Mechanism of Thermal Degradation of Some Polyphosphazenes

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ABSTRACT: The mechanism of degradation of poly[bis(trifluoroethoxy)phosphazene] (PBFP) and poly(diphenoxyphosphazene) (PBPP) has been examined by dynamic and isothermal thermogravimetry. The dynamic experiments were made between 50 and 750 °C at several heating rates from 2.5 to 80 °C/min and the isothermal measurements were made at 325, 340, 355, and 370 °C. The polymers and their degraded residues were characterized by gel permeation chromatography, infrared spectroscopy, and intrinsic viscosity. In PBFP, the overall activation energy for degradation (E_d) was between 23.2 (isothermal) and 26.6 (dynamic) kcal/mol. The order of reaction was 0.3 ± 0.1. Maxima in the rates of isothermal degradation occurred between 30% and 35% weight loss. On the basis of experimental results, the mode of initiation in PBFB was deduced as occurring at the chain ends. Sample molecular weight dropped rapidly with degradation, in harmony with a few random breaks occurring at weak points along the main chain after the degradation has been initiated at the chain ends. Literature results on the thermal degradation of PBFP under vacuum were shown to be consistent with a terminal initiation–chain-transfer mechanism. For PBPP, dynamic thermogravimetry provided two activation energies at all levels of weight loss. Between 0% and 5% weight loss, E_d's of 34 ± 1.5 and 29 ± 1.5 kcal/mol were found, and between 5% and 50% weight loss, E_d's of 37 ± 1.5 and 26 ± 1.5 kcal/mol were determined. The differential weight loss curves appeared skewed, and a 25% residue was present at 600 °C. Higher residues 31–35% were found in isothermal thermogravimetry, where an E_d of 32 kcal/mol was determined. The molecular weights of degraded samples remained almost constant up to degradation. A depolymerization mechanism with some degree of cross-linking is invoked to explain the thermal degradation behavior of the PBPP polymer.

Introduction

Stable linear poly(organophosphazenes) were first synthesized in 1965 by Allcock et al.,[1] and since then, various physical properties of polyphosphazenes, including polymerization and depolymerization, have been examined. A few investigators have studied the depolymerization/degradation of polyphosphazenes but the precise mechanism of thermal degradation remains unresolved.

MacCallum and Tanner[2] performed isothermal degradation experiments under vacuum on poly(diphenoxyphosphazene) (PBPP) followed by intrinsic viscosity measurements on the degradation products. They postulated (a) a low-temperature reaction, which is probably a depolymerization equilibration reaction, accompanied by another reaction at higher temperatures where other than the lower molecular weight phosphazene homologues are formed. Allen, Lewis, and Todd,[3] who made dynamic thermogravimetric measurements in nitrogen at 10 °C/min and isothermal measurements at 255 °C, concluded that in aryloxy polymers the side groups are involved in forming cross-links below the temperature at which the main chain degrades. From the isothermal degradation of a (trifluoroethoxy)phosphazene–(phenylphenoxy)phosphazene copolymer in air at 155 °C, Allen and Mortier[4] noted that a decreasing stability with increasing trifluoroethoxy content was apparent. In some studies,[2-4] a systematic kinetic analysis, based upon both isothermal and dynamic thermogravimetric measurements was not performed, nor were molecular weight–weight loss data obtained.

Allcock and Cook[5] investigated the thermal degradation of poly[bis(trifluoroethoxy)phosphazene] (PBFP) under isothermal conditions under vacuum at temperatures between 100 and 300 °C. Molecular weight measurements were carried out on the polymer residues and mass spectroscopy measurements made on the trapped volatile products. An overall degradation mechanism was proposed that qualitatively supports a random initiation and chain unzipping mechanisms. Allcock, Moore, and Cook[6] studied the degradation of PBPP and concluded that the reaction proceeds by a two-step process. First cleavage of the main chain occurs at weak points and then cyclization depolymerization is initiated from the chain ends of the linear fragments. Allcock et al.[5,6] obtained extensive molecular weight–weight loss data but did not test their experimental data against theoretical depolymerization rate equations, nor did they analyze the kinetics of the degradation.

Valaitis and Kyker[7,8] have studied the thermal degradation of a polyphosphazene containing a mixture of trifluoroethoxy and octafluoropentoxy substituents using both isothermal thermogravimetric and molecular weight measurements. These workers proposed that degradation by random scission occurred at a point in the chain followed by rapid depolymerization. The overall degradation was stated to to follow quasi-zero-order kinetics. Hagnauer and LaLiberte[9] performed isothermal degradation studies on poly[bis(m-chlorophenoxy)phosphazene] in static air and concluded that random scission took place at weak points in the chain backbone. However, they did not test for consistency between their molecular weight–weight loss data and theoretical models of degradation.

Recently, Zeldin, Jo, and Pearce[10] degraded PBFP isothermally under vacuum, and they also performed dynamic degradation experiments. They proposed a random initiation and partial unzipping mechanism to explain the mode of degradation of PBFP. In their work, maxima in the rates of degradation of PBFP were reported as occurring at 40% weight loss. Simha, Wall, and Bram[11] modeled degradation per se via random initiation where various zip lengths were involved. Maxima in the polymer degradation rates always occurred at or below 26% weight loss. In another study, a similar conclusion was arrived at by Boyd[12] if (a) terminal initiation occurs with chain transfer and (b) terminal initiation with some degree of random scission takes place. These possibilities have not been considered in ref 9.

