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# MACROMOLECULAR CHARACTERIZATION OF POLY[BIS(M-CHLOROPHENOXY)- PHOSPHAZENE]

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August 1976

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## ABSTRACT

The macromolecular structures and structure-property relationships of five poly[bis(*m*-chlorophenoxy)phosphazene] samples are critically analyzed. The polymers are found to have high molecular weights and broad, bimodal molecular weight distributions. Differences are observed in polymer chain structure (branching) and solubility characteristics. An intrinsic viscosity-molecular weight relationship is established for the linear polymer in chloroform solution at 25 C. The rate and mechanism for the thermal degradation in air of the polyphosphazenes are investigated and compared with that of polystyrene. Mechanical properties, thermal transitions, and thermal stability are markedly influenced by differences in the macromolecular and chemical structures of the polymers.

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## INTRODUCTION

In prior publications analyses revealed that organo-substituted polyphosphazenes have high molecular weights ( $\bar{M}_w > 10^6$ ) and broad molecular weight distributions ( $\bar{M}_w/\bar{M}_n > 10$ ).<sup>1-4</sup> However, the shape and detailed characteristics of the molecular weight distributions were not determined. The results of these studies also indicated that the polymers were probably not highly branched and should be amenable to fractionation. But it is not unexpected that branching might be present in organo-substituted polyphosphazenes since it is well-known that the inorganic precursor, polydichlorophosphazene, cross-links during polymerization if the reaction is carried out to high conversions (>75%) or in the presence of certain catalysts.<sup>4</sup> In this report the macromolecular structures and structure-property relationships of five poly[bis(*m*-chlorophenoxy)phosphazene] samples are critically analyzed. Also, the results of a preliminary study of the thermal degradation of the polymer are presented.

The polymer is generally white and fibrous in appearance. It is soluble in a variety of organic solvents and may be solution cast or compression molded to form films. It has a low glass transition temperature ( $T_g = -25$  C) and retains at least some crystallinity up to its decomposition temperature ( $T_d = 350$  C) although a first-order thermal transition, believed to represent a crystal-crystal transformation, is observed at 66 C.<sup>3,4</sup> Currently, this polymer is being considered for wire-coating, foam, and flame-retardant applications.

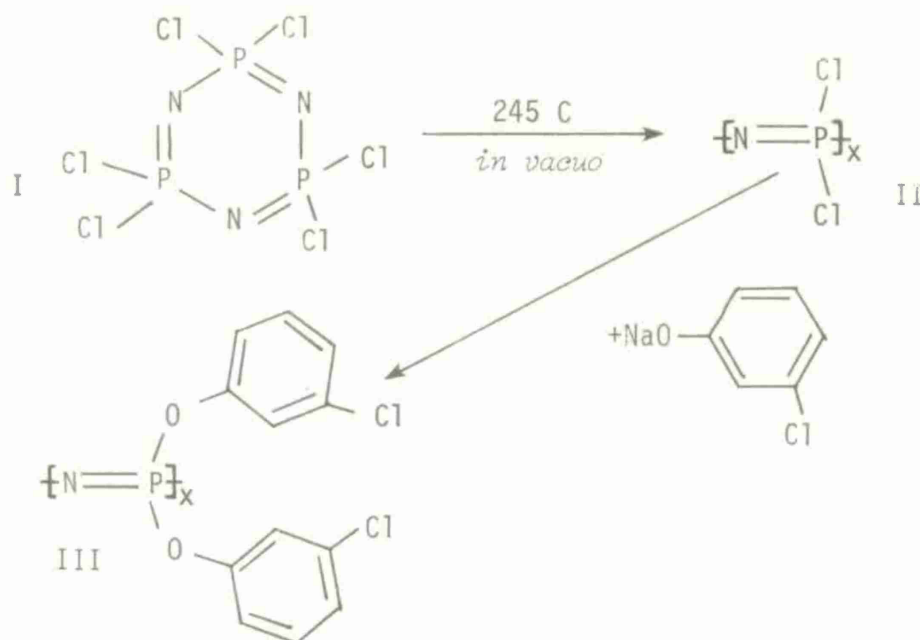
## EXPERIMENTAL

### Polymer Preparation

A detailed description of the preparation of poly[bis(*m*-chlorophenoxy)phosphazene] is given in Reference 3. Purified hexachlorocyclotriphosphazene (I) is polymerized in a sealed, evacuated glass tube at 245 C until the molten reaction mixture becomes so viscous that flow nearly ceases (ca 24 to 48 hours). The reaction mixture is then dissolved in benzene and the polydichlorophosphazene (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 and diglyme solution (ca 80 C). To promote complete substitution the temperature of the reaction mixture is then raised and maintained above 100 C for 24 hours. The polymer (III) is washed with water and methanol, dissolved in tetrahydrofuran, filtered, precipitated into methanol, and dried under vacuum.

1. HAGNAUER, G. L. *Macromolecular Characterization - Part I: Dilute Solution Characterization of Poly(fluoroalkoxy)phosphazenes*. Army Materials and Mechanics Research Center, AMMRC TN 72-10, April 1972.
2. HAGNAUER, G. L., and SCHNEIDER, N. S. *Dilute Solution Characterization of Polyfluoroalkoxyphosphazenes*. J. Polymer Sci., Part A-2, v. 10, 1972, p. 699-713.
3. SINGLER, R. E., HAGNAUER, G. L., SCHNEIDER, N. S., LaLIBERTE, B. R., SACHER, R. E., and MATTON, R. W. *Synthesis and Characterization of Polyaryloxyphosphazenes*. J. Polymer Sci., Polymer Chem. Ed., v. 12, 1974, p. 433-444.
4. SINGLER, R. E., SCHNEIDER, N. S., and HAGNAUER, G. L. *Polyphosphazenes: Synthesis-Properties-Applications*. Polymer Eng. Sci., v. 15, no. 5, 1975, p. 321-338.





Unknown differences in trimer purity and handling techniques, as well as controlled 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 1. The elemental analyses (Galbraith Labs, Knoxville, Tennessee) of 488-10, 1019-59, and 1019-78 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 samples 488-10, 1019-59, and 1019-78 are white, fibrous polymers; whereas samples 1011-187 and 1011-190 are tan-colored elastomers and are not completely substituted.

### Dilute Solution Techniques

All experiments were run at 25 C with freshly purified chloroform as the solvent unless stated otherwise. The chloroform was purified by extracting

Table 1. POLY[BIS(M-CHLOROPHENOXY)PHOSPHAZENE] SAMPLES

| Sample   | Trimer (I)<br>wt (g) | Polymerization<br>time/temp<br>hr/deg C | Yield (II)      | Substitution<br>time/temp<br>hr/deg C | Yield (III)     | Net<br>Yield<br>% | Elemental Analysis (%) |      |      |       | Remarks                          |
|----------|----------------------|-----------------------------------------|-----------------|---------------------------------------|-----------------|-------------------|------------------------|------|------|-------|----------------------------------|
|          |                      |                                         |                 |                                       |                 |                   | C                      | H    | N    | Cl    |                                  |
| 488-10   | 50                   | 20/240                                  | 19 g<br>(38%)   | 20/103                                | 25.4 g<br>(52%) | 20                | 47.99                  | 2.67 | 4.68 | 23.76 | Tough, white,<br>fibrous polymer |
| 1019-78  | 90                   | 29/245                                  | 44 g*<br>(49%)  | 22/125-7<br>7/125                     | 23 g<br>(40%)   | 20                | 48.07                  | 2.74 | -    | 23.17 | " " "                            |
| 1019-59  | 49                   | 32/245                                  | 11.3 g<br>(23%) | 24/125                                | 15 g<br>(51%)   | 12                | 48.05                  | 2.50 | -    | 23.31 | " " "                            |
| 1011-187 | 52                   | 46/245                                  | 12.3 g<br>(24%) | 24/110                                | 15.6 g<br>(49%) | 12                | 41.81                  | 2.54 | -    | 27.39 | Tough, tan,<br>rubbery polymer   |
| 1011-190 | 53                   | 46/245                                  | 14.2 g<br>(27%) | 24/105                                | 15.5 g<br>(42%) | 11                | 40.50                  | 2.51 | -    | 28.01 | " " "                            |

\*22 g was used for substitution



analytical grade chloroform with distilled water to remove the ethanol inhibitor, drying with  $\text{CaSO}_4$ , and then distilling over  $\text{CaSO}_4$ . Fisher spectrograde toluene and methanol were used for the theta-solvent study. Solutions were prepared in volumetric flasks and were heated for at least one hour at 50 C to ensure complete solubility.

Cannon-Ubbelohde dilution viscometers were employed for intrinsic viscosity determinations. The temperature was controlled at  $\pm 0.02$  C and solvent efflux times were sufficiently long to justify neglecting kinetic energy corrections. Intrinsic viscosities were calculated from the extrapolation of data at five different concentrations  $C$  (in grams per deciliter) using a least-squares computer program from the Huggins and Kraemer relations

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

$$\ln \eta_r / C = [\eta] - k'' [\eta]^2 C, \quad (2)$$

where  $\eta_{sp}$  is the specific viscosity and  $\eta_r$  the relative viscosity. Huggins constants were in the range  $0.35 < k' < 0.50$  with  $k' + k'' \approx 0.5$ , as expected for well-behaved solutions.

A Hewlett-Packard model 501 high-speed membrane (gel cellophane 600) osmometer was used to measure osmotic pressures  $\pi$  at 25 C with chloroform and at 37 C with toluene as the solvents. Osmometry data were evaluated using

$$(\pi/C)^{1/2} = (\pi/C)_0^{1/2} [1 + A_2 M_n C/2], \quad (3)$$

where  $A_2$  is the second virial coefficient; and  $M_n$ , the number-average molecular weight  $= RT/(\pi/C)_0$ , where  $R$  is the corrected gas content and  $T$  the absolute temperature.

A Bausch and Lomb FICA 50 instrument, operated with unpolarized light of wavelength  $\lambda_0 = 5461$  Å and calibrated with benzene ( $R_B = 16.3 \times 10^{-6}$ ), automatically measured scattered light intensities at preset angles between 30 and 150 degrees. Solutions were filtered through 0.45- $\mu$  Gelman Metrical 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  $(dn/dC) = 0.114$  ml/g. A computer program incorporating a polynomial equation for the least-squares analysis of data and a plotting routine for the construction of light scattering plots was used to evaluate weight-average molecular weights  $\bar{M}_w$ , second virial coefficients  $A_2$ , and z-average radii of gyration  $\langle S^2 \rangle_z^{1/2}$ . Figure 1 depicts the Zimm plot for polymer sample 488-10. Here the theoretical Zimm "grid" is constructed from determined values of  $\bar{M}_w$ ,  $A_2$ , and  $\langle S^2 \rangle_z$ . More precise values of  $\langle S^2 \rangle_z$  were determined according to the method of Yang<sup>5</sup> where  $KC/R_0 \sin(\theta/2)$  is plotted against  $1/\sin^2(\theta/2)$ .

A Waters ANAPREP gel permeation chromatograph (gpc) was used for both the fractionation and analytical gpc studies. For analytical work two different sets of 4-ft x 3/8-in. Styragel columns were used. Column set No. 1 had five columns

5. YANG, J. T. *An Improvement in the Graphic Treatment of Angular Light Scattering Data*. J. Polymer Sci., v. 26, 1957, p. 305-310.

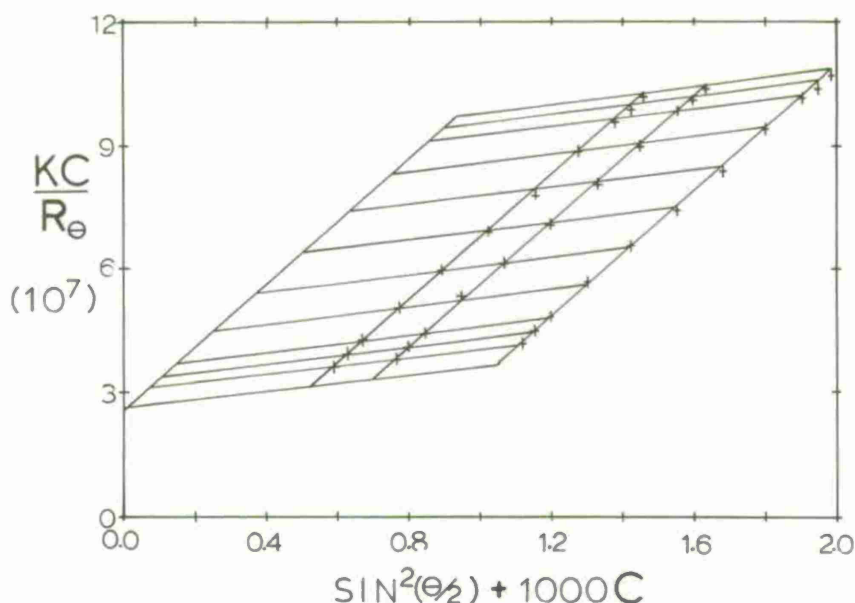


Figure 1. Zimm plot for sample 488-10 in chloroform solution.

