Thermal Stability of Phosphonitrilic Fluoroelastomers

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Synopsis

The thermal stability of the polymer prepared by substituting poly(dichlorophosphazene) with an excess of a 64/36 mole-% mixture of the sodium salts of 2,2,2-trifluoroethanol/2,2,3,3,4,4,5,5-octafluoropentanol were studied by thermogravimetric and gel permeation chromatography techniques. The primary mode of degradation of this polymer was shown to be via random scission. The overall degradation reaction corresponds to quasi-zero-order kinetics.

INTRODUCTION

A number of such elements as sulfur, phosphorus, silicon, etc., have been investigated as potential inorganic polymer backbones with thermal stabilities in excess of 250°C. However, as Economy and Mason[1] have pointed out, the utility of these elements is limited because of their inability to form chains longer than ten atoms. Furthermore, the bond strengths of these elements indicate that polymers from them may be less stable than carbon chains.

Heteroatoms appear to show significantly higher bond strengths and thus offer the possibility of obtaining polymers with improved thermal stabilities.[2,3] These heteroatoms also show relatively high ionic character which can lead to dipole interactions with neighboring chains thus resulting in brittle, glass-like behavior. These chain interactions may be minimized by encasing the metal ion in an organic shell. In the case of silicones, the stearic effects of alkyl groups diminish these chain interactions. If one considers the bond strengths of these inorganic elements alone, one may overestimate the stabilities of the resulting polymers since these inorganic bonds have an availability of bonding orbitals which may provide low-energy pathways to degradation reactions.[1]

The stability of polymeric materials has been judged on the ability of the polymer to retain its mechanical properties over an extended service time. It is also possible to establish a stability criterion of some value by following the weight loss of a polymer as a function of temperature or time. Experimentally, such weight loss data can be obtained from thermogravimetric analysis (TGA). However, because significant property changes may occur without a noticeable weight loss, great caution should be exercized in drawing conclusions from these data.[4] It is possible that the rate of weight loss may represent the rate of sublimation or distillation of degradation products rather than the rate of degradation of the polymer. The latter problem may be overcome if the rate of evaporation of the fragments is extremely fast as compared with the rate of formation of fragments.[5]

Information obtained from thermal weight loss data are quite valuable from the screening point of view. However, when combined with other information, such as molecular weight changes, this method of determining thermal stability may be extremely valuable and can serve as a basis for the calculation of the activation energies of the overall degradation reaction.

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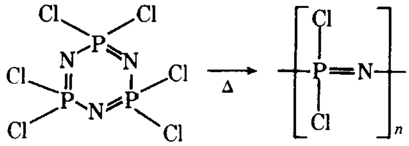
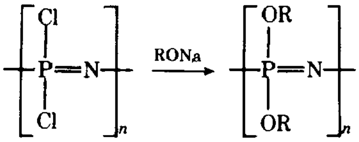
The polymer in this investigation is the outgrowth of the work initially carried out by Stokes and Allcock. It was first observed by Stokes[6] that trimeric phosphonitrilic chloride $(PNCl_3)_3$ could be polymerized at 200–300°C to form the elastomeric poly(dichlorophosphazene):



However, this inorganic rubber was usually obtained as a crosslinked material which was hydrolytically unstable; moist air causes the hydrolysis of the P—Cl bonds with subsequent degradation of the polymer to phosphoric acid and ammonia. Allcock[7,8] showed that an essentially linear polymer could be obtained if the polymerization is not carried to high conversion. This poly(dichlorophosphazene) may then be substituted with alcohols, phenols, or amines to obtain hydrolytically stable polymers:



The aim of the present investigation was to study the thermal stability of the polymer prepared from the reaction of poly(dichlorophosphazene) with an excess of a 64/36 mole-% mixture of the sodium salts of 2,2,2-trifluoroethanol/2,2,3,3,4,4,5,5-octafluoropentanol. The preparation of this polymer has been described elsewhere[9] and will not be discussed here. The thermal stability of this polymer was followed via TGA and gel permeation chromatography (GPC) in hopes of gaining a better understanding of the degradation process and improving the stability of the poly(organophosphazene) type of polymers.