In our study, the thermal degradation of PBFP and PBPP has been investigated by isothermal and dynamic thermogravimetry, respectively. The appropriateness of the kinetic parameters such as overall activation energy (E_d) and order (n) so determined were confirmed by curve fitting data with theory. Molecular weight changes with degradation time were fitted to theoretical equations developed by Boyd.[12] Thermal degradation of PBFP supports a mechanism of terminal initiation with some degree

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of scission occurring randomly at weak points along the backbone. The data of Zeldin et al.[10] have been reexamined and found to satisfy a degradation mechanism involving terminal initiation with chain transfer. The degradation of PBPP was noted to be even more complex, involving a dual mechanism, wherein depolymerization is accompanied or followed by cross-linking.

Theory. In general, isothermal rate data are analyzed according to the traditional method outlined by Madorsky.[13,27] From curves of weight loss rate vs. weight loss at different isothermal temperatures, the overall activation energy was determined from the equation

$$E_d = -2.3R[\mathrm{d}(\log \bar{k})/\mathrm{d}(1/T)] \qquad (1)$$

where $\bar{k}$ is the extrapolated initial rate[27] of weight loss, E_d is the overall activation energy for degradation, R is the gas constant, and T is the absolute temperature.

A general method for determining E_d directly from weight loss–temperature data at several heating rates was presented by Flynn and Wall.[14] The rate of loss is given by

$$\frac{\mathrm{d}C}{\mathrm{d}T} = \frac{A}{\beta} f(C) \exp\left[-\frac{E_d}{RT}\right] \qquad (2)$$

where C is the fractional weight loss = $(W_0 - W)/W_0 = 1 - W/W_0$, W is the sample weight at any instant, A is the preexponential factor, β is the heating rate, $f(C) = (1 - C)^n$ is a function of the fractional sample weight, and n is the order of the reaction. By the method of separation of variables and integration of eq 2, it follows that

$$\log\left[-\frac{(1-C)^{1-n} - 1}{1-n}\right] \simeq \log (AE_d/R) - \log \beta - 2.315 - 0.457(E_d/RT) \qquad (3)$$

when $n \neq 1$ or

$$\log [-\ln (1 - C)] \simeq \log (AE_d/R) - \log \beta - 2.315 - 0.457\left(\frac{E_d}{RT}\right) \qquad (4)$$

when $n = 1$. At constant weight loss (fixed C) for several heating rates, a plot of $\log \beta$ ($=\mathrm{d}T/\mathrm{d}t$) vs. $1/T$ exhibits a slope of

$$\frac{\mathrm{d}(\log \beta)}{\mathrm{d}(1/T)} \simeq -0.457\left(\frac{E_d}{R}\right) \qquad (5a)$$

or

$$E_d \simeq -4.35\left(\frac{\mathrm{d} \log \beta}{\mathrm{d}(1/T)}\right) \qquad (5b)$$

Equation 5 has been used to determine the magnitude of E_d from dynamic weight loss data.

Reich and Stivala[15] outline another technique whereby values of fractional weight loss (C) and corresponding temperatures (T) are used to calculate E_d's for arbitrary values of n. E_d values so obtained were plotted against respective n values, and the region bounded by the intersecting curves was used to simultaneously estimate E_d and n, and hence A. It is implicitly assumed here that the mechanism of degradation is invariant during the reaction. The parameters so obtained were then used to calculate a theoretical $1 - C$ vs. T curve, for comparison with the experimental one.

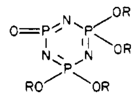
Experimental Section

1. Materials. Characterized poly[bis(trifluoroethoxy)phosphazene] (PBFP) and poly(diphenoxyphosphazene) (PBPP) used in this investigation were kindly provided by Dr. G. L. Hagnauer of the Army Materials and Mechanics Research Center, Watertown, MA. The following data were found:[28]

Table I
Mass Spectroscopic Results of PBFP

m/e	relative abundance	assignment
64	68	CF_2CH_2
69	30	CF_3
70	0	CF_3H
83	77	CH_2CF_3
84	0	CF_3CH_3
99	25	CF_3CH_2O (from trimer)
116.5	0	CF_3CH_2Cl
243	0	monomer
486	0	dimer
528	23	
532	23	
547	100	*a*
630	40	trimer with loss of OCH_2CF_3
631	27	
710	58	trimer with loss of fluorine
711	10	
729	100	trimer

a



($R = CH_2CF_3$).

(PBFP) Anal. Calcd: C, 19.77; H, 1.66; Cl, 0. Found: C, 19.88; H, 1.90; Cl, 0.032. Calorimetric data: T_g = −63 °C at 10 °C/min heating rate, $T(1)$ = 82.2 °C, T_m = 241.5 °C; $[\eta]^{25\,°C}$(acetone) = 0.284 dL/g; molecular weight average (broad) = 80 000.

(PBPP) Anal. Calcd: C, 62.34; H, 4.36; Cl, 0. Found: C, 62.84; H, 4.70; Cl, 0.006. Calorimetric data: T_g = 2 °C at 10 °C/min heating rate, $T(1)$ = 164 °C; molecular weight average (broad) = 660 000.

Infrared analyses were also made on these polymers, and mass spectroscopic information was obtained on degraded fragments. No chlorine-containing moieties or fragments were detected although traces of P–Cl, P–OH, and PONH groups were suspected. A mass spectrographic analysis of PBFP, for example, indicates that chlorine is absent (see Table I). Similarly, chlorine in a combined state was not identified in the volatiles from PBPP.