(20 feet) with porosity ratings of:  $5 \times 10^6$ ; two of  $(1.5 \text{ to } 7) \times 10^5$ ;  $10^5$ ; and  $(1.5 \text{ to } 5) \times 10^4$  Å as designated by the manufacturer (Waters Associates, Milford, Massachusetts). Column set No. 2 consisted of 6 columns (24 feet) with porosity ratings of: two of  $5 \times 10^6$ ; one of  $(1.5 \text{ to } 7) \times 10^5$ ;  $(1.5 \text{ to } 5) \times 10^4$ ;  $10^4$ ; and 700 to 2000 Å. A flow rate of 1 ml/min was maintained with chloroform as the eluent at 25 C. The column efficiency was measured as the number of theoretical plates per foot

$$N = (1/L) (4V_p/W)^2, \quad (4)$$

where  $V_p$  is the elution volume at the peak maximum and  $W$  is the peak width at its base for hexa(*m*-chlorophenoxy)cyclotriphosphazene ( $M = 900$  g/mole). Efficiency for column set No. 1  $N$  equaled 317 plates/ft and for No. 2  $N$  equaled 352 plates/ft. Elution volume  $V_e$  is designated in "counts" where 5 ml of eluate is 1 count. For column set No. 1 the exclusion volume is less than 25 counts and the "junk" peak first departs from the baseline at 49 counts. For column set No. 2 the exclusion volume is less than 32 counts and the junk peak begins to appear at 58 counts. Chromatograms having linear baselines were obtained using a diffractometer attenuation of 16X with solution concentrations of 0.25 g/dl.

After filtration through 5-μ Teflon filters, the solution (2 ml) was injected automatically onto the columns. A special calibration procedure (see GPC Calibration) using absolute molecular weights  $\bar{M}_n$  and  $\bar{M}_w$  of the polyphosphazene samples was used to obtain a calibration curve. The columns were also calibrated with a series of narrow distribution polystyrene standards obtained from Pressure Chemical Co., Pittsburgh, Pennsylvania, and Waters Associates, Milford, Massachusetts. Broad distribution NBS 706 and high molecular weight Waters No. 41746 ( $\bar{M}_n = 2 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 1.2$ ,  $\bar{M}_z/\bar{M}_w = 2.1$ ) polystyrene standards were run to assure the validity of the calibration curve.

A Hewlett-Packard model 9830 computer with in-house computer programs was used to analyze and plot data. A detailed description of the theory and programs used for gpc analysis will be presented in a future report.

## Fractionation

Two sets of gpc columns packed with untreated controlled-pore glass (CPG) beads (Electro-Nucleonics, Inc., Fairfield, New Jersey) were used to fractionate sample 488-10 with chloroform as the eluent at a flow rate of 1 ml/min. A stock solution (1 g/dl) was sequentially injected using a 2-ml injection loop. The first set of columns consisted of two 4-ft x 3/8-in. columns containing CPG 2000 and 740 Å packings. Fractions were collected for each injection at the elution volumes shown in Table 2. A total of 60 injections (1.2 g) were made on the first column set. The elution profile gradually shifted to lower elution volumes during the first 34 runs (Figure 2). Fractions 1A to 5A were collected from the first 40 injections and 1B to 5B were collected between injections 40 and 60. Fraction 5A was then refractionated on the second column set consisting of two 4-ft x 3/8-in. stainless steel columns with CPG 240 and 125 Å packings. Only a slight downward shift of the elution peak maximum was noted during separation. The fractions were recovered by slowly evaporating most of the chloroform and then precipitating the polymer with *n*-pentane. The precipitate was removed by centrifugation and dried under vacuum at 50 C. The weight fractions based on material recovered are given in Table 2.

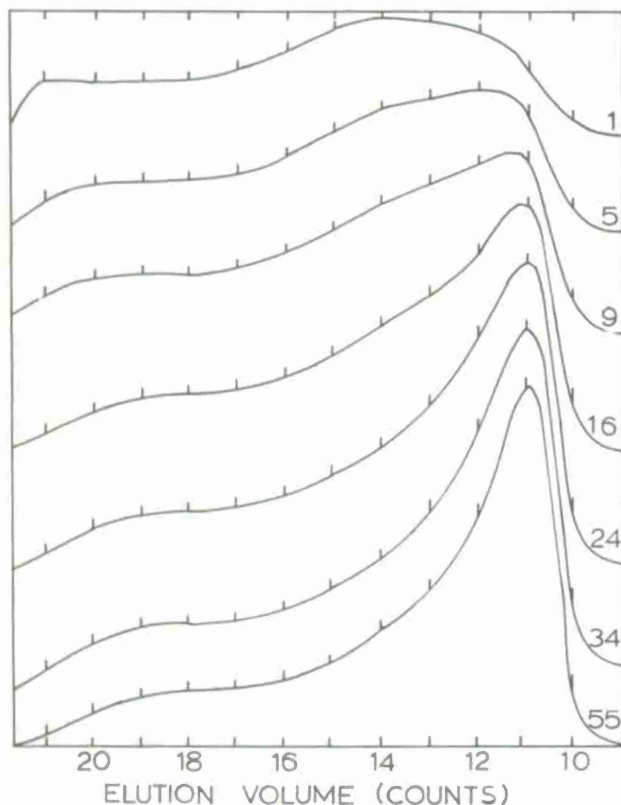


Figure 2. GPC chromatograms for fractionation with 2000, 740 Å CPG column set.

Table 2. FRACTIONATION

| Column Set | Fraction | Elution Volume (counts) | Weight Fraction Recovered |
|------------|----------|-------------------------|---------------------------|
| 2000, 740  | 1A and B | 10 - 11                 | 0.10                      |
|            | 2A and B | 12                      | .20                       |
|            | 3A and B | 13                      | .15                       |
|            | 4A and B | 14                      | .11                       |
|            | 5A and B | 15 - 23                 | .44                       |
| 240, 125   | 5A-1     | 10 - 11                 | .16                       |
|            | 5A-2     | 12                      | .50                       |
|            | 5A-3     | 13 - 15                 | .18                       |
|            | 5A-4     | 16 - 21                 | .16                       |



The gradual shift in the elution profile was a consequence of polymer being adsorbed by the porous glass packing. By extracting the CPG beads with THF, 140 mg of the polymer was recovered. Samples 740 and 2000 refer to polymer extracted from the respective CPG packings. Insufficient material was extracted from the 240 and 125 Å packings for analysis.

### GPC Calibration

The polystyrene and poly[bis(*m*-chlorophenoxy)phosphazene] calibration curves for column sets Nos. 1 and 2 are shown in Figure 3. For comparison the normalized gpc chromatograms of the unfractionated polymer 488-10 are illustrated also. The polystyrene calibration curves were constructed using a least-squares linear-regression analysis to fit the logarithm (base 10) of the molecular weight of polystyrene as a function of elution volume  $V_e$  (peak elution volume for the narrow distribution standards) to a third-order polynomial,

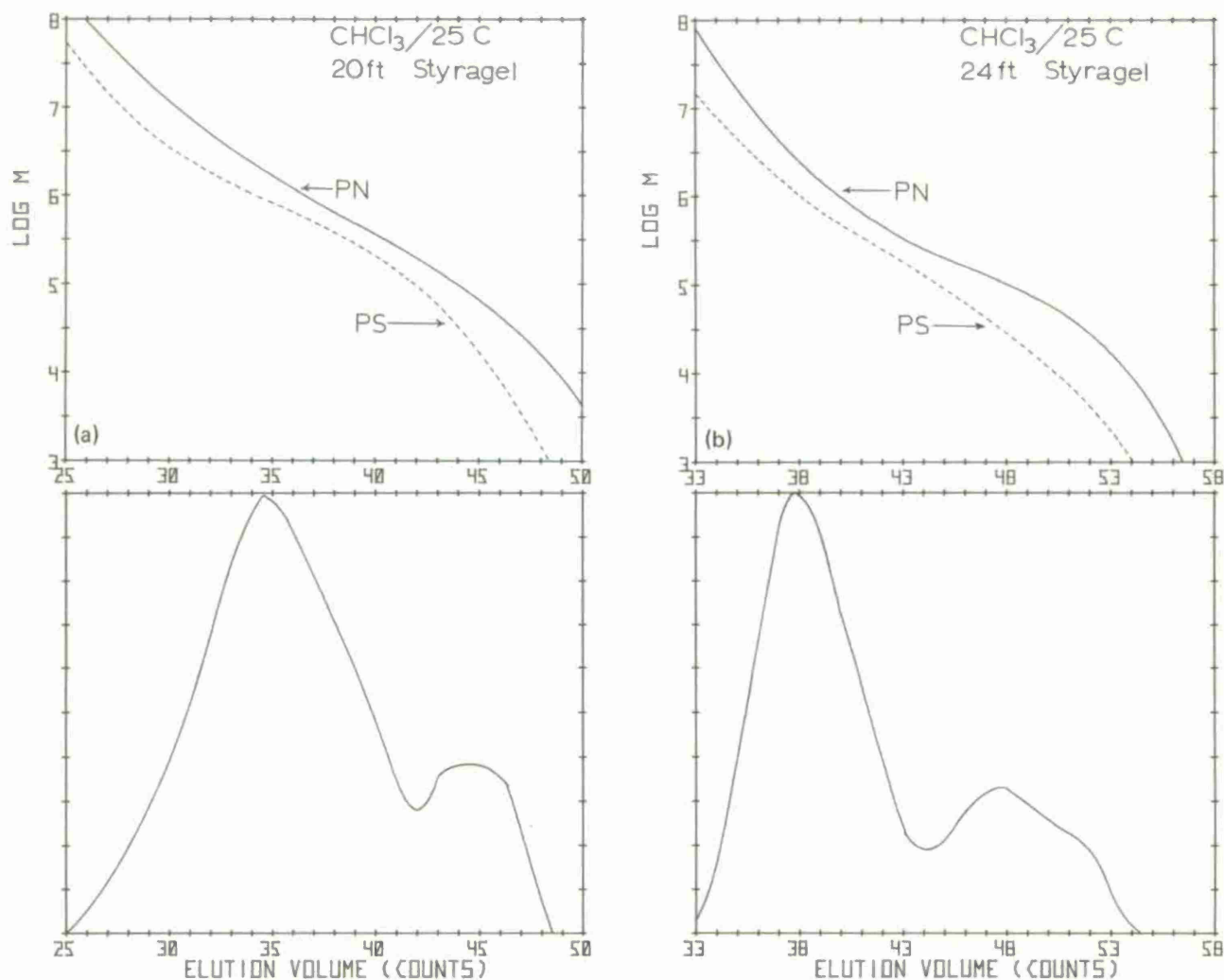


Figure 3. GPC calibration curves for polystyrene and for the polyphosphazene (upper portions) and normalized GPC chromatograms for sample 488-10 (lower portions) with (a) column set No. 1, and (b) column set No. 2.

$$\log_{10} M_{PS} = B(0) + B(1)V_e + B(2)V_e^2 + B(3)V_e^3. \quad (5)$$

The r-square correlation coefficient for this analysis was 0.9998. An iterative computer program was used to estimate the calibration curve for polyphosphazene. First, the polystyrene calibration was applied to evaluate  $\bar{M}_n$  and  $\bar{M}_w$  values from the polyphosphazene chromatograms. These parameters were compared with the absolute molecular weights of 488-10 and its fractions shown in Table 3. The variance between calculated and absolute molecular weights with change in molecular weight was then used to derive a new calibration curve which also was expressed as a third-order polynomial equation. The chromatograms were then re-analyzed using this revised calibration and different values of  $\bar{M}_n$  and  $\bar{M}_w$  were calculated. The variance between gpc and absolute molecular weight values was used to establish another calibration curve and the process was repeated until the variance between the set of calculated and absolute molecular weights neared a minimum. The correlation coefficient for the log-log plot of molecular weights (Figure 4) is  $r = 0.9937$  with a slope of 1.02. The number-, weight-, and z-average molecular weights were then evaluated from the gpc data. Molecular weights are reliable in the region between  $10^5$  and  $10^7$ . Consequently, little credibility is attributed to most of the  $\bar{M}_z$  values.