EXPERIMENTAL

The procedure used to study the thermal degradation of this poly(organophosphazene) was to follow the weight loss of the sample isothermally using TGA at several temperatures for 1-hr periods. At the end of this period, the TGA instrument was shut off and the unvolatilized portion of the sample was air cooled to room temperature. This residue was then analyzed by GPC. No insoluble material was observed in the GPC solutions and the areas of the chromatographs were uniform, thus giving us confidence that these residues were totally soluble.

Thermogravimetric Analysis

The weight loss of the sample was followed using a du Pont Model 950 TGA. Isothermal analyses were conducted with sample sizes of 8.8 to 11.7 mg both in air and nitrogen streams of 80 cc/min.

Gel Permeation Chromatography

A Waters Associates Model 100 GPC was used with four 4 ft × $^3/_8$ in. Styragel columns of nominal pore sizes of 10^4, 10^5, 10^6, and 10^7 Å to follow the molecular weight changes of the samples. A solvent flow rate of 0.7 ml/min was maintained with dimethylformamide as the solvent at 85°C. The concentrations were $^1/_8$% (w/v). A log weight-average molecular weight, $\overline{M}_w$, versus elution count calibration curve were obtained from light scattering measurements.

RESULTS AND DISCUSSION

The GPC traces of the original polymer sample and TGA residues of samples maintained for 1 hr at the indicated temperatures are shown in Figure 1. It is interesting to note that at the lower aging temperatures, the GPC peaks shift to the higher molecular weight side (lower GPC elution count) and only at the higher temperatures is the shift to the lower molecular weight side observed. It has been observed, however, that the shift to the high molecular weight side also occurs at the higher temperatures. It is only necessary to limit the pyrolysis to shorter time periods to observe this effect.

This initial increase in molecular weight may be due to the presence of residual P—Cl bonds in the polymer which may provide crosslinking sites. Allcock has detected the presence of small amounts of $ClCH_2CF_3$ in the thermolysis of poly[bis(trifluoroethoxy)phosphazene][10] and small amounts of chlorobenzene in the thermal breakdown of poly(diphenoxyphosphazene).[11] He explained the presence of the chlorocompounds as being due to residual P–Cl in the polymer which reacted with the substituant groups, thus allowing the possibility that intra- or intermolecular crosslinking did take place. If intermolecular crosslinking did take place, one can expect an increase in molecular weight as is observed in Figure 1. Figure 1 also shows the GPC trace of a sample of trimer substituted with a mixture of the sodium salts of several fluoro alcohols. The mixture of the sodium salts consisted of 80 mole-% of the sodium salt of 2,2,2-trifluoroethanol and 20 mole-% of about equal amounts of the sodium salts of 2,2,3,3-tetrafluoropropanol, 2,2,3,3,4,4,5,5-octafluoropentanol, and

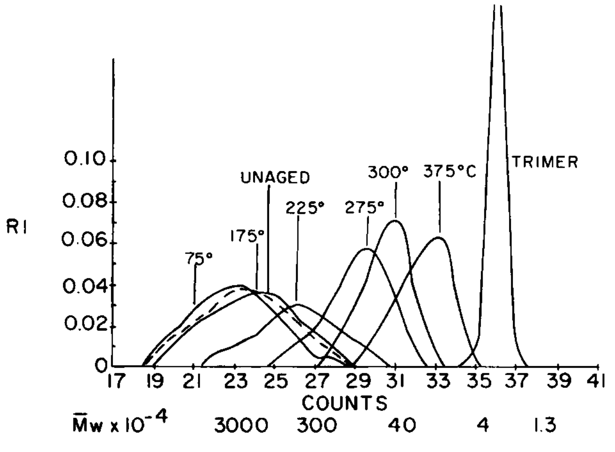


Fig. 1. Gel permeation chromatographs of original polymer, indicated by dotted lines, and of the residues of this polymer after 1 hr of aging at indicated temperatures.