2. Thermogravimetry (TG). The dynamic and isothermal thermogravimetric experiments were performed with a Perkin-Elmer TGS-2 with a first-derivative controller unit attached in series with a System-4 microprocessor controller and an X–Y_1–Y_2 recorder. All samples were heated at 50 °C for hours under vacuum to rid them of any low molecular weight species. Dynamic thermogravimetric measurements were made at heating rates of 2.5, 5, 10, 20, 40, and 80 °C/min between 50 and 750 °C with a helium gas flow of 160 cm^3/min. Sample weights were in the range 3–5 mg. At least two reproducible runs were obtained for each condition.

Isothermal thermogravimetric measurements were made at 325, 340, 355, and 370 °C for sample weights of 3–5 mg with a helium flow rate of 160 cm^3/min. In these measurements the furnace was preheated to the selected isothermal temperature, and then runs were initiated by quickly raising the preheated furnace assembly around the sample, which rapidly reached the degradation temperature. The decrease in sample weight was recorded as a function of time. Measurements were checked for reproducibility.

3. Gel Permeation Measurement (GPC). Measurements were made on PBFP to determine the change in molecular weight with degradation time. Results were compared with the intrinsic viscosity measurements on the same samples. A Water's 1600, with Bondagel-packed columns, was employed, with THF as the solvent phase. In addition, sample residues at different extents of degradation at 355 °C were used for intrinsic viscosity and infrared measurements.

4. Molecular Weight Measurements. Intrinsic viscosity ($[\eta]$) measurements were made with a Cannon-Ubbelohde viscometer at 25 ± 0.01 °C on the original PBFP and PBPP samples and

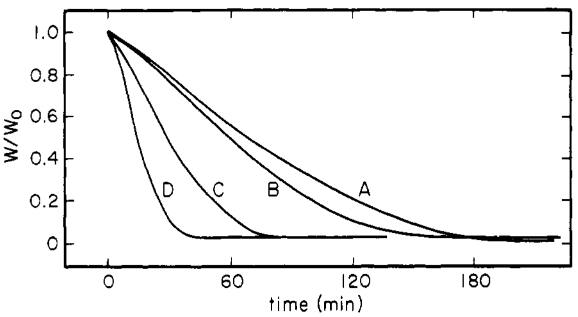


Figure 1. Fractional weight loss (W/W_0) vs. time (min) for the isothermal degradation of PBFP in helium at (A) 325, (B) 340, (C) 355, and (D) 370 °C. Helium flow rate was 160 cm^3/min.

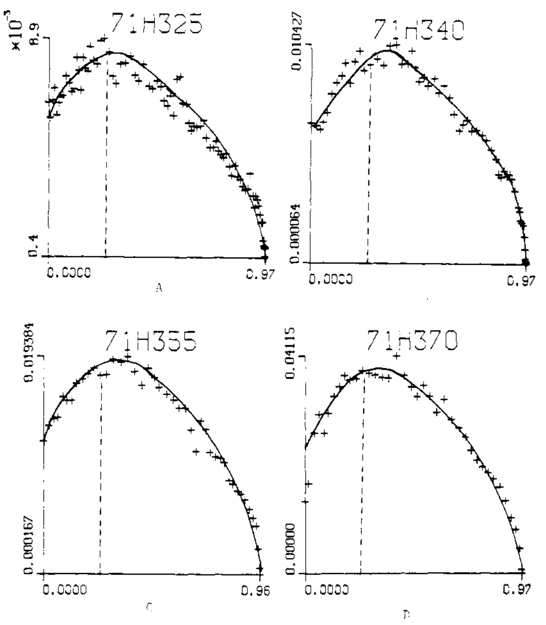


Figure 2. Isothermal weight loss rate (min^{-1}) vs. fractional conversion (W/W_0) for the degradation of PBFP in helium at (A) 325, (B) 340, (C) 355, (D) 370. Dotted vertical lines denote a 26% conversion level. Data were computer digitized from thermogravimetric curves of the type shown in Figure 1.

their residues obtained at 355 °C. Acetone was the solvent for PBFP and tetrachloroethane was used for PBPP. At each concentration, at least three efflux times were recorded at flow times where kinetic energy corrections were not required. The isothermal TG data were analyzed by using a computerized curve digitizer. Curves for the rate of weight loss based on the original sample weight and residue were computed and plotted as illustrated (for example) in Figure 2. Measurements were made on PBPP and its residues on a Water's ALC/GPC-244 using DuPont bimodal (60 and 1000 Å) silanized columns, with THF as the mobile phase. These measurements were kindly provided by Dr. G. L. Hagnauer for some of our samples.

Results and Discussion

A. Poly[bis(trifluoroethoxy)phosphazene] (PBFP). The fractional weight loss (fractional volatilization) vs. time curves from the isothermal degradation of PBFP are presented in Figure 1. The corresponding differential weight loss curves, Figure 2, exhibit maxima in the rates between 30% and 35% weight loss, i.e., greater than the 26% predicted by Simha et al.[11] and by Boyd[12] for only random-initiated degradation. Note, too, that Zeldin et al.[10] observed maxima at approximately 40% weight loss, and a similar peak has been reported for a fluoro elastomer of phosphonitrile[8] degraded in nitrogen. These results suggest that thermal initiation in PBFP takes place from chain ends, in contrast to random-scission initiation. The rates of weight loss, based upon polymer residue, are plotted in Figure 3, and from such data the extrapolated initial rates (k) were determined. An activation energy (E_d) of 23.0 kcal/mol was determined by using eq 1. Valaitis and Kyker[8] cite 27 kcal/mol for their polyphosphazene fluoro elastomer degraded in air. Experimental rate curves were compared with the calculated curves based upon zero-order kinetics, and fairly good agreement was found, suggesting a pseudo-zero-order reaction for this polyphosphazene homopolymer.