### Theta-Solvent Determination

The mixed-solvent methanol/toluene (26.1/73.9 v/v-%) appears to be a theta solvent<sup>6</sup> for the polyphosphazene at 30 C. The  $\theta$  condition was estimated by first titrating a 1-g/dl solution of sample 488-10 dissolved in toluene with the non-solvent methanol. The mixed-solvent composition was then adjusted and the temperature was varied until reversible precipitation was observed just below 30 C. To test the validity of the  $\theta$  condition both  $[\eta]$  and  $\langle S^2 \rangle^{1/2}$  were evaluated for several samples at different temperatures in the mixed solvent. The magnitudes of the parameters decreased as the temperature was lowered and approached a minimum

Table 3. DILUTE SOLUTION PARAMETERS

| Sample            | $[\eta]$<br>(dl/g) | $\bar{M}_w$<br>( $10^6$ ) | $A_2$<br>(ml-mol <sup>2</sup> /g <sup>2</sup> )<br>( $10^5$ ) | $\langle S^2 \rangle^{1/2}$<br>(Å) | $\bar{M}_n$<br>( $10^6$ ) | $A_2$<br>(ml-mol <sup>2</sup> /g <sup>2</sup> )<br>( $10^5$ ) | $\bar{M}_w$<br>( $10^6$ ) | GPC                   |                       |                           |
|-------------------|--------------------|---------------------------|---------------------------------------------------------------|------------------------------------|---------------------------|---------------------------------------------------------------|---------------------------|-----------------------|-----------------------|---------------------------|
|                   |                    |                           |                                                               |                                    |                           |                                                               |                           | $\bar{M}_w/\bar{M}_n$ | $\bar{M}_z/\bar{M}_w$ | $\bar{M}_{z+1}/\bar{M}_z$ |
| 488-10            | 1.95               | 3.89                      | 5.44                                                          | 906                                | 0.42*                     | 4.64                                                          | 3.56                      | 11.3                  | 5.7                   | 1.9                       |
| 1A                | 3.37               | 7.16                      | 3.89                                                          | 1190                               | -                         | -                                                             | 6.88                      | 7.4                   | 4.7                   | 2.1                       |
| 2A                | 2.80               | 6.34                      | 4.77                                                          | 1140                               | -                         | -                                                             | 5.93                      | 4.0                   | 4.3                   | 2.5                       |
| 3A                | 2.40               | 4.12                      | 4.50                                                          | 860                                | -                         | -                                                             | 3.51                      | 3.8                   | 3.2                   | 2.2                       |
| 4A <sup>†</sup>   | 1.84               | 2.97                      | 7.26                                                          | 678                                | -                         | -                                                             | 2.77                      | 3.4                   | 6.6                   | 3.8                       |
| 5A-1              | 1.61               | 1.85                      | 5.57                                                          | 483                                | -                         | -                                                             | 2.02                      | 2.2                   | 2.6                   | 2.3                       |
| 5A-2              | 1.20               | 1.79                      | 7.57                                                          | 503                                | 0.68                      | -                                                             | 1.81                      | 2.3                   | 2.9                   | 2.8                       |
| 5A-3 <sup>†</sup> | 1.16               | 1.17                      | 18.7                                                          | 440                                | 0.24                      | -                                                             | 1.17                      | 5.6                   | 5.5                   | 2.3                       |
| 5A-4 <sup>†</sup> | 0.493              | 0.56                      | 17.7                                                          | 378                                | 0.102                     | 47                                                            | 0.59                      | 7.8                   | 13.6                  | 2.1                       |
| 1B                | 3.02               | 6.84                      | 5.06                                                          | 1130                               | -                         | -                                                             | 6.23                      | 5.5                   | 4.5                   | 2.4                       |
| 2B                | 2.71               | 6.21                      | 5.44                                                          | 1080                               | -                         | -                                                             | 5.90                      | 5.6                   | 2.7                   | 2.0                       |
| 3B                | 2.10               | 4.11                      | 7.82                                                          | 817                                | -                         | -                                                             | 4.13                      | 3.5                   | 3.6                   | 2.0                       |
| 4B                | 1.85               | 2.41                      | 8.42                                                          | 590                                | -                         | -                                                             | 2.79                      | 2.2                   | 2.3                   | 2.1                       |
| 5B <sup>†</sup>   | 0.923              | 1.28                      | 7.01                                                          | 455                                | 0.162                     | 47                                                            | 1.37                      | 8.8                   | 4.9                   | 2.7                       |
| 740 <sup>†</sup>  | 1.44               | 3.00                      | 4.50                                                          | 707                                | -                         | -                                                             | 2.19                      | 10.8                  | 7.1                   | 3.0                       |
| 2000 <sup>†</sup> | 1.77               | 2.98                      | 5.80                                                          | 691                                | -                         | -                                                             | 2.41                      | 9.1                   | 8.2                   | 2.5                       |

\*Osmometry with toluene as the solvent at 37 C

<sup>†</sup>Bimodal distribution

(see Table 4) at 30°. Solutions were well-behaved above 30° as indicated by  $[\eta]$  determinations, but incipient precipitation was observed below 30°. Intrinsic viscosities  $[\eta]_0$  were evaluated for most samples in the  $\theta$  solvent.

## Thermal Studies

A Du Pont 990 DSC was used to identify and study shifts in the first-order thermal transition  $T(1)$  of the semicrystalline polyphosphazenes. The thermal degradation of the polymers in air was 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, Pennsylvania) was investigated 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 hole 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.

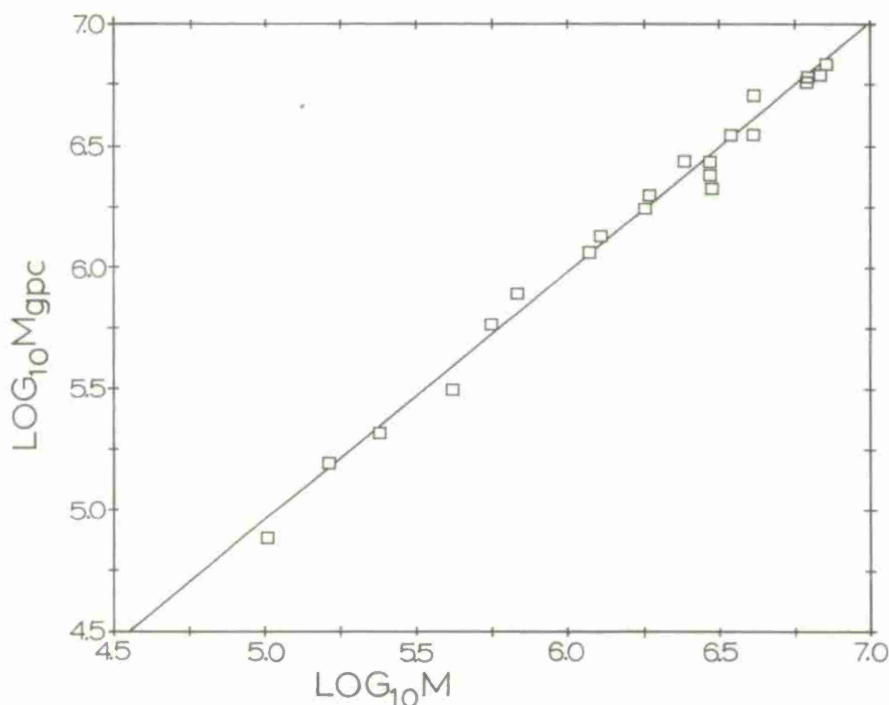


Figure 4. Comparison of molecular weights from gpc and absolute molecular weight analysis.

Table 4. POLYPHOSPHAZENE STRUCTURAL PARAMETERS

| Sample | $[\eta]$ | $\langle S^2 \rangle_z^{1/2}$ | $\langle S^2 \rangle_{z,0}^{1/2}$ | $\langle R^2 \rangle_z / n_z l^2$ | $\langle g \rangle_z$ | $B_w$ | $N_b$        | $x_w$ | $N_x$        |
|--------|----------|-------------------------------|-----------------------------------|-----------------------------------|-----------------------|-------|--------------|-------|--------------|
| 488-10 | 0.72     | 576                           | 440                               | 5.75                              | 0.583                 | 2.15  | $6.03(10^3)$ | 0.715 | $1.81(10^4)$ |
| 3A     | 0.73     | 420                           | 328                               | 5.52                              | 0.608                 | 1.93  | $7.12(10^3)$ | 0.645 | $2.13(10^4)$ |
| 5A-1   | 0.59     | 264                           | 224                               | 4.67                              | 0.719                 | 1.17  | $5.27(10^3)$ | 0.391 | $1.58(10^4)$ |



## RESULTS AND DISCUSSION

### Macromolecular Structure

The cumulative weight fraction and differential distributions of the unfractionated polymer 488-10 and two fractions are illustrated in Figure 5. Molecular weight is plotted logarithmically because of the broad distribution and large values of the molecular weights. The molecular weight distribution of 488-10 is bimodal and broad as indicated by the molecular weight ratio  $\bar{M}_w/\bar{M}_n = 11.3$ . Over half the weight of 488-10 is contributed by polymer molecules with  $M > 10^6$ . Peak maxima are located at  $10^5$  and  $1.6 \times 10^6$  g/mole. Although fractionation succeeded in narrowing the distribution, the fractions are still highly polydisperse with  $\bar{M}_w/\bar{M}_n > 2$ . More fractions should be collected for such a broad distribution. Failure to achieve more narrow distributions may be a consequence of (a) adsorption of the polymer during fractionation, (b) poor separation at the high molecular weight end of the distribution, and (c) the presence of branched polymer.

The fact that the polymer was adsorbed onto the glass packings during fractionation does not seem to have a particularly adverse effect on separation. The distributions of the adsorbed samples 740 and 2000 have the same shape as 488-10 with only slightly lower molecular weights. The lower molecular weights may be rationalized in terms of the gpc separation mechanism. Lower molecular weight polymers are more likely to be adsorbed because they are exposed to a greater surface area of the porous packing. The adsorption also did not seem to produce any significant differences in the molecular weight parameters of fractions collected at identical elution volumes during the first part 1A to 4A and the latter part 1B to 4B of the separation. The Mark-Houwink molecular weight-viscosity relationship

$$[\eta] = K\bar{M}_v^a, \quad (6)$$

where  $\bar{M}_v$  is the viscosity-average molecular weight and  $K$  and  $a$  are constants was determined from  $[\eta]$  and gpc data. By an iterative computer analysis of gpc data,  $\bar{M}_v$  was calculated for each sample assuming the values for  $a$ .

The  $\log [\eta]$  was then plotted against  $\log \bar{M}_w$  as a least-squares straight line. For the best estimate of  $a$  it was specified that the correlation  $r = 1$  assuming a linear relationship exists. Next  $K$  was determined by plotting  $[\eta]_{\text{gpc}}$  against the experimental value  $[\eta]_{\text{expt}}$ , where

$$[\eta]_{\text{gpc}} = \left( K \sum_{i=1}^n H_i M_i^a \right) / \left( \sum_{i=1}^n H_i \right) = K\bar{M}_v^a, \quad (7)$$

and  $H_i$  is the relative height of the chromatogram at elution volume  $V_i$  where polymer of molecular weight  $M_i$  elutes. The criteria for selecting  $K$  was that the slope of the linear plot must be 1 (Figure 6). For  $a = 0.70$  and  $K = 6.27 \times 10^{-5}$  the intercept of this plot is  $-0.006$  and the correlation coefficient is  $r = 0.961$ .