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol. The substituted trimer GPC traces are given as an aid in gauging the extent of degradation of the polymer.

In order to have some assurance that the rate of volatilization of the degradation products was at least as fast as the rate of formation of the degradation products, the substituted trimer as well as a mixture of the substituted cyclics ranging in size from trimer to nanomer were run on the TGA. A comparison of the rate of volatilization of the substituted cyclics and the rate of volatilization of the degradation products of the polymer is shown in Figure 2. It is apparent from this figure that the rate of volatilization of the substituted trimer, or cyclics as high as nanomer, are much faster than the degradation rate of the polymer. After 2 min about 98% of the trimer and about 87% of the cyclics mixture volatilized; however, after the same time period only about 2% of the polymer volatilized. This gave us confidence that the technique used is actually capable of measuring the rate of polymer degradation rather than just the rate of volatilization of the degradation products.

Conley[4] divides the thermal degradation of polymers into two major categories: random chain scission and depolymerization. Random chain scission is viewed as a reaction sequence approximating the reverse of polycondensation. Chain scission occurs at random points along the chain leaving fragments of relatively high molecular weight. However, each scission produces one new polymer molecule of lower molecular weight than the original polymer chain so that a rapid molecular weight loss is observed. For all practical purposes no monomer is liberated, and the weight loss of volatile products is nearly negligible.

In the depolymerization process, monomer units are released from the chain ends. This process can be viewed as the opposite of the propagation step of addition polymerization. The depolymerization process is often encountered with polymers produced from cyclic monomers.

Which of the two processes predominates or whether the two processes occur simultaneously depends on the polymer type, the temperature, and other degradation conditions. The relative importance of the two processes can be ascertained from plots such as shown in Figure 3, where percent of original molecular weight retained after 60 min of aging at the several temperatures is plotted

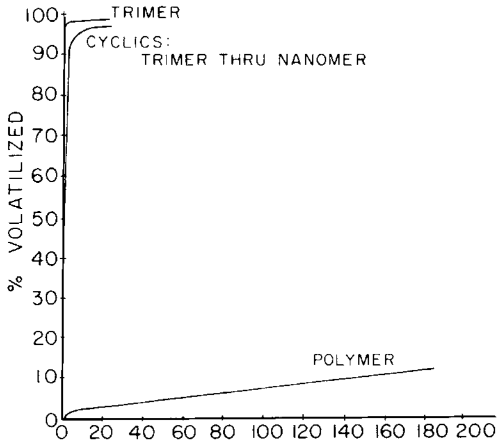


Fig. 2. Rates of volatilization of substituted trimer, other higher cyclics, and of the polymer degradation products.

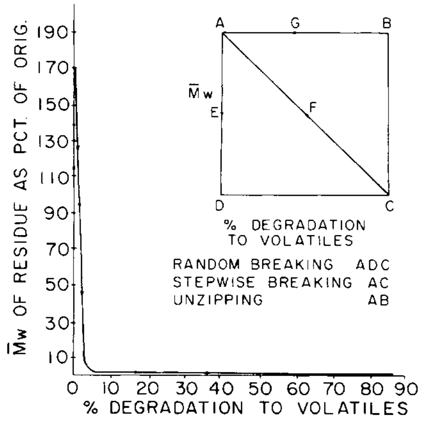


Fig. 3. Mechanism of thermal degradation.

versus percent degradation of polymer to low molecular weight volatile products. The inset in this figure represents graphically the type of degradation reactions discussed. The process of depolymerization is represented by line AB. Because relatively few chains are involved in this reaction at any given instant, the average molecular weight of the sample tends to remain essentially constant. Random scission is represented by line AD, where the molecular weight of the polymer drops rapidly without evolution of volatile products until a very low molecular weight is reached. Line AC represents the case where rupture of bonds near chain ends occurs or where random scission and depolymerization are simultaneously taking place. In the latter case, both a drop in molecular weight and a loss of volatile products occur to an appreciable extent.

