

## Poly[bis(*m*-chlorophenoxy)phosphazene]. Macromolecular Characterization and Degradation Studies\*

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### Synopsis

The macromolecular structures of five poly[bis(*m*-chlorophenoxy)phosphazene] samples are critically analyzed. There are significant variations in the solubility behavior and physical properties of the polymers. Property differences are attributed mainly to the incomplete nucleophilic substitution of the dichlorophosphazene polymer precursor. All the polymers are found to have high molecular weights and broad, bimodal molecular weight distributions. However, differences in branching are noted and the presence of thermally labile "weak links" on the polymer chain backbones is suspected. At 165°C in static air, the polyphosphazene degrades by a random degradation mechanism and for long exposure times is considerably more stable than polystyrene.

### INTRODUCTION

The synthesis and characterization of a number of poly(aryloxyphosphazenes) have been reported.<sup>1</sup> In general, the polymers displayed high intrinsic viscosities ( $[\eta] > 1$  dl/g) and were reported to have high molecular weights ( $\bar{M}_w > 10^6$ ) and broad molecular weight distributions ( $\bar{M}_w/\bar{M}_n > 10$ ). A more detailed analysis showed that one of these polymers, poly[bis(*m*-chlorophenoxy)phosphazene] (sample IIIe in ref. 1), has a bimodal molecular weight distribution with peak maxima located at<sup>2</sup>  $10^5$  and  $1.6 \times 10^6$  g/mole. The analysis also indicated that there was little, if any, branching present in the polymer. Since then, essentially the same techniques were used to prepare other samples of this polymer. However, significant differences in the solubility behavior and physical properties of the various preparations are observed. Indeed, in two instances, failure to complete the nucleophilic substitution of the dichlorophosphazene polymer precursor results in rubbery rather than fibrous products. In this paper, a detailed study is made of five such samples to determine whether their macromolecular structures are also different.

Currently, poly[bis(*m*-chlorophenoxy)phosphazene] is being considered for wire coating, foam, and flame retardant applications. The fully substituted polymer is white and fibrous in appearance and has a Limiting Oxygen Index (ASTM D2863) value<sup>3</sup> of 51. It is soluble in a variety of organic solvents and

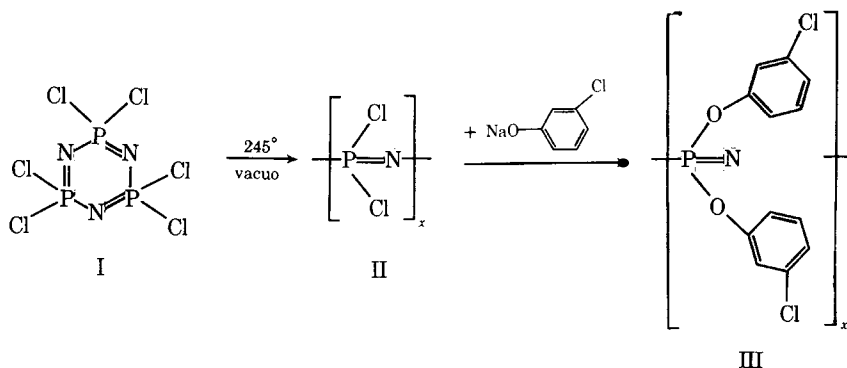
\* Based on presentation given at the Polyphosphazene Conference, AMMRC, Watertown, Massachusetts, May 1975.

may be solution cast or compression molded to form films. It has a low glass transition temperature ( $T_g = -37^\circ\text{C}$ ) and retains at least some crystallinity up to its decomposition temperature ( $T_d = 350^\circ\text{C}$ ). However, little is known of the polymer's stability at elevated temperatures and under conditions of shear. To simulate extreme environments such as the polymer is liable to encounter during processing or application, the degradation of three poly[bis(*m*-chlorophenoxy)phosphazene] samples is investigated by aging films of the polymers isothermally at  $165^\circ\text{C}$  in static air. Changes in macromolecular structure with exposure time are then correlated in an attempt to evaluate the degradation mechanism and rate. The results are compared with those of a high molecular weight polystyrene degraded under identical conditions.

## EXPERIMENTAL

### Polymer Preparation

A detailed description of the preparation of poly[bis(*m*-chlorophenoxy)phosphazene] is given in reference 1. Purified hexachlorocyclotriphosphazene (I) is polymerized in a sealed, evacuated glass tube at  $245^\circ\text{C}$  until the molten reaction mixture becomes so viscous that flow nearly ceases (ca. 24 to 48 hr). The reaction mixture is then dissolved in benzene and the poly(dichlorophosphazene) (II) is isolated from the unreacted trimer and low molecular weight cyclics and oligomers by precipitation with *n*-pentane. Next, the polymer (II) is dissolved in toluene and slowly added to an excess of sodium *m*-chlorophenoxide in diglyme solution (ca.  $80^\circ\text{C}$ ). To promote complete substitution, the temperature of the reaction mixture is then raised and maintained above  $100^\circ\text{C}$  for 24 hr. The substituted polymer (III) is washed with water and methanol, dissolved in tetrahydrofuran, filtered, precipitated into methanol, and dried under vacuum:



Unknown differences in trimer purity and variations in polymerization and substitution conditions may have affected the macromolecular structures of the polymers prepared for this study. Sample identities and synthetic details are given in Table I. The elemental analyses (Galbraith Labs, Knoxville, Tenn.) of samples A, B, and C are in excellent agreement with that predicted theoretically (C, 48.03; H, 2.69; N, 4.67; Cl, 23.63). It is also noted that

TABLE I  
Poly[bis(*m*-chlorophenoxy)phosphazenes]

Sam- ple	Weight of trimer I, g	Polymer- ization time/ temp., hr/°C	Yield II, g	Substitution time/temp., hr/°C	Yield III, g	Net yield, %	Elemental analysis				Remarks
							%C	%H	%N	%Cl	
A	50	20/240	19 (38%)	20/103	25.4 (52%)	20	47.99	2.67	4.68	23.76	tough, white, fibrous
B	90	29/245	44 (49%)	22/125-7 7/115	23 (40%)	20	48.07	2.74	—	23.17	tough, white, fibrous
C	49	32/245	11.3 (23%)	24/125	15 (51%)	12	48.05	2.50	—	23.31	tough, white, fibrous
D	52	46/245	12.3 (24%)	24/110	15.6 (49%)	12	41.81	2.54	—	27.39	tough, tan, rubbery
E	53	46/245	14.2 (27%)	24/105	15.5 (42%)	11	40.50	2.51	—	28.01	tough, tan, rubbery

samples A, B, and C are white, fibrous polymers, whereas D and E are tan-colored elastomers. Samples D and E are not completely substituted.

### Dilute Solution Techniques

Standard dilute solution techniques were used to characterize the polymers and degradation products with chloroform as the solvent at 25°C. Solutions were prepared in volumetric flasks and were heated for at least 1 hr at 50°C to ensure complete solubility. Cannon-Ubbelohde dilution viscometers were employed for intrinsic viscosity determinations. The temperature was controlled at  $\pm 0.02^\circ\text{C}$ , and solvent efflux times were sufficiently long to justify neglecting kinetic energy corrections. Intrinsic viscosities were calculated using a least-squares computer program from the Huggins and Kraemer relations:

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2C \quad (1)$$

$$\frac{\ln \eta_r}{C} = [\eta] - k''[\eta]^2C \quad (2)$$

where  $\eta_{sp}$  and  $\eta_r$  are the specific and relative viscosities, respectively.

A Bausch & Lomb FICA 50 instrument, operated with unpolarized light of wavelength  $\lambda_0 = 5461 \text{ \AA}$  and calibrated with benzene ( $R_B = 16.3 \times 10^{-6}$ ), automatically measured scattered light intensities at preset angles between  $30^\circ$  and  $150^\circ$ . Solutions were filtered through  $0.45 \mu$  Gelman Metricel ALPHA-6 filters directly into the measuring cell. The average value of the refractive index increment as determined using a Brice-Phoenix differential refractometer was  $(dn/dc) = 0.114 \text{ ml/g}$ . A computer program incorporating a polynomial equation for the least-squares analysis of data and a plotting routine for the construction of Zimm plots was used to evaluate weight-average molecular weights  $\bar{M}_w$ , second virial coefficients  $A_2$ , and  $z$ -average radii of gyration  $\langle S^2 \rangle_z^{1/2}$ .

GPC studies were performed using a Waters ANAPREP gel permeation chromatograph with a set of five 4-ft  $\times$   $\frac{3}{8}$ -in. Styragel columns having porosity ratings  $5 \times 10^6$ , 2 of  $(1.5-7) \times 10^5$ ,  $10^5$ , and  $(1.5-5) \times 10^4 \text{ \AA}$  as designated by the manufacturer (Waters Associates, Milford, Mass.). A flow rate of 1

ml/min was maintained with chloroform as the eluent at 25°C. Elution volume  $V_e$  is designated in "counts" where 5 ml of eluate is 1 count. The exclusion volume is less than 25 counts, and the "junk" peak first departs from the baseline at 49 counts. The columns were calibrated with a series of narrow-distribution polystyrene standards, and an iterative calibration procedure using the absolute molecular weight parameters  $\bar{M}_n$  (osmometry) and  $\bar{M}_w$  (light scattering) of the polymer fractions of sample A (sample IIIe in ref. 1) were applied to construct the polyphosphazene calibration curve (Fig. 1).<sup>2</sup>

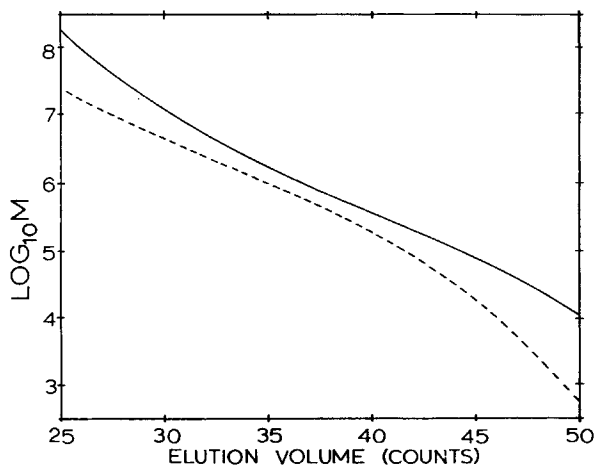


Fig. 1. GPC calibration curves for polystyrene (- - -) and for the polyphosphazene (—).