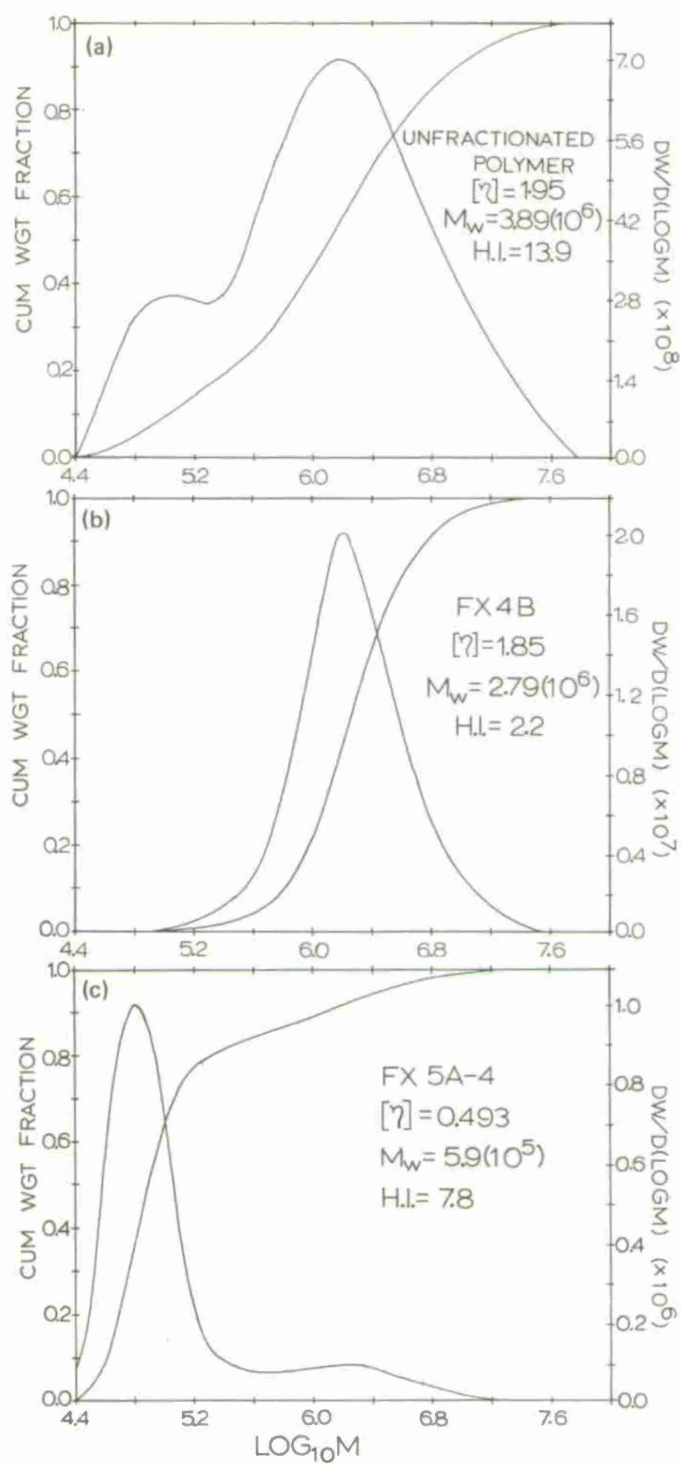


Figure 5. Molecular weight distributions of (a) sample 488-10, (b) fraction 4B, and (c) fraction 5A-4.

According to the universal calibration theory for gpc,<sup>7</sup> if  $K$  and  $a$  are correct, the plot of the logarithm of hydrodynamic volume  $[\eta] M_V = K\bar{M}^{1+a}$  versus  $V_e$  for the polyphosphazene should be superimposable on the same plot for polystyrene. With  $K = 7.16 \times 10^{-5}$  and  $a = 0.76$  for polystyrene in chloroform solution,<sup>8</sup> good agreement is observed (Figure 7) in the region ( $10^5$  to  $10^7$ ) where absolute molecular weight references were used for gpc calibration. The iterative computer approach was also used to determine the Mark-Houwink parameters under  $\theta$ -solvent conditions. The correlation between the experimental and calculated  $[\eta]_\theta$  parameters was poorer with  $r = 0.938$ , possibly because the  $\theta$ -solvent condition really does not apply to polymers with such broad and different molecular weight distributions. The values are  $K_\theta = (4.5 \pm 0.4) \times 10^{-4}$  and  $a = 0.48 \pm 0.04$ .

To estimate the extent of branching and/or cross-linking from dilute solution data, it is advisable to have well-characterized fractions of the branched polymer to compare with fractions of the corresponding linear polymer. Since the polyphosphazene fractions have high polydispersities and the linearity of the polymer is in question, an alternative is to consider model polymer chains which most likely represent the type of branching present in polyphosphazenes and which might be utilized to estimate the extent of branching. If the polymer is branched, the branches are probably randomly distributed with polydisperse chain lengths. Random-comb branched chains may be present with a distribution of branch lengths attached at random intervals to a much longer chain backbone. But it is unlikely that branching in such a comb-shaped polymer could be detected from the data in this study. Long-chain branching with randomly distributed, trifunctional branch units and branch lengths comparable to the length of the chain backbone should be detectable. Also, cross-links which are randomly distributed and tetrafunctional should have a measurable effect on experimental parameters.

The presence of long-chain branching and/or cross-linking may be indicated in plots of molecular weight versus  $[\eta]$  or  $\langle S^2 \rangle_z$ . The log-log plot of  $M_V$  versus  $[\eta]$  may become nonlinear with increasing molecular weight for a branched polymer. Curvatures in such plots are observed with as little branching as one branch per 2000 repeat units in low density polyethylene<sup>9</sup> and one cross-link per  $10^4$  repeat units in polystyrene.<sup>10</sup> For high extents of branching, especially under  $\theta$ -solvent conditions, the Mark-Houwink exponent  $a$  may be less than 0.5. Although a linear relationship between  $\log \bar{M}_V$  and  $\log [\eta]$  was assumed in the gpc analysis for  $K$  and  $a$ , the good agreement between  $[\eta]_{\text{expt}}$  and  $[\eta]_{\text{gpc}}$  was indicative of a linear or not highly branched polymer. Assuming  $\bar{M}_w \approx \bar{M}_V$ , a direct comparison of  $[\eta]$  with  $\bar{M}_w$  (LS) also gives a linear relation (Figure 8) in chloroform solution with  $a = 0.67$ . Finally, under  $\theta$  conditions the parameter  $a = 0.48 \pm 0.04$  indicates little, if any, branching.

For flexible, linear polymers

$$\langle S^2 \rangle \propto M^{1+\epsilon} \quad (8)$$

7. GRUBISIC, Z., REMPP, P., and BENOIT, H. *A Universal Calibration for Gel Permeation Chromatography*. J. Polymer Sci., v. B5, 1967, p. 753-759.
8. BRANDRUP, J., and IMMERGUT, E. H. *Polymer Handbook*. John Wiley & Sons, New York, Section IV, 1966, p. 10.
9. HAMA, T., YAMAGUCHI, K., and SUZUKI, T. *Long Chain Branching and Solution Properties of Low Density Polyethylene*. Die Makromolekulare Chemie, v. 155, 1972, p. 283-298.
10. THURMOND, C. D., and ZIMM, B. H. *Size and Shape of the Molecules—Artificially Branched Polystyrene*. J. Polymer Sci., v. 8, no. 5, 1952, p. 477-494.

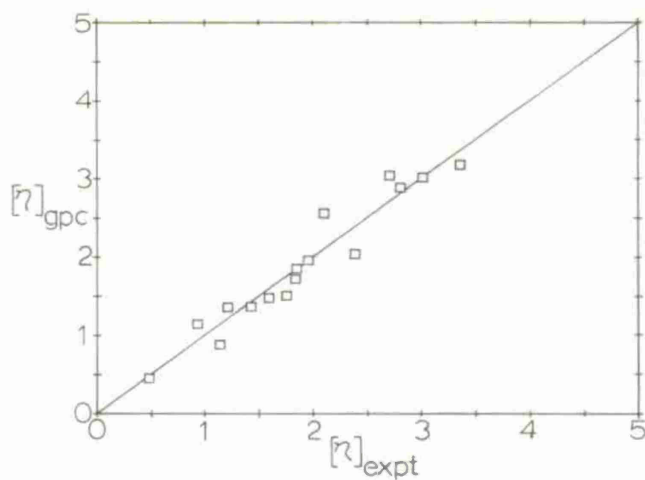


Figure 6. Correlation between intrinsic viscosities calculated from gpc data and determined experimentally.

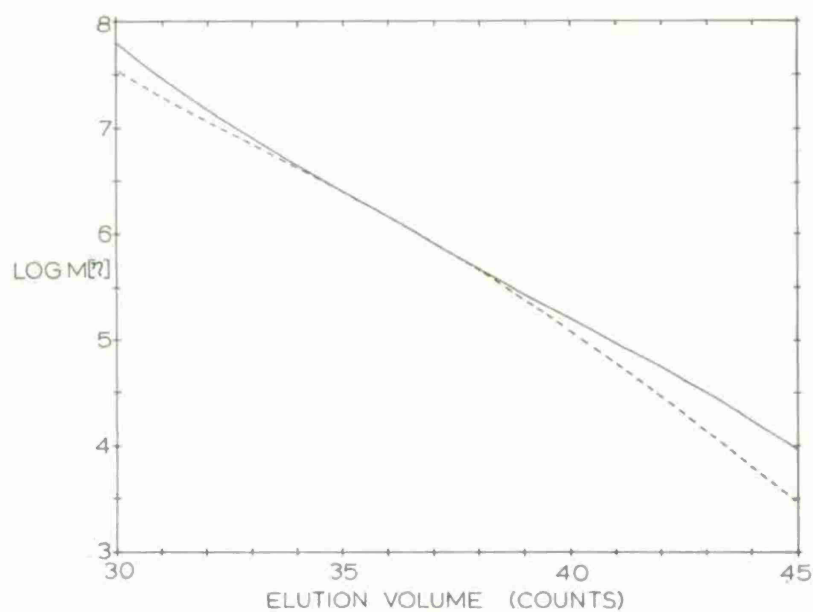


Figure 7. GPC universal calibration plot for polystyrene (-----) and for the polyphosphazene (—) with column set No. 1.

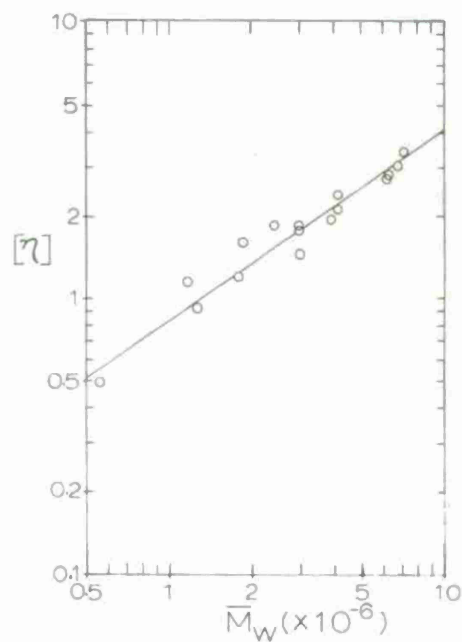


Figure 8. Mark-Houwink plot for the polyphosphazene in  $\text{CHCl}_3$  solution.



where  $\epsilon$  takes into consideration the excluded volume effect.<sup>6</sup> Generally,  $0 < \epsilon \leq 0.2$  and  $\epsilon = 0$  for polymers under  $\theta$ -solvent conditions. If a polymer is sufficiently branched, its molecular weight exponent may be less than one. The log-log plot of  $\bar{M}_z$  (gpc) versus  $\langle S^2 \rangle_z$  is linear with a slope of 1.04 and correlation of  $r = 0.91$ . The correlation is poor because of the error inherent in determining  $\bar{M}_z$  (gpc). The slope is 1.02 and the correlation is better  $r = 0.989$  when  $\log \bar{M}_w$  (LS) versus  $\log \langle S^2 \rangle_z$  is plotted (Figure 9). If the light scattering data of fraction 5A-4 are excluded in Figure 9 because of the sample's broad distribution ( $\bar{M}_z/\bar{M}_w = 13.6$ ), the slope becomes 1.17, i.e.,  $\epsilon = 0.17$ . No branching is evident from the appearance of this data. However, the polydispersity effect and perhaps the fact that the molecular weight data covers only a limited range may be masking to some extent the effects of branching on the  $M - [\eta]$  and  $M - \langle S^2 \rangle_z$  relations.