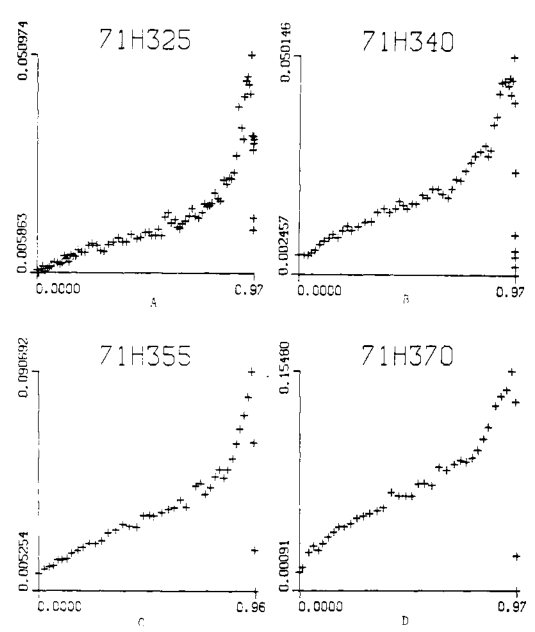


Figure 3. Rate of weight loss data (min^{-1}) based upon residue fraction vs. fractional conversion for the isothermal degradation of PBFP in helium (150 cm^3/min flow rate) at (A) 325, (B) 340, (C) 355, and (D) 370 °C. Data were computer digitized and plotted.

Table II
Average Kinetic Parameters from Dynamic Thermogravimetry

% wt loss	E_d, kcal/mol	n	A, 1/min
0-20	16 ± 0.4	0.3 ± 0.1	2.5 × 10^4
beyond 20	23.4 ± 1.5	0.3 ± 0.1	4.5 × 10^6

Using the method of Flynn and Wall,[14] we determined an activation energy value of 26.6 kcal/mol (eq 5) from the dynamic degradation data of PBFP in helium. Dynamic thermogravimetric data analyzed by the technique outlined by Reich and Stivala[15] provided the E_d, n, and A values for PBFB degradation at 5, 10, and 20 °C/min. The average of these parameters from the three different heating rates are summarized in Table II.

With the parameters listed in Table II and eq 3, the temperatures of degradation were calculated at different weight loss levels, so providing a degradation curve for comparison with the experimental results. Figure 4 illustrates the agreement obtained for a heating rate of 10 °C/min. Heating rates of 5 and 20 °C/min provide equally good agreement.

The E_d values determined from isothermal thermogravimetry were ~23.2 kcal/mol. From the dynamic TG method of Flynn and Wall,[14] values of ~26.6 kcal/mol resulted. The method of Reich and Stivala gave ~23.4 kcal/mol above 20% weight loss. The data compare favorably. However, a low E_d value (~16 kcal/mol) also was obtained by the latter technique below 20% weight loss. This is surprising in view of the fact that the weight loss curves (not shown) do not indicate a dual reaction mechanism as they are superposable by a lateral shift, nor do

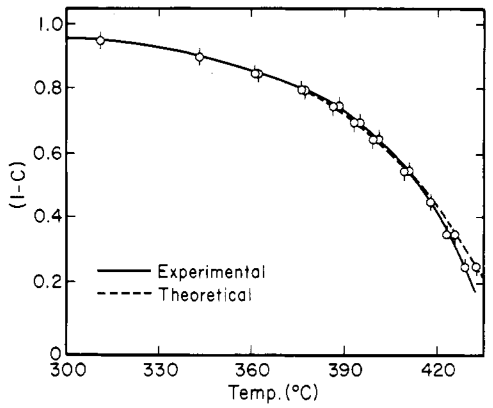


Figure 4. Experimental vs. calculated fractional weight loss (1 - *C*) curves as a function of temperature (°C) for the degradation of PBFP at 10 °C/min.

Table III
Molecular Weight of PBFP

% wt loss	time, min	$[\eta]$, dL/g	$[\eta]/[\eta]_0$	$\overline{M}_n{}^a$	$\overline{M}_n/\overline{M}_{n,0}$
0	0	0.284	1	49 490	1
2	1.52	0.1411	0.5	19 730	0.4
4	3.2	0.1216	0.43	16 210	0.33
10	7.2	0.0944	0.33	11 615	0.235

[a] The $\overline{M}_n$ values have been determined following Zeldin et al.[10]

the differential weight loss curves display a shoulder.

Generally, low E_d values, typically ≤30 kcal/mol, are more consistent with a chain-end-initiated degradation mechanism. In the case of the thermal depolymerization of poly(dichlorophosphazene), E_d = 22–26 kcal/mol,[16] and for the chain-end unzipping mechanism of PMMA,[17] E_d values less than 30 kcal/mol are found. A lower activation energy is needed in the initiation degradation step as opposed to pure random scission, occurring other than at chain weak points. This further supports our conclusion that the mode of initiation in PBFP is more likely to occur at chain ends than by random scission.

