the two techniques.

The data were also analyzed by the approach utilized by Reich. It is possible to determine the order of the reaction, n, and the activation entropy by this method. n was calculated from Eq. (4). The measured values of S_1/S_2 at $W_{1,c} = 0.80$ and $W_{2,c} = 0.20$ were determined from the slope of the 10°C/min TGA curves and then
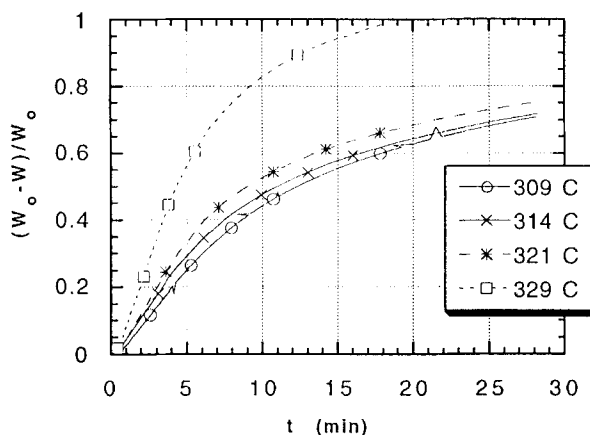

FIG. 12. Isothermal weight loss fraction vs time at various temperatures for block copolymer 19.
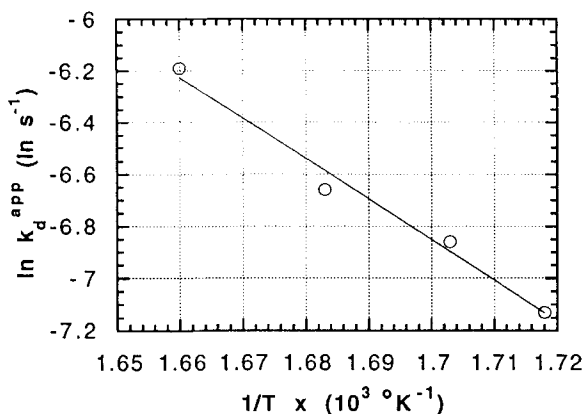
FIG. 13.   Arrhenius plot for block copolymer 19 determined for isothermal kinetics.

used to calculate *n*. Equations (5)-(8) were then used to determine E_d and $\Delta S^{\ddagger}$ at various depolymerization conversions, as shown in Figs. 14 and 15.

Although some scatter is present due to the inherent inaccuracies in measuring the slope at a given point, the general shape of Fig. 14 obtained by the Reich method is similar to Fig. 10, where E_d was determined by the Magill modification of the Flynn and Wall method except that the activation energies are a few kcal/mol lower. Magill reported 16 kcal/mol at 0-20% weight loss and 23.4 kcal/mol above 20% weight loss by the Reich method, which was less than the 26.5 kcal/mol which he
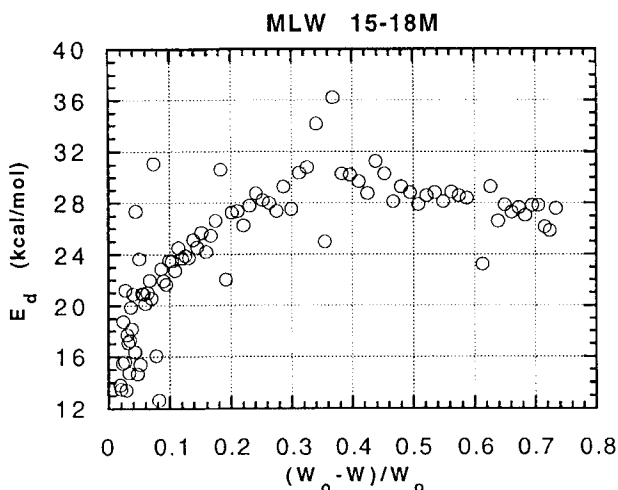