A comparison of unperturbed chain dimensions calculated theoretically and determined experimentally under  $\theta$ -solvent conditions is informative. Assuming a freely rotating chain of high molecular weight unperturbed by solvent interactions, the characteristic ratio<sup>6</sup>

$$C_\infty = \langle R^2 \rangle_0 / n\ell^2 = \frac{(1 + \cos\theta')(1 + \cos\theta'')}{(1 - \cos\theta' \cos\theta'')} = 3.36, \quad (9)$$

where  $\langle R^2 \rangle_0$  is the unperturbed mean-square end-to-end distance,  $n$  is the number of P-N bonds of length  $\ell = 1.6\text{\AA}$  in the chain backbone, and  $\theta'$  and  $\theta''$  are the supplements of bond angles  $\angle \text{PNP} = 127^\circ$  and  $\angle \text{NPN} = 119^\circ$ . Since

$$\langle S^2 \rangle_{z,0} = \langle R^2 \rangle_{z,0} / 6 \quad (10)$$

for randomly coiled polymers and  $n_z = M_z/150 - 1$ , the characteristic ratio may be determined from light-scattering data  $\langle R^2 \rangle_{z,0} / n_z \ell^2$ . As shown in Table 4, the experimental values of the characteristic ratio are larger than the theoretical

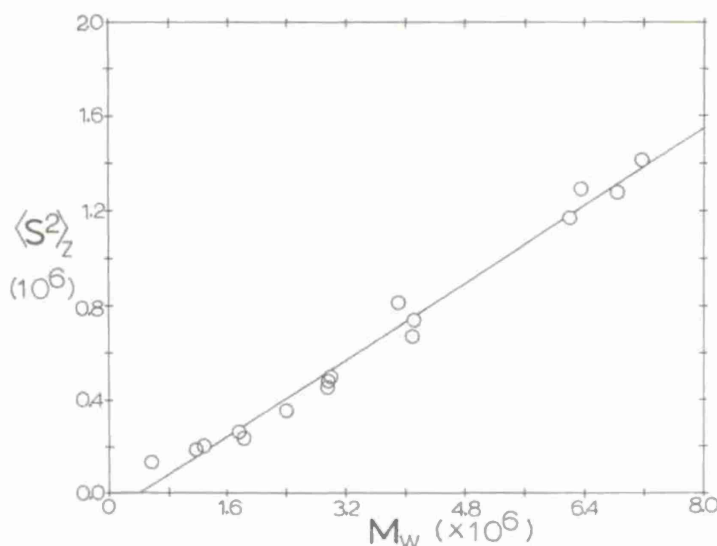


Figure 9. Plot of  $\langle S^2 \rangle_z$  versus  $\bar{M}_w$  (LS) for the polyphosphazene in  $\text{CHCl}_3$  solution.



value for the freely rotating chain and are in the range 4 to 10 usually observed for polymers. The unperturbed root-mean-square radii of gyration  $\langle S^2 \rangle_{z,0}$  for polyphosphazenes with freely rotating bonds are calculated for several samples (Table 4) using Eqs. 9 and 10. The experimental dimensions are larger than those calculated. These results suggest that the polymers are not highly branched since even a moderate amount of long-chain branching or cross-linking greatly reduces the dimensions of a branched polymer  $\langle S^2 \rangle_{z,b}$  when compared to the dimensions of the same linear polymer  $\langle S^2 \rangle_{z,l}$  of identical molecular weight. According to Zimm and Stockmayer<sup>11</sup>

$$\langle S^2 \rangle_{z,b} = \langle g \rangle_z \langle S^2 \rangle_{z,l} \quad (11)$$

where  $\langle g \rangle_z = (1+B_w/3)^{-1}$  and  $B_w$  is the weight-average number of branches per long-chain branched polymer, or where  $g_z = (1+X_w)^{-1}$  and  $X_w$  is the weight-average number of cross-links. Assuming that  $\langle S^2 \rangle_{z,l} \approx \langle S^2 \rangle_{z,\theta}$ , the extent of branching or cross-linking necessary to reduce  $\langle S^2 \rangle_{z,\theta}$  below its respective freely rotating model value may be estimated by supposing

$$\langle g \rangle_z = \langle S^2 \rangle_{z,0} / \langle S^2 \rangle_{z,\theta} \quad (12)$$

The number of chain repeat units per branching unit  $N_B = \bar{M}_w / (300 B_w)$  or per cross-linking unit  $N_X = \bar{M}_w / (300 X_w)$  are shown in Table 4. By this reasoning, about one branch or cross-link per  $10^4$  repeat units should have a detectable effect on chain dimensions and may be considered as an upper limit for branching in this polymer.

## Structure-Properties Relations

In the previous section the macromolecular structure of sample 488-10 was described in detail. It was concluded that the polymer has very little, if any, long-chain branching. Results derived from the characterization of 488-10, including the gpc calibration curve and intrinsic viscosity-molecular weight relationship, may now be utilized in analyzing the macromolecular structures of other poly[bis(m-chlorophenoxy)phosphazene] samples (Table 5). The gel permeation

Table 5. DILUTE SOLUTION PROPERTIES

| Sample                       | LIGHT SCATTERING   |                        |                                                   |                                   | GPC                   |                        |                       |                       |                       | Comments   |
|------------------------------|--------------------|------------------------|---------------------------------------------------|-----------------------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|------------|
|                              | $[\eta]$<br>(dl/g) | $\bar{M}_w$            | $\langle S^2 \rangle_z^{1/2}$<br>(Å) <sup>2</sup> | $B_2$<br>(ml-mol/g <sup>2</sup> ) | $\bar{M}_n$           | $\bar{M}_w$            | $\bar{M}_z$           | $\bar{M}_w/\bar{M}_n$ | $\bar{M}_z/\bar{M}_w$ |            |
| 488-10                       | 1.95               | 3.89(10 <sup>6</sup> ) | 906                                               | 5.44(10 <sup>-5</sup> )           | 3.2(10 <sup>5</sup> ) | 3.56(10 <sup>6</sup> ) | 2.0(10 <sup>7</sup> ) | 11.3                  | 5.7                   | Linear     |
| 1017-78                      | 1.66               | 6.13(10 <sup>6</sup> ) | 1280                                              | 5.3(10 <sup>-5</sup> )            | 2.5(10 <sup>5</sup> ) | 2.2(10 <sup>6</sup> )  | 1.6(10 <sup>7</sup> ) | 8.8                   | 7.3                   | Branched   |
| 1019-59*                     | 2.10               | 2.64(10 <sup>6</sup> ) | 733                                               | -0.9(10 <sup>-5</sup> )           | 5.1(10 <sup>5</sup> ) | 2.6(10 <sup>6</sup> )  | 8.4(10 <sup>6</sup> ) | 5.1                   | 3.2                   | Associates |
| 1011-187                     | 1.27               | 2.34(10 <sup>6</sup> ) | 740                                               | 1.33(10 <sup>-4</sup> )           | 3.9(10 <sup>5</sup> ) | 2.24(10 <sup>6</sup> ) | 1.5(10 <sup>7</sup> ) | 5.7                   | 6.9                   | Linear     |
| 1011-187<br>(one year later) | 0.99               | -                      | -                                                 | -                                 | 1.0(10 <sup>5</sup> ) | 5.45(10 <sup>5</sup> ) | 2.2(10 <sup>6</sup> ) | 5.3                   | 4.0                   |            |
| 1011-190                     | 1.21               | 1.80(10 <sup>6</sup> ) | 648                                               | 8.7(10 <sup>-5</sup> )            | 2.4(10 <sup>5</sup> ) | 2.02(10 <sup>6</sup> ) | 1.2(10 <sup>7</sup> ) | 8.3                   | 6.1                   | Linear     |
| 1011-190<br>(one year later) | 0.73               | -                      | -                                                 | -                                 | 9.8(10 <sup>4</sup> ) | 5.28(10 <sup>5</sup> ) | 1.8(10 <sup>6</sup> ) | 5.4                   | 3.4                   |            |

\*Light scattering for 1019-59 was run in THF at 25 C because the CHCl<sub>3</sub> solution could not be filtered through a 0.45-μ Millipore filter

11. ZIMM, B. H., and STOCKMAYER, W. H. *The Dimensions of Chain Molecules Containing Branches and Rings*. J. Chem. Phys., v. 17, 1949, p. 1301-1314.

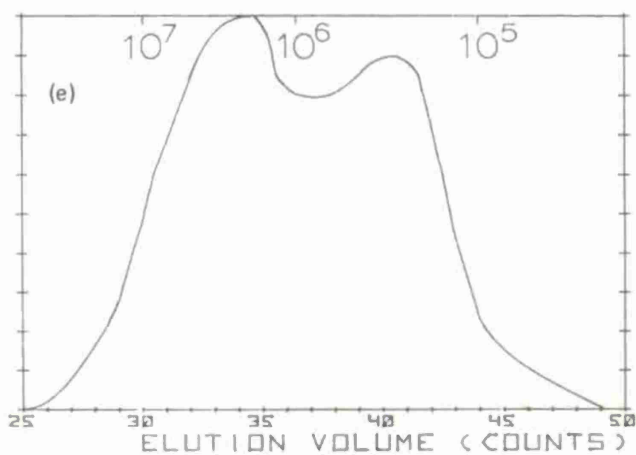
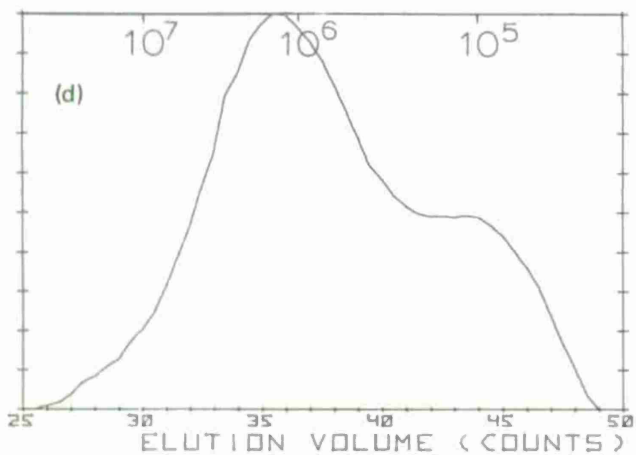
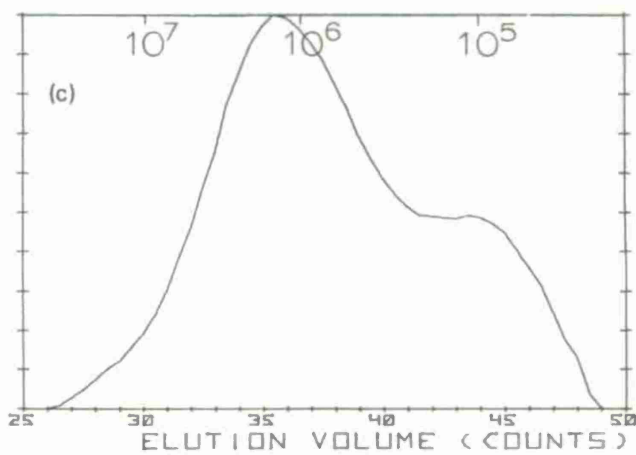
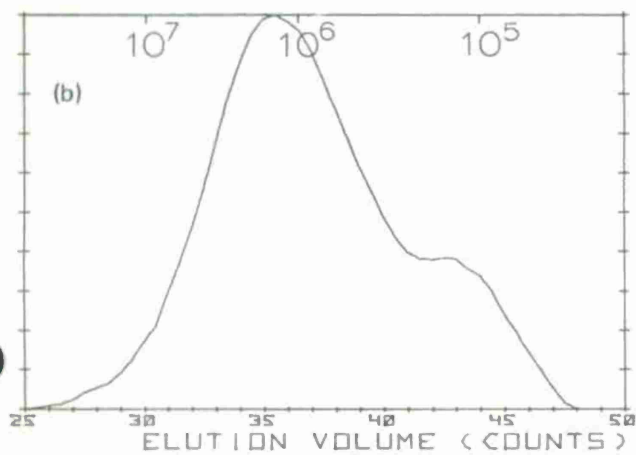
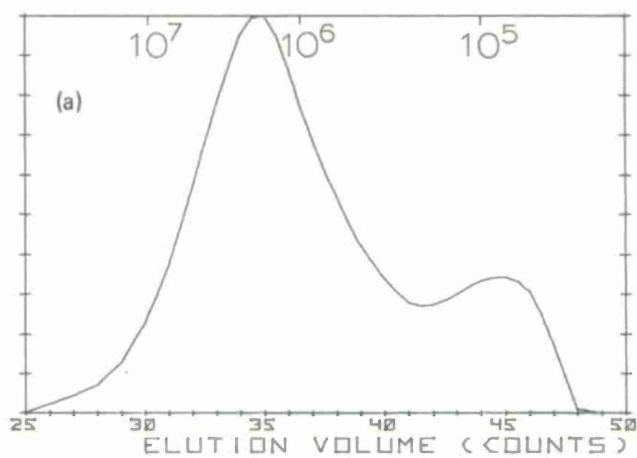


Figure 10. GPC chromatograms of samples (a) 488-10, (b) 1019-78, (c) 1019-59, (d) 1011-187, and (e) 1011-190.

chromatograms for these samples are depicted in Figure 10. The chief characteristics that the samples have in common are high molecular weights and broad, bimodal molecular weight distributions.