Although we have some reservations about the order of the reaction when the degradation process(es) is complex and molecular weight distribution broad, the magnitude of *n* is still significant. MacCallum,[18] in his analysis of the kinetics of polymer degradation, has shown that for a randomly initiated degradation process, the reaction order with respect to the sample weight lies between 1 and 2, whereas for end-initiated degradation reactions, the order is in the range 0–1. From our isothermal measurements we presume that the reaction follows pseudo-zero-order kinetics and from the dynamic TG measurements we obtain a value of 0.3, which is again consistent with chain-end-initiated kinetics.

The intrinsic viscosity in acetone at 25 ± 0.1 °C of PBFP starting materials and samples degraded by 2, 4, and 10% are summarized in Table III. The rapid decrease in molecular weight with degradation has been noted for thermal degradation initiated at chain ends[11] in two instances, namely, (1) terminal initiation with chain transfer and (2) terminal initiation with some degree of random scission.

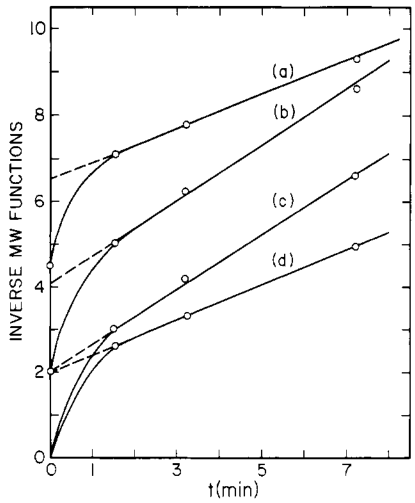


Figure 5. Inverse molecular weight functions vs. time (*t*, min) for PBFP samples. Symbols denote the appropriate ordinate function: (a) $M^{-1/2}$; (b) $\bar{M}_n{}^{-1}$; (c) $1/\bar{M}_n - 1/\bar{M}_{n,0} \times 10^5$; (d) $1/\bar{M}_n{}^{1/2} - 1/\bar{M}_{n,0}{}^{1/2} \times 10^3$.

The most clear-cut distinction may, in principle, be drawn between transfer and random scission from the molecular weight change of the polymer with degradation. Boyd[12] has shown that if the degradation is by random scission, then eq 6 holds, whereas if chain transfer is responsible for the rapid drop in molecular weight, then eq 7 applies.

$$1/\bar{M}_n - 1/\bar{M}_{n,0} = k_r t \tag{6}$$

$$1/\bar{M}_n{}^{1/2} - 1/\bar{M}_{n,0}{}^{1/2} = k_c t \tag{7}$$

A constant *N* or *N'* can be added to the right-hand side of eq 6 and 7, respectively, to account for the presence of weak links.[18] However, in the absence of such defects, a plot of $1/\bar{M}_n$ vs. *t* (see Figure 5b) or $1/\bar{M}_n{}^{1/2}$ vs. *t* (see Figure 5a) should yield a straight line passing through the origin. At short times, we note that both of these plots exhibit nonlinear behavior, in line with the weak-link concept. If weak links are absent, plots of $1/\bar{M}_n - 1/\bar{M}_{n,0}$ vs. *t* (Figure 5c) or $1/\bar{M}_n - 1/\bar{M}_{n,0}{}^{1/2}$ vs. *t* (Figure 5d) should also pass through the origin, but they do not. The linear portion of these plots (Figure 5c,d) intercepts the ordinate axis, as in accord with other plots dealing with polyphosphazenes[7,9] or where weak links[19] are suspected in other polymer backbones. If weak points are randomly distributed, then the sharp drop in molecular weight initially is attributed to random scission at these defects following thermal initiation at the chain ends. The E_d values ~23–26 kcal/mol are consistent with this picture since purely random scission involves higher activation energies.

The rapid decline in molecular weight of PBFP initially (<1.5 min) is very important mechanistically, but the changes that occur beyond this time (Table III) are noteworthy, too. Analyses of the data according to eq 6 and 7 both yield straight lines, compounding the difficulties of differentiation between transfer and random-scission processes. Indeed both mechanisms may be operative here. From an analytical viewpoint, no new chemical species were found in the infrared spectrum since this spectrum was identical with that of the original polymer, indicating that PBFP essentially degrades by splitting of the main chain. It appears then that the thermal degradation of PBFP in our work involves thermal initiation, followed by random scission at weak points.

Zeldin et al.[10] from the isothermal degradation of PBFP under vacuum concluded that PBFP degraded via a random-scission and partial unzipping mechanism. However, their observations appear inconsistent with random initiation[11,12,18] and specifically criteria such as (a) maxima in the rate of weight loss at approximately 40%, (b) order of reaction (*n* = 0.8), and (c) relatively high values for E_d (vide infra).