FIG. 14.   Activation energy vs fraction conversion for block copolymer Sample 19 as calculated by the Reich method.
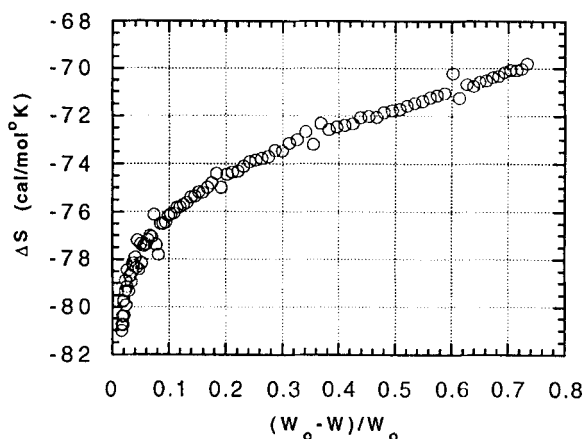
FIG. 15. The activation entropy at various conversions as determined by the Reich procedure for Sample 19.

reported by the Flynn–Wall analysis [7]. A gradual increase in E_d was noted using both the Reich and Flynn–Wall methods for Samples 8–12 and 17–20.

The calculated values of n, E_d, and $\Delta S^{\ddagger}$ obtained using the Reich technique are shown in Table 2.

It can be noted in Fig. 1 that in addition to the change in thermal stability with Φ_m (the fraction of repeating units bearing 2-methoxyethoxy groups), the steepness of the decomposition curve decreases with m. This is manifested in the calculated order of the decomposition (n) shown in Table 2. As stated above, these values were calculated based on $W_{1,c} = 0.80$ and $W_{2,c} = 0.20$. However, the order changes through the course of the depolymerization. For instance, for Sample 9, n is 1.4 for $W_{1,c}/W_{2,c} = 0.75/0.25$, 0.7 for 0.70/0.30, and 0.4 for 0.60/0.40. This demonstrates that there are two polymerization processes taking place that have relatively different contributions at different temperatures. The derivative curves of TGA exhibit a

TABLE 2. Activation Parameters Calculated from the Reich Method

Sample	T_d, °K [a]	n	E_d (10%), kcal/mol	E_d (Lim),[b] kcal/mol	$\Delta S^{\ddagger}$, cal/mol·°K
3	637	0.05	22	28	−76.5
9	590	1.3	24	36	−75.4
10	586	1.9	34	45	−74.7
17	610	0.6	24	24	−76.4
18	590	1.2	21	26	−76.2
19	577	1.9	23	28	−76.1

[a]10% decomposition in argon at 10°K/min.
[b]Limiting value at high conversions (>20%).

hint of bimodality for all of these samples at a 2.5°C/min scan rate. This also indicates the presence of a contribution from two or more decomposition processes.

Another possible process is the rearrangement of the phosphazene moieties to phosphoramides, hence creating a weak point in the backbone. Although Papkov proposed this type of rearrangement in PBFP [9], the alkoxyalkoxy groups are far more likely to shift in these copolymers due to the smaller electron-withdrawing nature of these groups. Phosphoramide isomers have been found during the Staudinger reaction for alkoxy-substituted phosphoranimines [12, 13, 26]. However, phosphoramides have not been noted in the case of tris-2,2,2-trifluoroethoxy-N-trimethylsilylphosphoranimine. Rearrangement reactions could be responsible for the aforementioned increase in n at higher conversions in the case of the copolymers with 2-methoxyethoxy substituents. The reaction order is typically 1–2 for random initiation [6, 7]. Thus at >50% conversion, there may be an increasing contribution from rearrangement reactions followed by depolymerization. Since the molecular weight remains relatively constant (in fact, it continues to increase slightly), the contribution from such a process is either relatively small or the molecular weight remains constant due to simultaneous crosslinking processes.

Another observation is that the activation entropies change with Φ_m. This is indicative of a change in the "orderliness" of the transition state. Although there is considerable variation in the values of E_d calculated by the Reich method, if one assumes that the relative values of E_d (and $\Delta H^{\ddagger} = E_d + RT$) obtained from the Flynn and Wall technique are accurate, then the differences in $\Delta S^{\ddagger}$ are enough to account for the apparent discrepancies between the calculated E_ds and the observed thermal stabilities.