As mentioned previously (see Table 1), samples 1011-187 and 1011-190 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 (percent carbon) suggest that the substitution of sample 1011-187 was only 72% completed and 1011-190 was only 68% completed. 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 indicate that significant polymer chain degradation occurred on storage (Table 5); nevertheless, both samples still have relatively high molecular weights ( $\bar{M}_w > 5 \times 10^5$ ).

Samples 488-10, 1019-78, and 1019-59 are white, fibrous polymers that form tough, flexible films when cast from THF or chloroform solution. The polymers are essentially completely substituted according to elemental analysis and no deterioration or change in molecular weight occurred after more than one year in storage. The solubility characteristics of 1019-59 are different from the other polymers. Anomalous viscosity constants and abnormal light-scattering values suggest that 1019-59 associates in chloroform solution. The gpc results (Figure 10c) are also probably influenced by the anomalous solution behavior. A further abnormality in solution behavior may be indicated in THF solution where a slightly negative second virial coefficient was determined. The reason for 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 backbone, resulting from incomplete substitution.<sup>12</sup> However, if such is the case, why then do samples 1011-187 and 1011-190 display normal solution behavior?

One major difference in the macromolecular structures of the five polymers is that 1019-78 appears to be branched. Branching is apparent in that the  $[\eta]$  value of 1019-78 is smaller than 488-10's value even though 1019-78 has a significantly larger  $\bar{M}_w$  (LS) value, and that the gpc value  $\bar{M}_w$  is considerably smaller than the respective light scattering value for 1019-78.

The extent of branching may be estimated from dilute solution data by assuming a branching model. As discussed in the previous section, a likely model for polyphosphazene branching is a polymer with 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  $[\eta]_l$  is related to the intrinsic viscosity of a branched polymer  $[\eta]_{br}$  (assuming equivalent molecular weights) by a branching function  $g$  such that

$$g^{\frac{1}{2}} = [\eta]_{br} / [\eta]_l. \quad (13)$$

12. GIGIO, E., POMPA, F., and RIPAMONTI, A. *Molecular Conformation of Linear Phosphonitrile Chloride*. J. Polymer Sci., v. 59, 1962, p. 293-300.



Branched and linear polymers of the same type and molecular weight may be related by combining the Mark-Houwink equation for the linear polymer (Eq. 6) with Eq. 13, which gives

$$[\eta]_{br} = KM_{\lambda}^a g^{\frac{1}{2}}, \quad (14)$$

where for random, trifunctional, long-chain branching<sup>13</sup>

$$g = \langle g_3 \rangle_w = \frac{6}{\lambda M} \left[ \frac{1}{2} \frac{(2 + \lambda M)^{\frac{1}{2}}}{(\lambda M)^{\frac{1}{2}}} \ln \frac{(2 + \lambda M)^{\frac{1}{2}} + (\lambda M)^{\frac{1}{2}}}{(2 + \lambda M)^{\frac{1}{2}} - (\lambda M)^{\frac{1}{2}}} - 1 \right], \quad (15)$$

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 there is an equivalence between the hydrodynamic volumes of linear and branched polymers

$$M_{\lambda} [\eta]_{\lambda} = M_{br} [\eta]_{br}, \quad (16)$$

the gpc calibration curve may be revised for analysis of the branched polymer by plotting  $\log(M/g^{\frac{1}{2}})$  versus  $V_e$ . Such a calibration curve is then applied in analyzing the gpc chromatogram of the branched polymer (Figure 10b).

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 to the respective light-scattering value. For sample 1019-78 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  $\bar{M}_w/\bar{M}_n = 24.5$ .

Poly[bis(*m*-chlorophenoxy)phosphazene] is a semicrystalline polymer that exhibits two first-order thermal transitions separated by about 300 C. A well-defined lower first-order transition  $T(1)$  has been reported at 66 C.<sup>3,4</sup> Optical microscopy reveals that crystallinity is retained above  $T(1)$  and persists up to a higher temperature transition  $T_m \approx 370$  C which seems to be the true melting temperature and is near the polymer's decomposition temperature. X-ray analysis indicates that  $T(1)$  is a major crystal disorder process, and DSC studies show that  $T(1)$  is sensitive to side group structure and that changes in  $T(1)$  are usually parallel to those in glass transition  $T_g$ .<sup>3</sup> At temperatures slightly above  $T(1)$  the polymer is sufficiently soft to be compression molded into coherent films. This suggests that  $T(1)$  probably represents an upper temperature limit for engineering applications of the polymer in an unmodified form.

DSC experiments were run on solution cast films of the semicrystalline samples 488-10, 1019-78, and 1019-59 to determine what effect, if any, polymer structure might have on  $T(1)$ . Significant differences in  $T(1)$  were observed (Table 6).  $T(1)$  is highest for the branched polymer which also has the highest molecular weight; but the molecular weight effect is not expected to be important since all the samples have very high molecular weights. In general, branching introduces

13. ZIMM, B. H., and KILB, R. W. *Dynamics of Branched Polymer Molecules in Dilute Solution*. J. Polymer Sci., v. 37, 1959, p. 19-42.

Table 6. T(1) THERMAL TRANSITION (DEG C)

| Sample  | Solution-Cast Film | Heat-Treated Film<br>(68 hr 165 C in air) |       |
|---------|--------------------|-------------------------------------------|-------|
|         | T(1)               | T(1)                                      | T(1') |
| 488-10  | 67                 | 67                                        | 67    |
| 1019-78 | 81                 | 91                                        | 101   |
| 1019-59 | 76                 | 81                                        | 87    |

disorder into crystal lattices and should thereby lower, rather than raise, the crystalline transition temperature. The T(1) value for 1019-59 may somehow be related to the effect causing the polymer's anomalous behavior in chloroform solution. However, at present no satisfactory explanation is available to explain the observed variation in T(1). Perhaps, trace amounts of cyclic trimer or other impurities are present in the samples and give rise to the variation. Also, since incomplete substitution results in rubbery, noncrystalline polymers (e.g., 1011-187 and 1011-190), a few unsubstituted sites (<1%) in the polymer chains may be sufficient to introduce imperfections in crystal lattices and thereby lower T(1).

Thermal aging studies (to be discussed in the next section) show that the polymer films become brittle after exposure at 165 C in air. The studies also indicate that thermally "weak links," which may be the consequence of incomplete substitution and branching, are present in the polymer chain backbones and that exposing the polymer films for more than 10 hours at 165 C in air effectively destroys all such weak links. DSC scans on an exposed (68 hours) film of 1019-78 are illustrated in Figure 11. On the first scan it is noted that T(1) appears at 92 C. After annealing the sample by slowly cooling it through the transition region and then rerunning the DSC, a second transition peak appears at 101 C. The higher temperature peak disappears when the polymer is rapidly quenched and reappears if the polymer is annealed. If the film is aged for 222 hours, the two endotherms occur at the same temperatures but the higher temperature transition seems to predominate. If the film aged for 222 hours is dissolved in THF and recast to form a new film, the film is no longer brittle and the two endotherms reappear at the same temperatures upon annealing. A similar behavior is observed for sample 1019-59, but the two endotherms occur at lower temperatures. No significant shift in T(1) is observed for 488-10 with thermal aging.

The thermal aging experiments suggest a means by which the upper temperature limit for engineering applications of the polyphosphazenes might be extended. Annealing stabilizes the higher T(1) transition temperature crystalline form in the heat-treated samples. Increased exposure time reduces the polymer's molecular weight (see next section) which in part may explain the enhanced formation of the higher temperature T(1) endotherm observed for sample 1019-78 after 222 hours exposure. Variations in the T(1) transition are still observed after heat aging the three samples. In the two samples the heat treatment raised T(1) and at the same time created twin T(1)-type endotherms separated by almost 10 C. It is not known whether the twin T(1) transitions result from differences in molecular structure (cyclics, oligomers?) or from distinct crystalline modifications of the polymer.

Both TGA and DSC experiments were run on the polymer films in air and no significant differences in thermal stability were observed. No major thermal events (e.g., scission endotherm or oxidation exotherm) were evident from the DSC



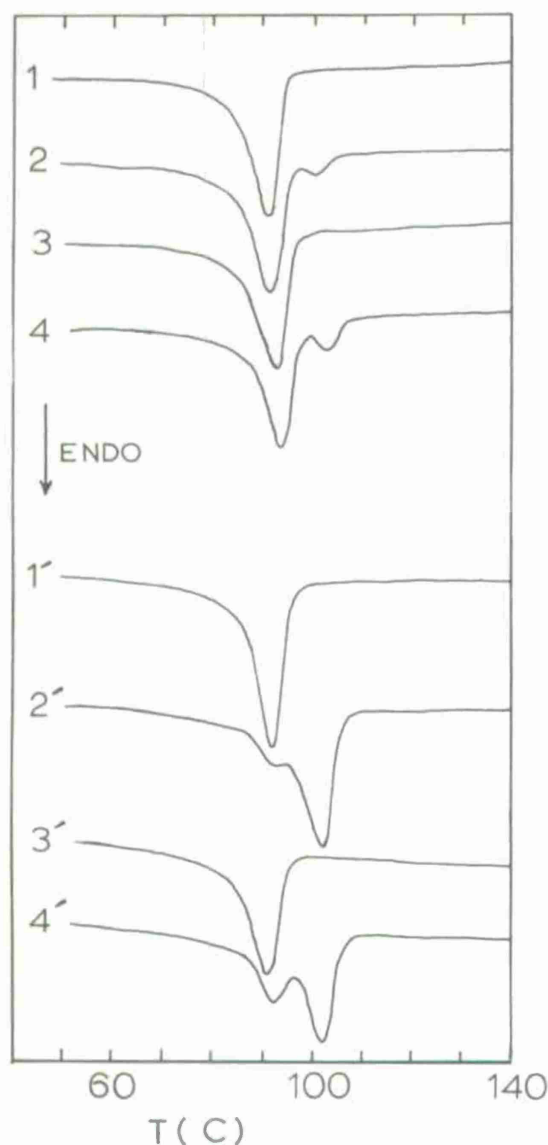


Figure 11. DSC scans of sample 1019-78 after heat aging 68 hours at 165 C (1) first scan, (2) after annealing, (3) after rapid quench, (4) after annealing again; and after heat aging 222 hours at 165 C (1') first scan, (2') after annealing (3') after rapid quench, (4') after annealing again.

analysis up to the temperature region where weight loss starts to occur. The polyphosphazene appears to be more thermally stable at elevated temperatures in air than polystyrene (Figure 12).

### Polymer Chain Degradation

The engineering properties of a polymer material depend on the polymer's ability to sustain its high molecular weight over long periods of exposure. The processability of a polymer depends on its stability at elevated temperatures and under conditions of shear. Preliminary studies show that poly(aryloxy)phosphazenes may require temperatures above 150 C for compression molding. Although poly-[bis(*m*-chlorophenoxy)phosphazene] has a thermal decomposition temperature  $T_d \approx 350$  C in air (Figure 12), chain scission and weight loss under isothermal conditions may occur at considerably lower temperatures. To simulate extreme environments such as the polymer is liable to encounter during processing or application, the