Table IV
Molecular Weight Data for PBFP

	W/W_0						
	1.0	0.9	0.86	0.75	0.71	0.65	0.35
$\overline{M}_n$	305 000	61 500	46 400	20 600	15 400	13 900	12 700
$\overline{DP}$	1255	253	191	85	63	57	52
$\overline{DP}/\overline{DP}_0$	1	0.207	0.152	0.068	0.050	0.045	0.041

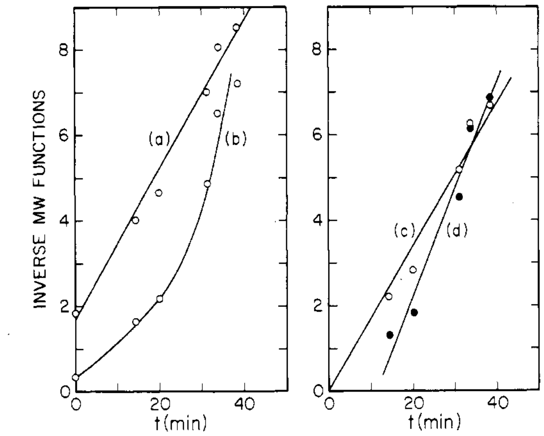


Figure 6. Inverse molecular weight functions vs. time (t, min) for PBFP data.[10] Symbols denote the appropriate ordinate function: (a) $M_n^{-1/2}$; (b) $\bar{M}_n^{-1}$; $1/\bar{M}_n^{1/2} - 1/\bar{M}_{n,0}^{1/2} \times 10^3$; (d) $1/\bar{M}_n - 1/\bar{M}_{n,0} \times 10^5$.

The molecular weight–weight loss data in Table IV indicate a rapid drop in molecular weight.

Once degradation is initiated at chain ends, the rapid drop in molecular weight may arise through chain transfer or via limited but random scissions. Figure 6a,b is a plot of $1/\bar{M}_n$ and $1/\bar{M}_n^{1/2}$ vs. time,[29] where in Figure 6a the plot of $1/\bar{M}_n^{1/2}$ vs. time yields a straight line, favoring a chain-transfer mechanism. the plot of $1/\bar{M}_n^{1/2} - 1/\bar{M}_{n,0}^{1/2}$ vs. time (Figure 6c) is linear, passing through the origin as expected.

Since Zeldin et al.[10] obtained higher E_d values, 45 kcal/mol (isothermal) and 39 kcal/mol (dynamic), there may exist intrinsic sample differences between their material and that employed in our work. The discrepancy of approximately 20 kcal/mol in overall E_d's may be explained by an activation energy for chain transfer of this magnitude. However, the difference in the maxima of the rate of weight loss and the value of the order of reaction tend to support our proposed mechanism even though (i) terminal initiation followed by chain transfer (our analysis of their data)[10] and (ii) random chain scissions coupled with partial chain unzipping qualitatively indicate the same rapid decrease in molecular weight with weight loss or time. It is also important to point out here that the mechanism proposed by us for our PBFP material (terminal initiation coupled with limited breaks at defect regions of the chain) intrinsically shows the same reduction in molecular weights.

On the basis of a terminal initiation–chain transfer mechanism, Boyd[12] developed an equation for the rate of weight loss

$$\frac{1}{W}\frac{\mathrm{d}W}{\mathrm{d}t} = -k_E[-\sigma^0 n^0 \tilde{n}^{1/2} + 1 + \gamma]/[1 \tilde{\mp} \tilde{\gamma}\tilde{n}(n^0\gamma^0)] \qquad (8)$$

where W is the total number of repeat units in the sample (when multiplied by the molecular weight of a repeat unit (m_0) it is the sample weight), k_E is the rate constant for end-group initiation, x is the number-average degree of polymerization, $\tilde{n} = n/n^0$, γ is the reciprocal average zip length, $\tilde{\gamma} = \gamma/\gamma^0$, σ^0 is the transfer parameter, and superscript zero indicates initial values.

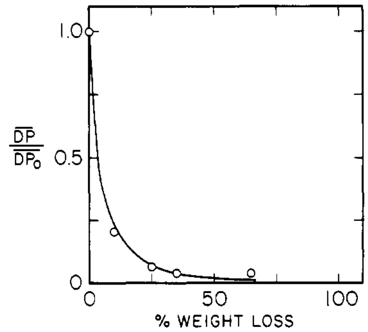


Figure 7. Relative molecular weight fraction $\bar{DP}/\bar{DP}_0$ vs. percent weight loss.[10]

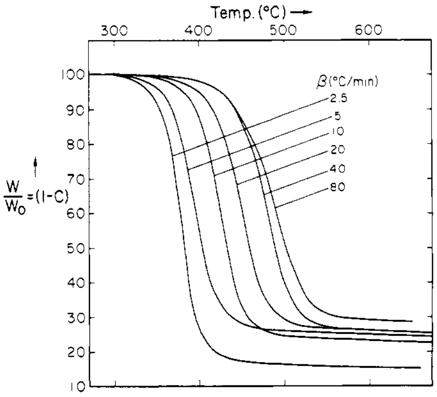


Figure 8. Percent weight loss (1 − C) vs. temperature (°C) for PBPP specimens at different heating rates (°C/min) from 2.5 to 80 °C/min in helium.

Using Boyd's approach and making the assumption that the zip length is comparatively long, we are able to derive the following simplifying equation, relating fractional weight and degree of polymerization:

$$\ln\left(\frac{W}{W_0}\right) = \frac{-2\tilde{\gamma}[1 + \sigma^0 x^0/2]}{(\sigma^0 n^0)(x^0\gamma^0)}\left(\frac{1}{\tilde{x}^{1/2}} - 1\right) \qquad (9)$$

Application of this equation yields good agreement between experimental and predicted fractional molecular weights as a function of weight loss (see Figure 7). We therefore conclude that there is significant evidence in favor of a thermal initiation–chain-transfer mechanism to explain the degradation behavior of PBFP.