The Mechanism of Thermal Decomposition

All of the data discussed above is consistent with a chain-end initiation mechanism followed by complete unzipping to cyclic trimer. Magill proposed chain-end initiation followed by partial unzipping to trimer, followed by transfer reactions for the PBFP produced by the anionically initiated polymerization of phosphoranimines [7]. However, this is based only on the depolymerization kinetics. It was not possible to draw precise mechanistic conclusions due to the unknown nature of the end groups for that polymer. Based on Papkov's studies [9], it would seem that the proposed transfer reactions could occur at phosphoramide defects in the backbone which could result from the hydrolysis of incompletely substituted P—Cl bonds. Since such defects are almost certainly not present in the polymers synthesized from phosphoranimines, complete unzipping can occur.

In addition, the nature of the end gorups on polyphosphazenes synthesized by the anionically initiated polymerization of phosphoranimines has been studied by NMR [17]. As previously mentioned, the P-terminal end consists of pentavalent phosphorus with three alkoxy groups and the N-terminal chain end initially bears a trimethylsilyl group. However, the latter chain end may be hydrolyzed to a phosphate end group upon workup. The observation that the block copolymer composition affects the thermal stability may indicate that the depolymerization occurs at the P-terminal end of the polymer chain and may therefore have a cationic depolymerization mechanism.
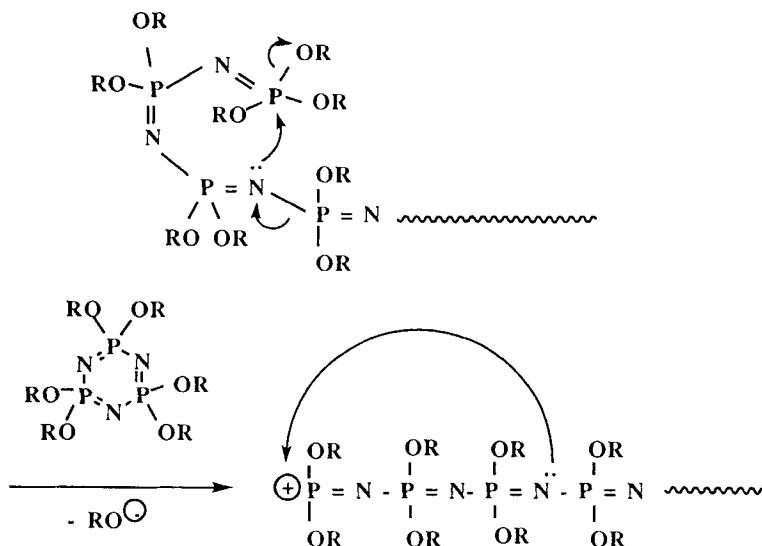
The relative constancy of the molecular weight vs depolymerization conversion contraindicates a significant contribution from the random electrophilic attack of the P-terminal chain end on the backbone nitrogens. Immediate recombination of the alkoxide would yield a linear decrease in molecular weight and thus depropagation of the initiated chain would be faster than recombination. Another possibility is that both of the above processes contribute to the overall decomposition and tend to counterbalance each other. The aforementioned crosslinking is another complicating factor. As mentioned above, there is some evidence for competitive decomposition processes such as the rearrangement to phosphoramides or oxidation.

CONCLUSIONS

1.   The thermal stability of the polyphosphazene copolymers synthesized by the anionically initiated polymerization of phosphoranimines decreases proportionally to the fraction of the repeating units bearing 2-methoxyethoxy groups.

2.   The molecular weight vs fractional conversion plots and the analysis of the decomposition products indicate that depolymerization occurs by chain end initiation followed by complete unzipping to cylic trimer. This behavior is different than for the PBFP homopolymer synthesized by the ring-opening process and is attributed to an absence of defective units in the backbone. The fact that the block copolymer structure (AB vs BA) affects the thermal stability may indicate that the depolymerization occurs at the P-terminal end of the polymer chain and may therefore have a cationic depolymerization mechanism.

3.   Activation energies are on the order of 22-35 kcal/mol and vary with decomposition conversion. Activation energies of this magnitude are consistent with a chain end initiation mechanism.

4.   There is no direct correlation between the calculated activation energies and the observed polymer stability. This has been attributed to the contribution of activation entropy.

5.   Increasing quantities of residual mass at higher alkoxyalkoxy side-group concentrations are attributed to transetherification or transesterification reactions leading to crosslinking.

ACKNOWLEDGMENTS

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