Chromatograms were reproducible and showed no significant change with solution concentrations ranging from 0.1 to 1.0 g/dl. No polymer was adsorbed onto the Styragel packings, and no changes were observed in eluent flow rate or column back pressure during this investigation.

### Degradation Studies

The thermal degradation of the polymers in air were investigated using a Du Pont 951 TGA and a Perkin-Elmer DSC-1B programmed at heating rates of 10°C/min. The isothermal degradation of the polyphosphazenes and a standard polystyrene ( $2 \times 10^6$  g/mole, Pressure Chemical Co., Pittsburgh, Penn.) was studied at 165°C in air. Films of uniform thickness (10 mil) were prepared by solution (THF) casting the polymers onto glass plates. The films were then cut into strips, weighed (ca. 30 mg), and placed in small glass ampoules. Samples in the open ampoules were exposed in a modified oven and were removed over varying time intervals through a small opening on top of the oven. After cooling, the samples were dissolved by adding chloroform to the ampoules. Solutions were then transferred to 10-ml volumetric flasks and diluted to volume. Finally, the structure of each sample was characterized using viscometry and GPC. Membrane osmometry and light-scattering techniques were occasionally employed to ensure that the molecular weight parameters being determined by GPC were correct.

## RESULTS AND DISCUSSION

## Macromolecular Characterization

Results from the dilute solution characterization of sample A and its fractions<sup>2</sup> were utilized in analyzing the macromolecular structures of the other poly[bis(*m*-chlorophenoxy)phosphazene] samples (Table II). The gel permeation chromatograms for these samples are depicted in Figures 2A–E. The chief characteristics that the polymers have in common are high molecular weights and broad, bimodal molecular weight distributions. No polymer chain branching was indicated in sample A.<sup>2</sup> It is possible to discern whether significant branching is present in the other samples by comparing their characterization parameters with those of sample A, assuming that sample A has

TABLE II  
Dilute Solution Parameters

Sample	$[\eta]$ , dl/g	Light scattering			GPC					Comments
		$\bar{M}_w$	$(S^2)^{1/2}$ , Å	$A_{21}$ , ml-mole/g <sup>2</sup>	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$	
A	1.95	$3.89 \times 10^6$	906	$5.44 \times 10^{-5}$	$3.2 \times 10^5$	$3.56 \times 10^6$	$2.0 \times 10^7$	11.3	5.7	linear
B	1.66	$6.13 \times 10^6$	1280	$5.3 \times 10^{-5}$	$2.5 \times 10^5$	$2.2 \times 10^6$	$1.6 \times 10^7$	8.8	7.3	branched 511 repeat units per branch
C <sup>a</sup>	2.10	$2.64 \times 10^6$	733	$-0.9 \times 10^{-5}$	$5.1 \times 10^5$	$2.6 \times 10^6$	$8.4 \times 10^6$	5.1	3.2	associates
D	1.27	$2.34 \times 10^6$	740	$1.33 \times 10^{-4}$	$3.9 \times 10^5$	$2.24 \times 10^6$	$1.5 \times 10^7$	5.7	6.9	linear
D <sup>b</sup>	0.99	—	—	—	$1.0 \times 10^5$	$5.45 \times 10^5$	$2.2 \times 10^6$	5.3	4.0	—
E	1.21	$1.80 \times 10^6$	648	$8.7 \times 10^{-5}$	$2.4 \times 10^5$	$2.02 \times 10^6$	$1.2 \times 10^7$	8.3	6.1	linear
E <sup>b</sup>	0.73	—	—	—	$9.8 \times 10^4$	$5.28 \times 10^5$	$1.8 \times 10^6$	5.4	3.4	—

<sup>a</sup> Light scattering for C was run with tetrahydrofuran as the solvent at 25°C.

<sup>b</sup> Sample after one year.

very little, if any, long-chain branching. Branching is apparent only in sample B, since the  $[\eta]$  value of B is smaller than that of sample A even though B has a significantly larger light-scattering  $\bar{M}_w$  value and since the GPC value of  $\bar{M}_w$  is considerably smaller than the respective light-scattering value for B.