The behavior of the polyphosphazene under investigation is shown by the main curve of Figure 3. It is recalled, from the GPC traces in Figure 1, that at the mild aging conditions there is an initial increase in molecular weight. This is also shown in Figure 3. The latter figure also shows a small weight loss (~2%) during this initial degradation time, which is represented in this figure by a small displacement from the ordinate. This initial weight loss is due to volatilization of residual trimer and higher oligomers. The presence of these low molecular weight species in the original sample has been observed by GPC analyses.

Substantial weight loss is not observed until the scission process yields quite low molecular weight polymer (~30,000 g/mole). At this point the depolymerization reaction predominates and the molecular weight of the degraded polymer remains essentially constant.

Figures 4 and 5 show the TGA data plotted as cumulative weight loss, expressed in percent of original weight of the sample, as a function of time of degradation at several temperatures in air and nitrogen, respectively. Careful inspection of the curves in an air atmosphere shows that the rate is quite rapid during the first 2% weight loss and then proceeds at almost a constant slower rate until about 80% of the starting sample is degraded. After this time the rate slows down considerably. Under a nitrogen atmosphere the initially fast rate is followed by a relatively slow degradation rate until about 20% weight loss. Above the first 20% weight loss, the degradation rate again increases until about 80% weight loss, when the rate slows down again.

The variation in the rate of degradation becomes even more obvious if the average rates of volatilization for short time intervals are computed. The mean

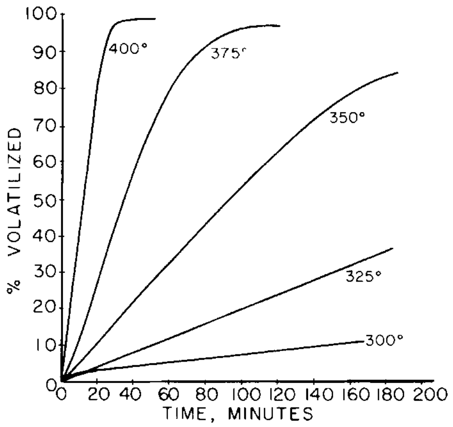


Fig. 4. Cumulative degradation as function of time in air.

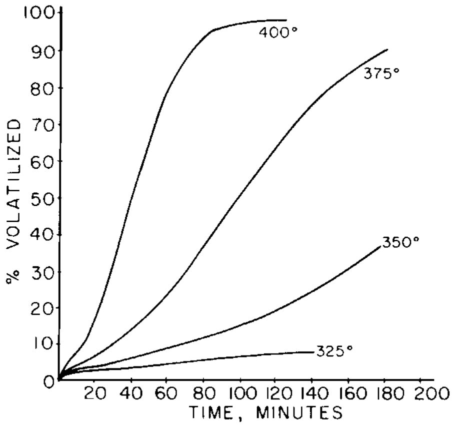


Fig. 5. Cumulative degradation as function of time in nitrogen.

rates of volatilization for short time intervals, as percent of original weight volatilized per minute, K_1, are plotted versus percent of original sample volatilized in Figures 6 and 7 in air and nitrogen, respectively. It is seen that the rates first fall off, as the residual trimer is volatilized, and then rise with percent loss of weight and reach a maximum. The rates then fall again with increasing degree of degradation. Comparing these curves, it is clear that the rates of degradation are faster in air than nitrogen and that these rates increase with increasing temperature.