B. Poly(diphenoxyphosphazene) (PBPP). The dynamic thermogravimetric data expressed as fractional weight loss–temperature data for PBPP in helium are plotted in Figure 8. The curves are complex and not superposable via lateral shifting. The differential weight loss curves exhibit distinct shoulders, suggesting that more than one mechanism is involved. Two activation energies, corresponding to two mechanisms, were found (see Figure 9) when data were analyzed according to Flynn and Wall.[14] Up to 5% degradation, E_d's of 29 ± 1.5 and 34 ± 1.5 kcal/mol were obtained. Between 5 and 50% weight loss,

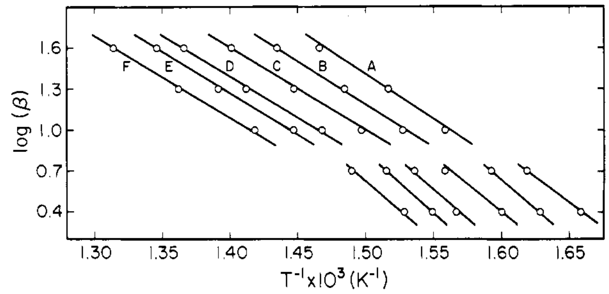


Figure 9. log (rate of heating β) (°C/min) vs. reciprocal temperature (K^{-1}) for the degradation of PBPP in helium for conversion levels (A) 2.5%, (B) 5%, (C) 10%, (D) 20%, (E) 30%, and (F) 50%.

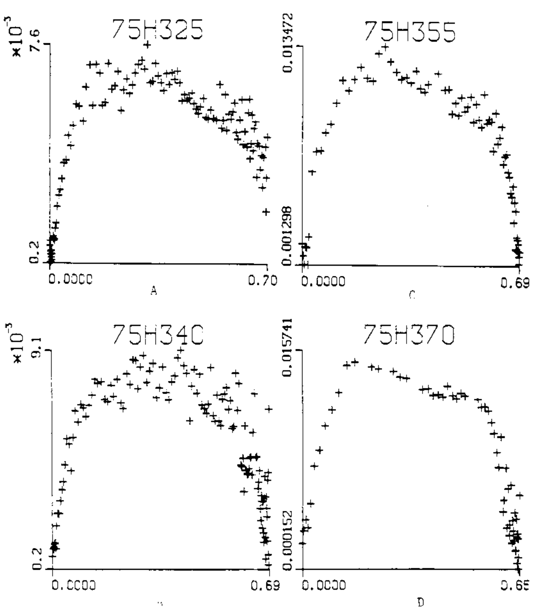


Figure 10. Rate of weight loss ($\min^{-1}$) (based on residue) vs. fractional conversion (abscissa) for isothermal degradation of PBPP in helium at (A) 325, (B) 340, (C) 355, (D) 370 °C. Data were computer digitized and plotted.

E_d's of 26 ± 1.5 and 37 ± 1.5 kcal/mol were derived. The higher E_d's correspond to the lower heating rate (below 10 °C/min) and the lower E_d's arise above this rate. Residue levels about 25% and 33% correspond to dynamic and isothermal test conditions, respectively. Compared with PBFP, values ~3% were obtained under similar environmental conditions; these levels signify that cross-linking is operative and that the side-group chemistry is important. It is gratifying to see that an E_d of 31 kcal/mol was determined from our isothermal analysis of rates of volatilization of PBPP in helium, in good agreement with results obtained in our dynamic measurements.

Typical isothermal degradation rates (Figure 10) exhibit maxima around 20% volatilization (weight loss), after which the rate falls to approximately 55%, but reaching zero change in weight about the 70% level. Contrast, for example, the PBFP results (Figure 3), where little or no weight loss stabilization occurs (i.e., no cross-linking reaction takes place). Elsewhere it is known that cross-linking enhances thermal stability since the depolymerization tends to be "blocked" by cross-links.

The degradation curves for PBPP above 340 °C follow the pattern of the rate of volatilization vs. percent of sample volatilized, as reported for isotactic poly(propylene oxide)[21] and for poly(trivinylbenzene),[22] especially where cross-linking definitely occurs. An interesting paper by Winslow and Matreyek[23] on the pyrolysis of cross-linked styrene copolymers points up some discrepancies in the literature.[24,25] The former work[23] shows that cross-linking is favored over volatilization, presumably involving hydrogen transfer with concomitant carbon formation with a gain in heat-resistant residue.

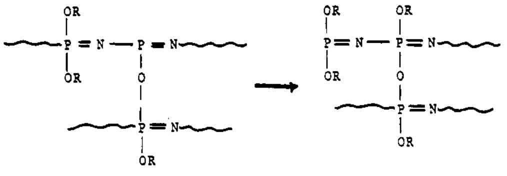


Figure 11. Schematic illustration of cross-linking in PBPP.

Table V
Molecular Weight Data for PBPP

% wt loss	0	1.2	4.2	10.1	20
$\overline{M}_w \times 10^5$	6.6	6.8	6.2	7.6	7.9
$\overline{M}_w/\overline{M}_{w,0}$	1.00	1.03	0.94	1.15	1.2

Supporting evidence for degradation with cross-linking comes from GPC data of PBPP in Table V. The molecular weights are relative, since polystyrene standards only were used for calibration, but the molecular weight ratios are significant for comparison of chain lengths changes during degradation even though these are minor up to 20% weight loss. Note, too, that degraded samples only dissolved with difficulty in tetrachloroethane at 120 °C.