The extent of branching may be estimated from dilute solution data by assuming a branching model. A likely model for polyphosphazene branching is a polymer with randomly distributed, trifunctional branching units and long-chain branches. It is well known that long-chain branched polymers have a more compact configuration in solution than do linear chains of the same type and that the intrinsic viscosity of a linear polymer  $[\eta]_{\text{lin}}$  is related to the intrinsic viscosity of a branched polymer  $[\eta]_{\text{br}}$  (assuming equivalent molecular weights) by a branching function  $g$  such that<sup>4</sup>

$$g^{1/2} = \frac{[\eta]_{\text{br}}}{[\eta]_{\text{lin}}} \quad (3)$$

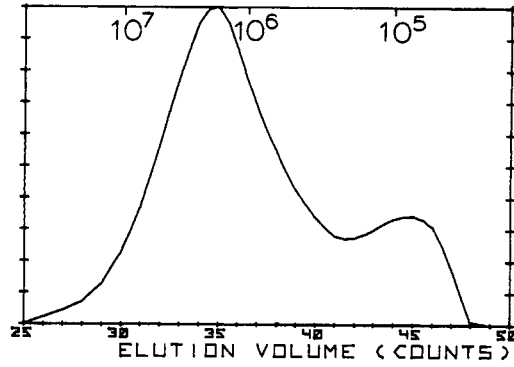
Branched and linear polymers of the same type and molecular weight may be related by combining the Mark-Houwink equation for the linear polymer  $[\eta]_{\text{lin}} = KM^a_{\text{lin}}$  with eq. (3), which gives

$$[\eta]_{\text{br}} = KM^a_{\text{lin}} g^{1/2} \quad (4)$$

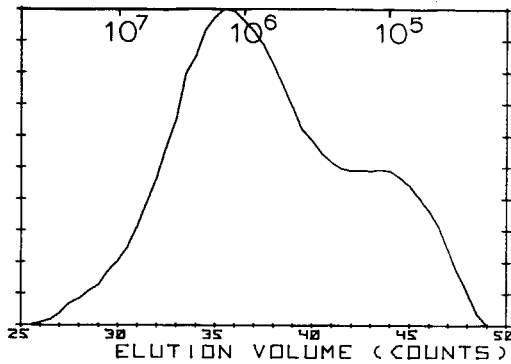
where for random, trifunctional, long-chain branching<sup>5</sup>

$$g = \langle g_3 \rangle_w = \frac{6}{\lambda M} \left\{ \frac{(2 + \lambda M)^{1/2}}{2(\lambda M)^{1/2}} \ln \frac{(2 + \lambda M)^{1/2} + (\lambda M)^{1/2}}{(2 + \lambda M)^{1/2} - (\lambda M)^{1/2}} - 1 \right\} \quad (5)$$

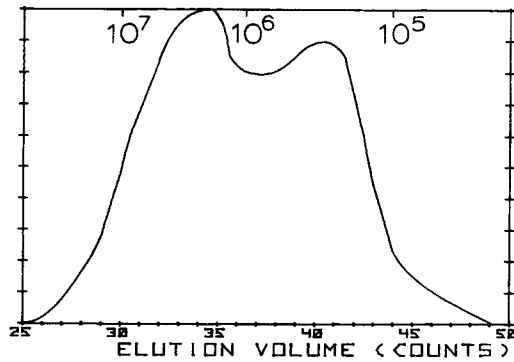
and  $\lambda$  is the branching parameter such that  $\lambda M$  is the weight-average number of branched repeat units per polymer molecule. Since in theory<sup>6</sup> there is an



(a)

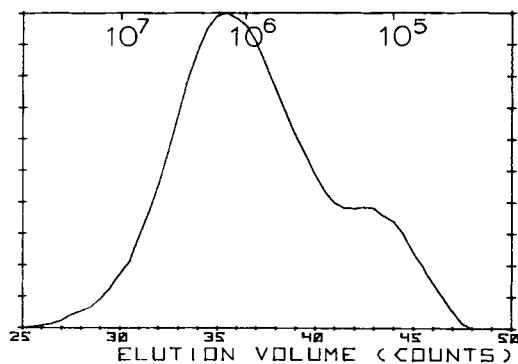


(b)

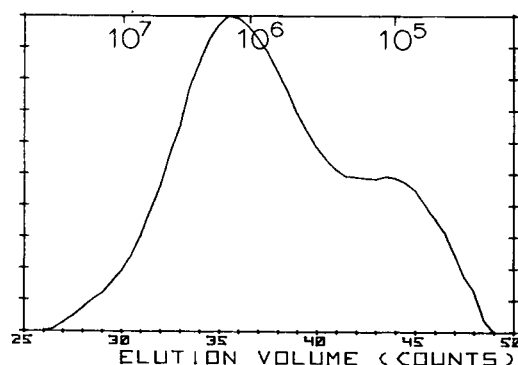


(c)

Fig. 2 (continued)



(d)



(e)

Fig. 2. GPC chromatograms for samples A, B, C, D, and E.

equivalence between the hydrodynamic volumes of linear and branched polymers

$$M_{\text{lin}}[\eta]_{\text{lin}} = M_{\text{br}}[\eta]_{\text{br}} \quad (6)$$

The GPC calibration curve may be revised for analysis of the branched polymer by plotting  $\log(M/g^{1/2})$  versus  $V_e$ . Such a calibration curve is then applied in analyzing the GPC chromatogram of the branched polymer (Fig. 2B). In practice, an iterative procedure is used where the value of  $\lambda$  is varied until the  $\bar{M}_w$  value calculated from the GPC analysis is in close agreement with the respective light-scattering value. For sample B, the branching parameter  $\lambda = 2.8 \times 10^{-6}$ , which may also be expressed as the number of repeat units per branch point,  $1/(\lambda M_0) = 1190$ , where  $M_0 = 300$  g/monomer repeat unit. The number-average molecular weight  $\bar{M}_n$  determined by GPC upon application of the branching model is essentially unchanged. However, the molecular weight distribution is quite broad, as indicated by the molecular weight ratio  $\bar{M}_w/\bar{M}_n = 24.5$ .