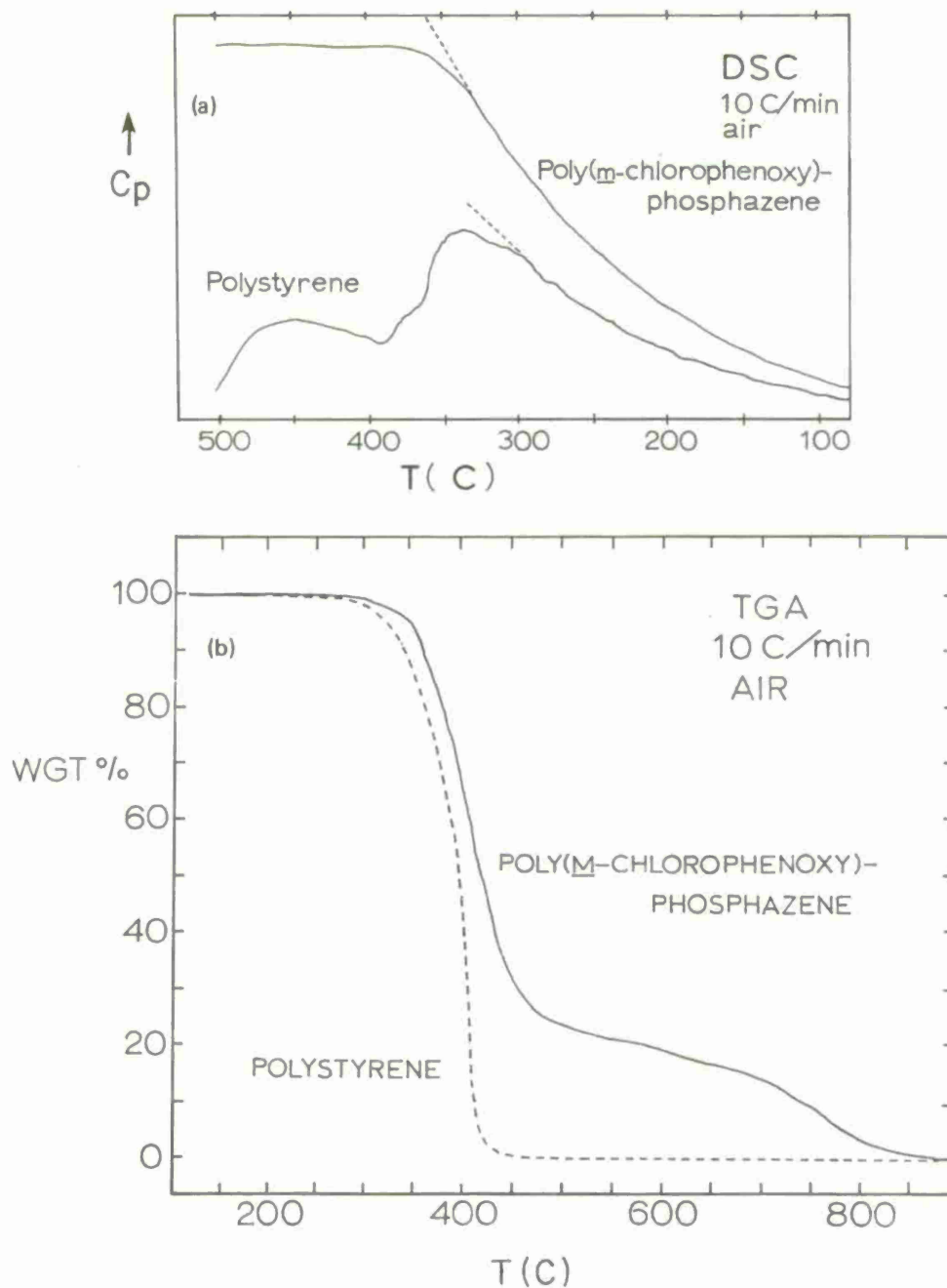


Figure 12. (a) DSC and (b) TGA of poly[bis(*m*-chlorophenoxy)phosphazene] and polystyrene degradation in air at 10 °C/min.

degradation of poly[bis(*m*-chlorophenoxy)phosphazene] was investigated by aging solution cast films of the polymer isothermally at 165 °C in static air. The marked reduction in intrinsic viscosity after heat aging (Figure 13) indicates that significant chain degradation occurs at 165 °C.

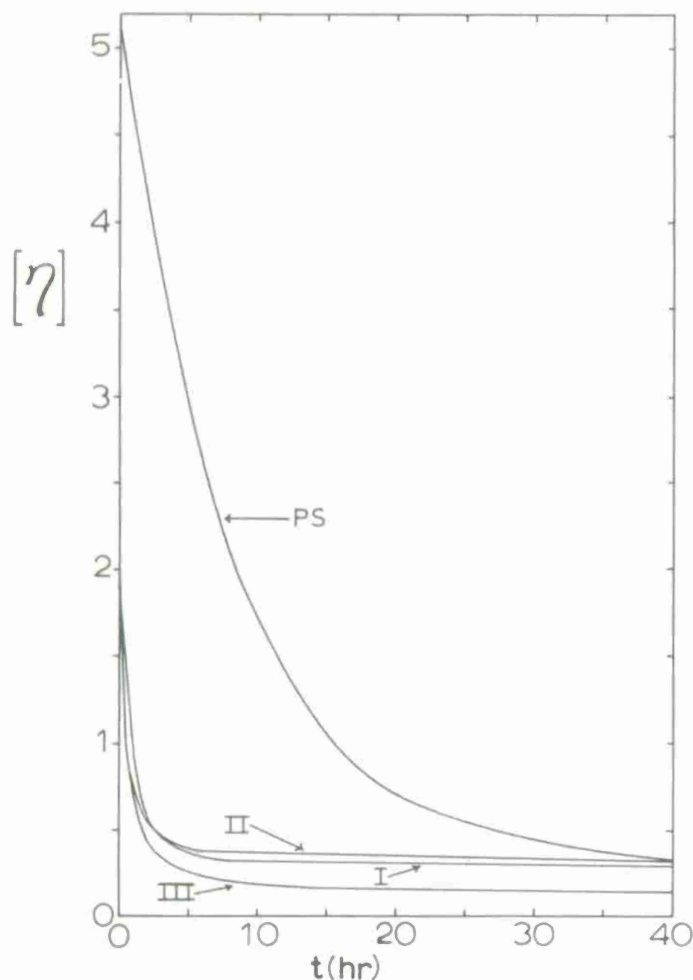


Figure 13. Plot of  $[\eta]$  versus heat-aging period in air at 165 C for polystyrene (PS), 488-10 (I), 1019-78 (II), and 1019-59 (III).

There are two fundamental mechanisms by which polymers generally degrade—random degradation and chain depolymerization.<sup>14</sup> In random degradation, chain rupture or scission occur 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 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 unzippering type mechanism does not occur since no low molecular weight residue was produced. That is, no significant weight loss was observed after exposing films for one month at 165 C and no cyclic or phenol formation was observed. Figure 14 illustrates changes in the molecular weight distribution of sample 488-10 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 (Figure 15). For a random degradation mechanism the heterogeneity index  $\bar{M}_w/\bar{M}_n$  is expected to approach a value of 2 with

14. BILLMEYER, F. W. *Textbook of Polymer Science*. John Wiley & Sons, New York, 2nd ed., 1971, p. 369.

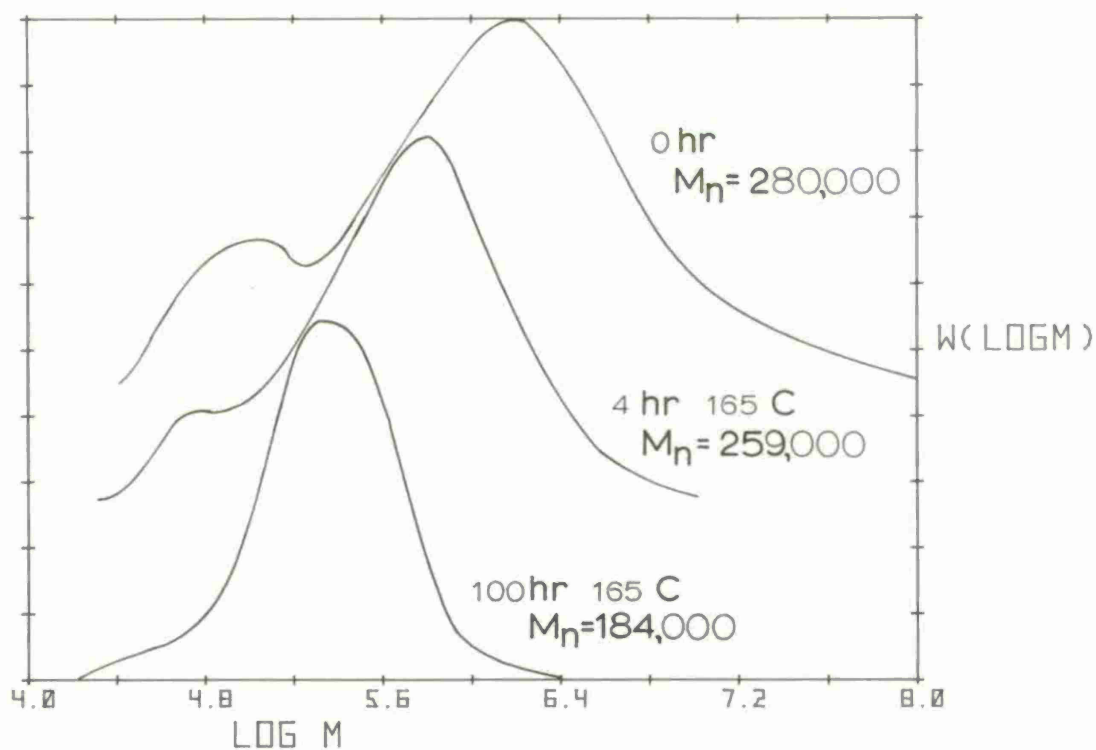


Figure 14. Change in the molecular weight distribution of sample 488-10 upon heat aging at 165 C in air.

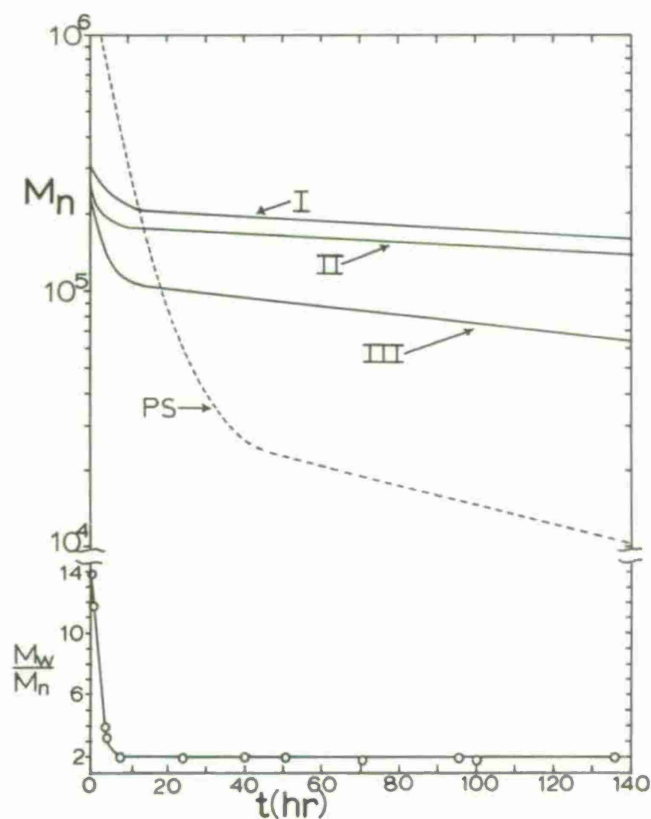


Figure 15. Plot of  $\bar{M}_n$  versus heat-aging period  $t$  in air at 165 C for polystyrene (PS), 488-10 (I), 1019-78 (II), and 1019-59 (III). Plot of  $\bar{M}_w/\bar{M}_n$  versus  $t$  for 488-10.



increasing exposure time. As shown at the bottom of Figure 16, sample 488-10 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 cross-link or gel formation.

Since polystyrene is known<sup>15</sup> to undergo random degradation at 165 C, a standard, narrow distribution polystyrene sample ( $M = 2 \times 10^6$ ) was selected for comparison of degradation behavior with samples 488-10 (I), 1019-78 (II), and 1019-59 (III). The greatest change in molecular weight for the polyphosphazenes occurs within the first ten hours of exposure. The ratio  $\bar{M}_w/\bar{M}_n$  is sharply reduced within the first four hours and  $\bar{M}_w/\bar{M}_n = 2$  after ten hours exposure for all three polyphosphazenes. Since the molecular weight distribution of 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  $X_n = \bar{M}_n/\bar{M}_0$  ( $\bar{M}_0$  is the repeat unit molecular weight) provides some indication of a polymer's relative stabilities. Comparing the original number of chain repeat units  $X_{n,0}$  with the value after 240 hours exposure  $X_{n,240}$  (Table 7), the extent of degradation is considerably greater for polystyrene.