The infrared spectra of the original and the degraded samples up to 10% and even at 42% weight loss exhibit no significant changes in spectral features. This evidence suggests that PBPP, like PBFP, essentially degraded via backbone breakdown as opposite to side-group splittings. The P–O–P band is expected between 870 and 1000 cm^{-1} if (see schematic in Figure 11) cross-linking occurs via possible pathways that arise from the reaction of unsaturated fragments or chain components created during degradation. However, the band is not observed since it is overlapped by the stronger P–OC_6H_5 peak at 855–994 cm^{-1}. Still, there is support for a dual-degradation mechanism in PBPP involving (i) a depolymerization stage, which accounts for the observed weight loss, and (ii) a cross-linking reaction, relating to the high residue level in degraded samples.

Overall, the difficulties associated with this work are obvious. Narrow molecular weight specimens are essential to obtain a definitive understanding of physical properties of PBPP and other polyphosphazenes. On the theoretical side[26] more consideration must be given to the role of cross-linking in order to extend and test the consistency of kinetics with models of polymer degradation.

Conclusions

1. The mode of initiation in PBFP occurs at chain ends; afterward, further breakdown of the chain takes place by limited random scission (a) at weak points along the chain (our sample) and by (b) chain transfer (our analysis of the data of Zeldin et al.[10]).

2. The thermal degradation behavior of PBPP occurs by depolymerization with cross-linking which increases with the extent of degradation, finally resulting in an insoluble residue.

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(27) Madorsky[13] has shown that from isothermal measurements, an accurate value of E_d can be obtained if the residues have the same average MW and MWD (as the original sample). These conditions strictly hold only at 0% weight loss.

(28) Most of this chemical analysis was kindly provided by the Army Materials and Mechanics Research Center.

(29) Although the molecular weight–weight loss data were obtained from thermolysis at 350 ± 2 °C under vacuum, weight loss–time (isothermal degradation) data were obtained by degradation under vacuum at 355 °C. Still, the molecular weight–time results plotted in Figure 6 provide a good first approximation.

Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 1. (Hydroxypropyl)cellulose in Dimethylacetamide

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ABSTRACT: The phase diagrams of (hydroxypropyl)cellulose (HPC) in water at 20 °C and in dimethylacetamide (DMAc) between 20 and 130 °C were determined up to concentrations of ~80% polymer. Phase equilibria were determined via optical microscopy, viscosity, ultracentrifugation, and analytical techniques. The molecular weight of the HPC samples investigated varied between 132 000 and 479 000. Fractions of these samples were used to determine the persistence length of HPC in DMAc from intrinsic viscosity measurements at 25 and 70 °C. The critical polymer volume fraction v_2^* at which a cholesteric mesophase appears is ~0.35 at room temperature and increases, in DMAc, with temperature. v_2^* is not greatly affected by molecular weight. The ratio of the critical compositions in the biphasic region is considerably smaller than observed for other polydisperse systems. The persistence length of HPC in DMAc was found to be 65 Å (±15 Å) at 25 °C and 45 Å at 70 °C. An approximate correction for excluded volume effects would lower the above figure by ~15 Å. The results are discussed in terms of recent theories of liquid crystalline solutions. Provided the axial ratio of the solute is calculated on the basis of the Kuhn statistical segment, the body of the results is satisfactorily described by the Matheson–Flory theory of semirigid mesogens and by the lattice theory of hard rods with anisotropic dispersion forces.

Several reports have appeared in recent years concerning the liquid crystalline behavior of concentrated solutions of cellulose and its derivatives. Flory[1] was probably the first to comment on the possibility of mesophase formation for cellulosic polymers. The patent literature[2] describes the use of anisotropic solutions of cellulose derivatives for the production of fibers endowed of superior mechanical properties. More recent patents[3] describe a process whereby cellulose dissolved in aqueous solutions of a cyclic amine oxide is spun to yield high-tenacity fibers. The latter technology appears to hold the greatest promise since it represents a new direct route for the obtainment of regenerated cellulose fibers. The use of nematic solutions of synthetic polymers such as poly(*p*-benzamide) (PBA) for the preparation of ultrahigh-modulus and -strength fibers is now well established[4,5] and prompted interest in the development of similar technologies for the cellulosic polymers.

More fundamental investigations have also been reported. In pioneering work, Werbowyj and Gray[6,7] reported the phase diagram of (hydroxypropyl)cellulose (HPC) in water. They observed the formation of iridescent colors, typical of cholesteric mesophases, above a polymer volume fraction $v_2^* = 0.37$. This critical concentration was unaffected by the degree of polymerization of HPC in the molecular weight range 60×10^4 to 1×10^6. Onogi et al.[8] and Asada[9] have recently reported structural and rheooptical measurements of liquid crystalline solutions of HPC. Spherulitic structures were observed in these solutions, and shearing appeared to greatly improve the order of the cholesteric texture.

The phase diagram of cellulose acetate (CA) in trifluoroacetic acid was investigated by Navard et al.,[10] and that of cellulose in *N*-methylmorpholine *N*-oxide (MMNO) was considered by Chanzy and Peguy.[11] These studies indicated that, at variance with the HPC/H_2O system mentioned above, the critical concentration was dependent upon the degree of polymerization (DP). For cellulose, the critical concentration decreased from 45% to 20% (w/w)

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