As mentioned previously, samples D and E are rubbery polymers. The absence of crystallinity in these samples is apparently a consequence of incomplete chloride replacement during the substitution reaction. Calculations based on elemental analysis (%C) suggest that the substitution of samples D

and E was only 72% and 68%, respectively. The two samples also deteriorated upon storage at room temperature in closed glass specimen jars. After one year, the polymers had turned a dark-brown color and had a strong phenolic odor. Intrinsic viscosity and GPC analyses indicated that significant polymer chain degradation occurred on storage (Table II); nevertheless, both samples still had relatively high molecular weights ( $\bar{M}_w > 5 \times 10^5$ ).

Samples A, B, and C are essentially completely substituted according to elemental analyses, and no deterioration or change in molecular weight occurred after more than one year in storage. Samples A and B display good solubility properties with chloroform as the solvent. Huggins constants evaluated from intrinsic viscosity data were in the range of  $0.35 < k' < 0.5$  with  $k' + k'' \approx 0.5$ , as expected for well-behaved solutions; and a linear concentration dependence was observed in plots of light-scattering data yielding positive  $A_2$  values. However, sample C behaves anomalously in chloroform solution. Dilute solutions filter ( $0.45 \mu$ ) with difficulty and some loss of polymer, and nonlinear Zimm plots are obtained indicating abnormally large  $\bar{M}_w$  values. The polymer also has an unusually large Huggins constant ( $k' = 0.95$ ) which is most likely the consequence of large intermolecular interactions or association between polymer molecules. GPC results (Fig. 2C) are also probably influenced by the anomalous solution behavior. No polymer association is indicated when sample C is in tetrahydrofuran solution although a slightly negative second virial coefficient is observed. The exact cause of the association phenomenon is uncertain, but it may be due to the presence of a few polar substituents (P—OH, P=O, or >N—H) on the polymer chain backbones which interact specifically when the polymer is in a relatively nonpolar, low-dielectric solvent like chloroform.

### Polymer Chain Degradation

TGA and DSC experiments were run at  $10^\circ\text{C}/\text{min}$  in air, and no significant differences were observed in the thermal stabilities of A, B, and C. No major thermal events (e.g., scission endotherm or oxidation exotherm) were evident from the DSC analysis up to the temperature region where weight loss starts to occur. The polyphosphazene has a thermal decomposition temperature  $T_d \approx 350^\circ\text{C}$  and appears more stable at elevated temperatures than polystyrene (Figs. 3a and b). However, chain scission and weight loss may occur under isothermal conditions at considerably lower temperatures. For example, weight loss is observed with long exposure times down to  $200^\circ\text{C}$ . And processing studies show that poly(aryloxyphosphazenes) may be compression molded at temperatures between  $150^\circ$  and  $200^\circ\text{C}$ . Therefore, it was decided to study the thermal degradation of poly[bis(*m*-chlorophenoxy)phosphazene] at  $165^\circ\text{C}$  in static air. The marked reduction in intrinsic viscosity after heat aging (Fig. 4) indicates that significant chain degradation occurs at  $165^\circ\text{C}$ .

There are two fundamental mechanisms by which polymers generally degrade—random degradation and chain depolymerization.<sup>8</sup> In random degradation, chain rupture or scission occurs at random points along the polymer chain, producing fragments which are usually much larger than a single repeat unit. Chain depolymerization involves the successive release or “unzippering” of low molecular weight units from chain ends. The two types of