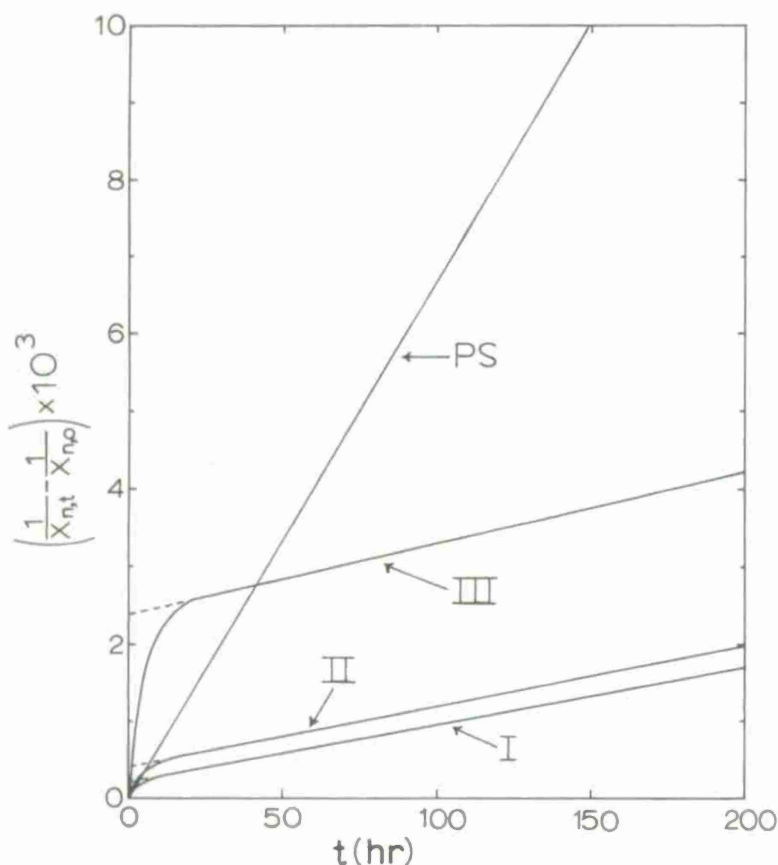


Figure 16. Plot of  $(1/X_{n,t} - 1/X_{n,0})$  versus heat-aging period  $t$  for polystyrene (PS), 488-10 (I), 1019-78 (II), and 1019-59 (III).

15. CAMERON, G. C., and MacCALLUM, J. R. *Thermal Degradation of Polystyrene*. Reviews in Macromolecular Chemistry, G. B. Butler, K. F. O'Driscoll, and M. Dekker, ed., New York, v. 2, 1967, p. 350.

Table 7. POLYMER DEGRADATION

| Sample  | $X_{n,0}$ | $X_{n,240}$ | $k$<br>( $\text{hr}^{-1}$ ) | $b$            | $N_{1000}$ |
|---------|-----------|-------------|-----------------------------|----------------|------------|
| 488-10  | 1070      | 315         | $7.5(10^{-6})$              | $2.0(10^{-4})$ | 0.4        |
| 1019-78 | 833       | 291         | $8.0(10^{-6})$              | $4.0(10^{-4})$ | 0.8        |
| 1019-59 | 1700      | 189         | $9.0(10^{-6})$              | $2.4(10^{-3})$ | 4.8        |
| PS      | 19,000    | 56          | $6.7(10^{-5})$              | 0              | 0          |

The polyphosphazenes are originally in the form of white, translucent films. After heat aging, the films retain their shapes but become brittle and gradually change color from white to tan (2 to 4 hours), to brown (40 hours), and finally to dark brown (100 hours). After ten days exposure at 165 C, the polyphosphazene films still retain their original shapes and have high molecular weights; however, the polystyrene is 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

$$1/X_{n,t} - 1/X_{n,0} = kt, \quad (17)$$

where  $X_{n,t}$  is the number-average number of chain repeat units at time  $t$  and  $X_{n,0}$  at  $t = 0$ , and  $k$  is the first-order rate constant for bond scission. As shown in Figure 16, 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  $t < 10$  hours and the linear portions do not extrapolate to zero. Similar plots have been obtained for other polymers. 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. 17 becomes

$$1/X_{n,t} - 1/X_{n,0} = b + kt, \quad (18)$$

where  $b$  is the ordinate intercept in Figure 17 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  $N_{1000} = 2(10^3)b$ . 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 1019-59 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 1019-59 (III) curve 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, polydichlorophosphazene, 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 oxophosphazane bonds may form in the polymer backbone. It is possible that the anomalous solubility behavior and large  $N_{1000}$  value of 1019-59 may be related to a high phosphazane concentration in the polymer. It is interesting that after a short period of exposure ( $t < 2$  hours), during which most of the weak links are believed to rupture, sample 1019-59 no longer behaves anomalously in solution. Another source of weak links appears to be branch points in the polymer chains. Before heat aging, sample 1019-78 is branched but after one hour 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 polymer were heat aged for 24 hours, dissolved in THF, recast as films and heat aged an additional 24 hours. Duplicate films which were not redissolved after the first 24-hour 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 re-exposure compared to the films which are not recast.

However, no important differences in the molecular weights of the polymers were 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 tie chains.

Preliminary tests suggest that poly[bis(*m*-chlorophenoxy)phosphazene] is especially susceptible to mechanical degradation. Sample 1019-78 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  $M_w = 4.0 \times 10^5$ . 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 hours 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 macromolecular structures and structure-property relationships of five poly[bis(*m*-chlorophenoxy)phosphazene] samples were analyzed. The polymers were found to have high molecular weights and broad, bimodal molecular weight distributions. The GPC fractionation failed to yield fractions with narrow molecular



weight distributions because of adsorption on the porous glass bead substrate. Fractionation with THF rather than chloroform as the eluent is advised. The unusually high molecular weight and broad distribution of the polymer also made it difficult to obtain narrow fractions. To elucidate polymer chain structure (branching, flexibility, conformation, etc.) and the solution thermodynamics of poly[bis(*m*-chlorophenoxy)phosphazene], fractions of linear polymer with narrow molecular weight distributions ( $\bar{M}_w/\bar{M}_n < 1.2$ ) are required. This report suggests that such fractions might be obtained by fractionating polymers which are first thermally aged or milled to rupture branch points to establish a most probable distribution.

Detailed investigations of both the polymerization and substitution reactions are required. The procedure used to synthesize the polymers for this study did not produce consistent products. Differences in branching, solubility behavior, stability, and thermal transition temperatures  $T(1)$  were observed. Two of the polymer samples were incompletely substituted and degraded slowly on storage at room temperature. Substitution affects polymer crystallinity to the extent that the polymer becomes a rubber if insufficient substitution is achieved. It is suggested that the transition temperature  $T(1)$  is sensitive to partial substitution and that  $T(1)$  increases with the extent of substitution. Thermal aging at 165 C and annealing also tend to raise the  $T(1)$  temperature.

The high molecular weights and bimodal distribution may have a significant effect on the physical properties of these polymers. The cause of the bimodal distribution is unknown. Although an ionic mechanism has been proposed,<sup>16</sup> the exact operation of the mechanism in the polymerization reaction is uncertain. Heterogeneities in the bulk polymerization, impurities in the cyclic trimer,<sup>17</sup> or surface catalyst effects<sup>18</sup> during polymerization may be creating the bimodal distribution. Also, variations in reaction conditions for the nucleophilic substitution of polydichlorophosphazene with *m*-chlorophenoxide are known to affect the molecular weight distribution.<sup>19</sup> Perhaps a better understanding of the polymerization and substitution reactions would provide clues to controlling the macromolecular structures of polyphosphazenes. Another approach to control the structure and thereby ensure a more uniform product is to either heat age or mechanically degrade the polymer.

The polyphosphazene appears more thermally stable at elevated temperatures in air than polystyrene. No major thermal events, such as a scission endotherm or oxidation exotherm, are evident up to the temperature ( $T_d = 350$  C) at which weight loss begins. However, films of the polymer become brittle and gradually turn brown at lower temperatures. At 165 C in air the polymer degrades by a random degradation mechanism. The polyphosphazene chains were found to contain

16. ALLCOCK, H. R., and BEST, R. J. *Phosponitrilic Compounds. I. The Mechanism of Phosponitrilic Chloride Polymerization. Capacitance, Conductance, and Electro-Spin Resonance Studies.* Can. J. Chem., v. 42(2), 1964, p. 447-455.
17. ALLCOCK, H. R., GARDNER, J. E., and SMELTZ, K. M. *Polymerization of Hexachlorocyclotriphosphazene. The Role of Phosphorus Pentachloride, Water, and Hydrogen Chloride.* Macromolecules, v. 8, 1975, p. 36-42.
18. EMSLEY, J., and UDY, P. B. *Polymerization of Hexachlorotriphosphonitrile, (NPCl<sub>2</sub>)<sub>3</sub>.* Polymer, v. 13, December 1972, p. 593-594.
19. LaLIBERTE, B. R., and HAGNAUER, G. L. *Nucleophilic Substitution of Cyclic and Polymeric Dichlorophosphazenes with M-Chlorophenoxide.* Army Materials and Mechanics Research Center, AMMRC TR 76-17, June 1976.



weak links which rupture nearly 400 times faster than regular P-N bonds at 165 C. Both chain branching units and phosphazane units introduced by hydrolysis are believed to represent weak links. Another approach to control macromolecular structure and obtain lower molecular weight polymers might be to introduce a prescribed number of weak links in the polymer by selectively hydrolyzing polydichlorophosphazene before or during the substitution reaction. The weak links in the substituted polymer may then be ruptured to produce a more uniform, lower molecular weight polymer.



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Robert E. Singler, Susan J. Kalian, and  
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Technical Report AMMRC TR 76-25, August 1976, 30 pp -  
illus-tables, D/A Project 1T161102AH42,  
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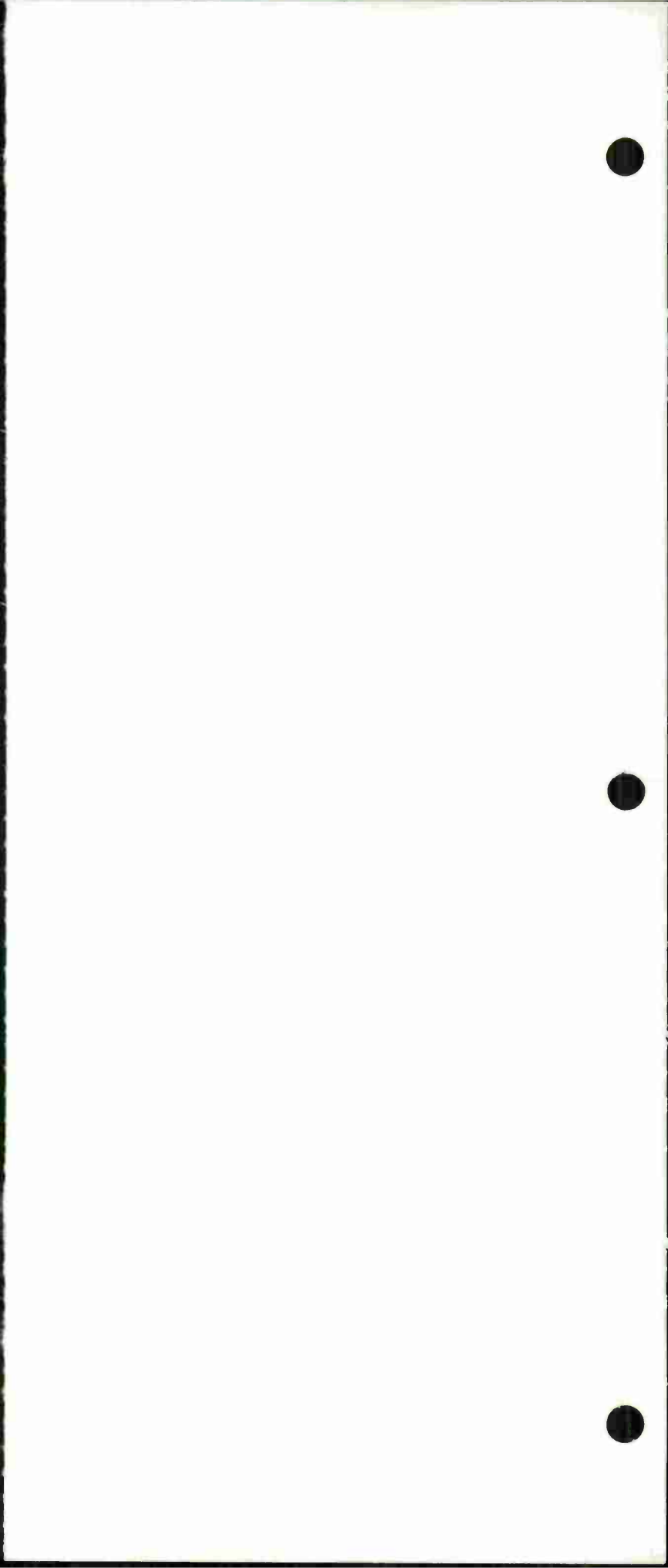
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