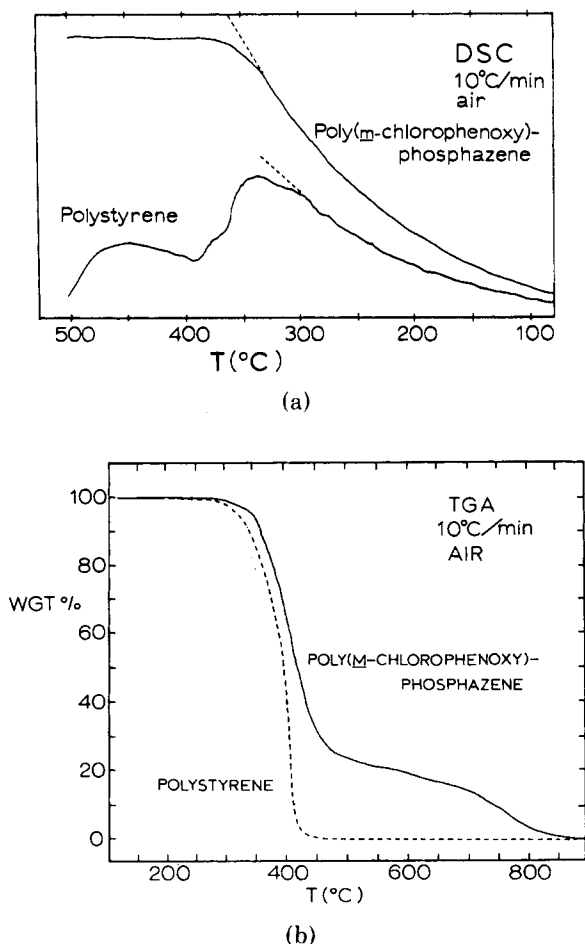


Fig. 3. (a) DSC and (b) TGA of poly[bis(*m*-chlorophenoxy)phosphazene] and polystyrene.

mechanisms may operate separately or in combination. It is possible to differentiate between the two mechanisms, and initial observations suggest that poly[bis(*m*-chlorophenoxy)phosphazene] degrades by random degradation. A chain depolymerization or "unzipping" type mechanism does not occur since no low molecular weight residue is produced. That is, no significant weight loss is observed after exposing films for one month at  $165^{\circ}\text{C}$ , and no cyclic or phenol formation is observed. Figure 5 illustrates changes in the molecular weight distribution of sample A upon exposure. The molecular weight distribution gradually shifts from a bimodal to a nearly "most probable" type distribution. The  $\bar{M}_w$  value drops by an order of magnitude in a relatively short period of time, whereas  $\bar{M}_n$  decreases more gradually (Fig. 6). For a random degradation mechanism, the heterogeneity index  $\bar{M}_w/\bar{M}_n$  is expected to approach a value of 2 with increasing exposure time. As shown at the bottom of Figure 6, sample A appears to degrade according to a typical random scission mechanism. Finally, no insoluble polymer was created during heat treatment, and there was no indication of crosslink or gel formation.

Since polystyrene is known<sup>9</sup> to undergo random degradation at  $165^{\circ}\text{C}$ , a

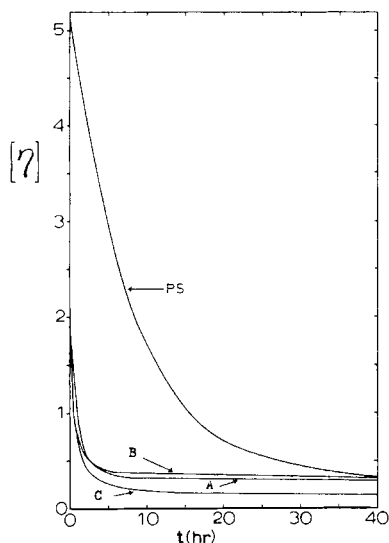


Fig. 4. Plot of  $[\eta]$  vs. heat aging period in air at  $165^{\circ}\text{C}$  for samples A, B, and C and polystyrene (PS).

standard, narrow-distribution polystyrene sample ( $M = 2 \times 10^6$ ) was selected for comparison of degradation behavior with samples A, B, and C. The greatest change in molecular weight for the three polyphosphazenes occurs within the first 10 hr of exposure. The ratio  $\bar{M}_w/\bar{M}_n$  is sharply reduced within the first 4 hr, and  $\bar{M}_w/\bar{M}_n \approx 2$  after 10 hr of exposure for all three polyphosphazenes. Since the molecular weight distribution of the polystyrene was originally narrow ( $\bar{M}_w/\bar{M}_n < 1.2$ ), its distribution gradually broadens with  $\bar{M}_w/\bar{M}_n$ , approaching 2. For long exposure times, polystyrene appears to degrade at a higher rate than the polyphosphazenes. The change in the number-average number of chain repeat units,  $X_n = \bar{M}_n/M_0$  ( $M_0$  is the repeat unit molecular weight), provides some indication of the relative stabilities of the polymers. Comparing the original number of chain repeat units,

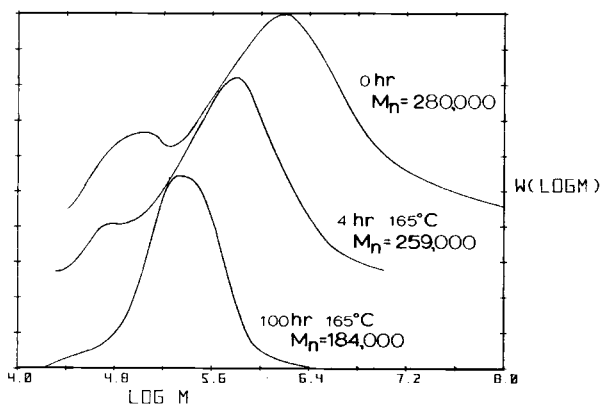


Fig. 5. Change in the molecular weight distribution of sample A upon heat aging at  $165^{\circ}\text{C}$  in air.

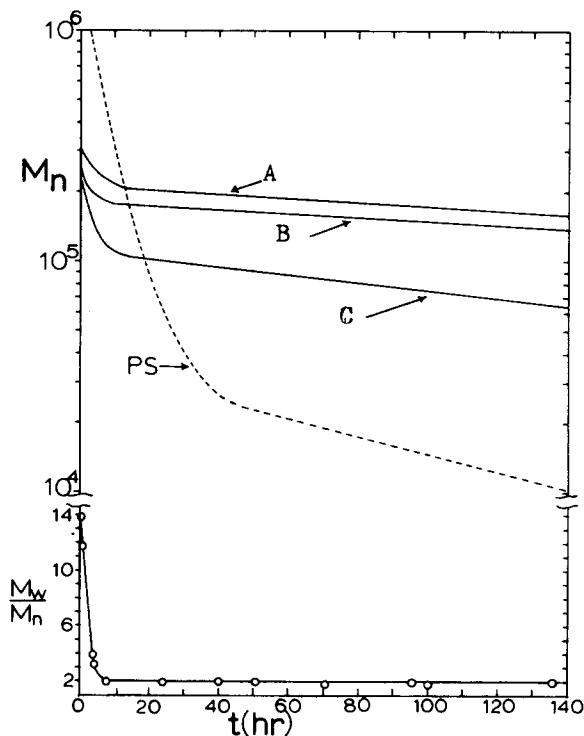


Fig. 6. Molecular weight change with heat aging period  $t$  for samples A, B, and C and polystyrene (PS).

$X_{n,0}$ , with the value after 240 hr of exposure,  $X_{n,240}$  (Table III), the extent of degradation is considerably greater for polystyrene. The polyphosphazenes were originally in the form of white, translucent films. After heat aging, the films retained their shapes but became brittle and gradually changed color from white to tan (2–4 hr) to brown (40 hr) and finally to dark brown (100 hr). After ten days of exposure at 165°C, the polyphosphazene films still retained their original shapes and were of high molecular weight; however, the polystyrene had formed a viscous, yellow oil.

The most revealing evidence for a random degradation mechanism comes from examining the change in  $\bar{M}_n$  with exposure time  $t$ . For a purely random scission process, the following equation should apply:<sup>9</sup>

$$\frac{1}{X_{n,t}} - \frac{1}{X_{n,0}} = kt \quad (7)$$

TABLE III  
Polymer Degradation

Sample	$X_{n,0}$	$X_{n,240}$	$k, \text{hr}^{-1}$	$b$	$N_{1,000}$
A	1070	315	$7.5 \times 10^{-6}$	$2.0 \times 10^{-4}$	0.4
B	833	291	$8.0 \times 10^{-6}$	$4.0 \times 10^{-4}$	0.8
C	1700	189	$9.0 \times 10^{-6}$	$2.4 \times 10^{-3}$	4.8
PS	19000	56	$6.7 \times 10^{-5}$	0	0

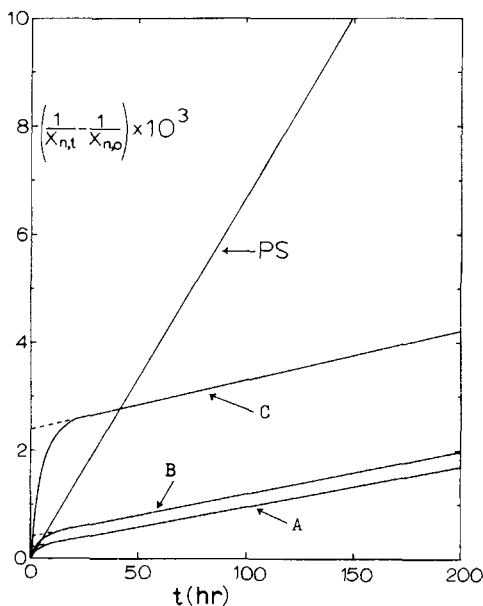


Fig. 7. Plot of  $(1/X_{n,t} - 1/X_{n,0})$  vs. heat aging period  $t$  for samples A, B, and C and polystyrene (PS).

where  $X_{n,t}$  and  $X_{n,0}$  are the number-average numbers of chain repeat units at time  $t$  and  $t = 0$ , respectively; and  $k$  is the first-order rate constant for bond scission. As shown in Figure 7, the random degradation mechanism applies to polystyrene. A linear plot is obtained with an intercept at "zero" when  $1/X_{n,t} - 1/X_{n,0}$  is plotted against  $t$ . However, plots of the polyphosphazene data are not linear for  $t < 10$  hr, and the linear portions do not extrapolate to "zero." Similar plots have been obtained for other polymers.<sup>9</sup> The seemingly anomalous behavior has been explained as due to the presence of "weak links" in the polymer chain backbone which break rapidly and preferentially in the initial period of exposure. If such weak links are present, eq. (7) becomes<sup>9</sup>

$$\frac{1}{X_{n,t}} - \frac{1}{X_{n,0}} = b + kt \quad (8)$$

where  $b$  is the ordinate intercept in Figure 7 and is a measure of the weak link concentration. The number-average number of weak links for a polymer molecule with 1000 repeat units is defined as  $N_{1000} = 2000 \times b$ . The rate constant is determined from the slope of the linear portion of the plot. The degradation rates for the three polyphosphazenes are similar; but the rate for polystyrene is nearly ten times greater than that of poly[bis(*m*-chlorophenoxy)phosphazene] at 165°C. Sample C has the largest concentration of weak links. The rate of weak link scission is estimated to be  $3.6 \times 10^{-4} \text{ hr}^{-1}$  from the initial slope of the curve of sample C near  $t = 0$ . That is, weak links rupture at a rate of approximately 400 times that found after the weak links are broken.

It is quite plausible that weak links are present in the polyphosphazenes. Both hexachlorocyclotriphosphazene and the polymer precursor poly(dichlo-

rophosphazene) are susceptible to hydrolysis. Although precautions are taken during synthesis, adventitious moisture may contaminate the polymer and P—OH, P=O, or >N—H groups may form. Specifically, thermally labile oxo phosphazane bonds may form in the polymer backbone. It is possible that the anomalous solubility behavior and large  $N_{1000}$  value of sample C is related to a high phosphazane concentration in the polymer. It is interesting that after a short period of exposure ( $t < 2$  hrs), during which most of the weak links are believed to rupture, sample C no longer behaves anomalously in solution. Another source of weak links appears to be branch points in the polymer chains. Before heat aging, sample B is branched. After 1 hr at 165°C, branching is no longer evident.

A special experiment was conducted to determine whether the rapid, initial decay in molecular weight of the polyphosphazenes is related to their crystalline structure. Amorphous regions in the semicrystalline polymers may be particularly susceptible to thermo-oxidative degradation. The brittleness of the polymer films after exposure suggests that tie chains between crystalline regions may have been ruptured. To test this theory, films of the polymers were heat aged for 24 hr, dissolved in THF, recast as films, and heat aged an additional 24 hr. Duplicate films which were not redissolved after the first 24-hr heat-aging period were exposed under identical conditions. If amorphous regions in the films are highly susceptible to degradation, the recast films should experience a significant decline in molecular weight upon reexposure compared to the films which are not recast. However, no important differences in the molecular weights of the polymers are observed after the second heat treatment. Therefore, it is concluded that, although amorphous regions might be more susceptible than crystalline regions to thermal degradation, a different phenomenon must be responsible for the large decrease in molecular weight on first exposing the polyphosphazenes at 165°C. It is probable that weak links are more inclined to occur in amorphous regions of the polymers, since they would tend to disrupt crystal formation, and that the brittleness of the heat-aged films is a consequence of weak links rupturing the chains.

Preliminary tests suggest that poly[bis(*m*-chlorophenoxy)phosphazene] is especially susceptible to mechanical degradation. Sample B was rolled (20 passes) on a small compounding mill at room temperature and then recharacterized. The polymer formed a tough, flexible, white film. Sufficient orientation occurred such that the film was notably stronger parallel to the rolling direction. The mechanical treatment significantly reduced the polymer's molecular weight, with  $[\eta] = 0.49$  dl/g,  $\bar{M}_n = 1.89 \times 10^5$ , and  $\bar{M}_w = 4.0 \times 10^5$ . Also, branching was no longer evident after the treatment, and GPC showed only a single, "most probable" distribution peak. The effect of milling appears equivalent to heat aging the polymer for about 24 hr at 165°C. It is likely that the reduction in molecular weight with mechanical treatment is a further consequence of the presence of weak links in the polymer chains.

## COMMENTS

The synthetic procedure used to prepare the polymer for this study did not produce consistent products. Two of the samples were incompletely subst-

intututed and degraded slowly on storage at room temperature. Differences in crystallinity, branching, solubility behavior, and thermal degradation were observed. It is possible that structural differences in the unsubstituted poly(dichlorophosphazenes)(II) influenced the extent of substitution and contributed to the variations in properties. A critical examination of both the polymerization and substitution reactions is required.

All of the polymers have high molecular weights and broad, bimodal molecular weight distributions. The cause of the bimodal distribution is unknown. Although an ionic mechanism has been proposed,<sup>10</sup> the exact operation of the mechanism in the polymerization reaction is uncertain. Heterogeneities in the bulk polymerization, impurities in the cyclic trimer,<sup>11</sup> or surface catalysis effects<sup>12</sup> during polymerization may be creating the bimodal distribution. Variations in reaction conditions for the nucleophilic substitution of poly(dichlorophosphazene) are also known to affect the molecular weight distribution.<sup>13</sup>

The polyphosphazene appears more thermally stable at elevated temperatures in air than polystyrene. The polyphosphazene chains contain "weak links" which may be chain branching units and/or phosphazane units introduced by hydrolysis. Perhaps the macromolecular structure of polyphosphazenes can be controlled by introducing prescribed amounts of "weak links" in the polymers through selective hydrolysis of poly(dichlorophosphazene) before or during the substitution reaction. The "weak links" in the substituted polymer might then be ruptured during processing to produce a more uniform, lower molecular weight polymer.

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