In a similar treatment, if the mean rates of loss of weight, as percent of the mean weight of the residues, K_2, are plotted for the same time intervals, the set of curves shown in Figures 8 and 9 are obtained. Comparison of these curves leads to the same conclusion as with Figures 6 and 7, as it should. It is also seen again that when the extent of degradation is high, as is the case of the curve at 350°C in air, the rates of degradation fall off. This reduction in rate of degradation at high extents of degradation has been noted by other investigators[10–12] with similarly substituted polyphosphazene as well as with a number of aryloxy-substituted phosphazene polymers. In our studies, the reduction in degradation rate may be due to the formation of incombustible residues; it was found

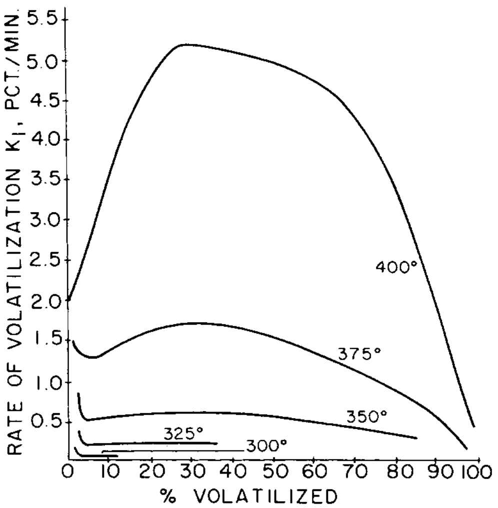


Fig. 6. Rate of degradation as percent of original weight in air.

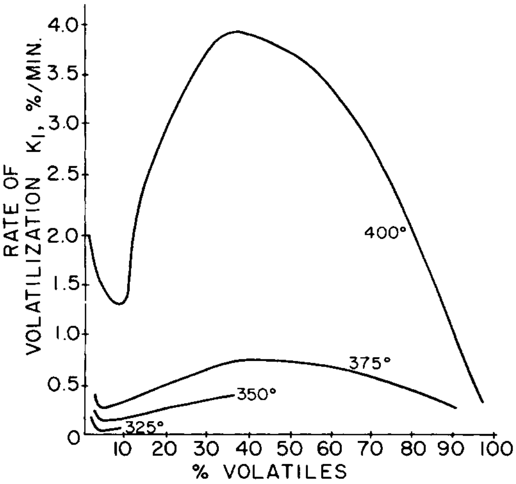


Fig. 7. Rate of degradation as percent of original weight in nitrogen.

that even extensive pyrolysis at 400°C yielded 1% to 2% incombustible residue.

As is pointed out by Madorsky,[13] the rate of loss of weight by volatilization at different temperatures may be used to calculate activation energies only when the residues corresponding to the rates used have the same average molecular weights and molecular weight distributions (MWDs). However, as was shown earlier (Fig. 3), the molecular weight of the residues decreases unevenly with percent loss of weight. The condition of the same average molecular weights and MWDs, however, is met at zero degradation where the same material is used for all temperature experiments. By extrapolating the early straight-line portions of the rate curves to zero degradation, one is able to obtain initial rates of volatilization wherein all samples have the same molecular weight, molecular weight distribution, and composition. If the maxima rates or any other rates are chosen, the above requirements are not met.

By the use of the Arrhenius equation

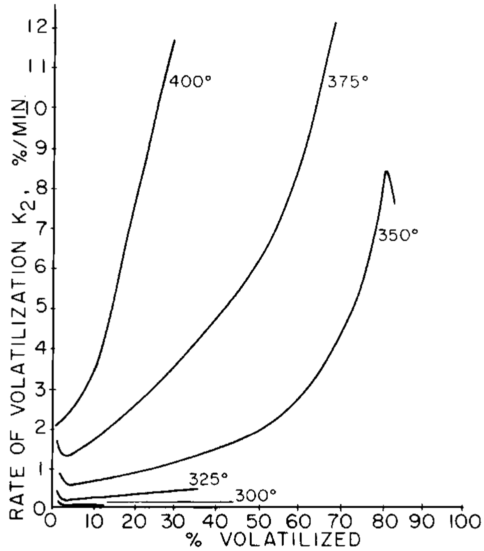


Fig. 8. Rate of degradation as percent of residue in air.

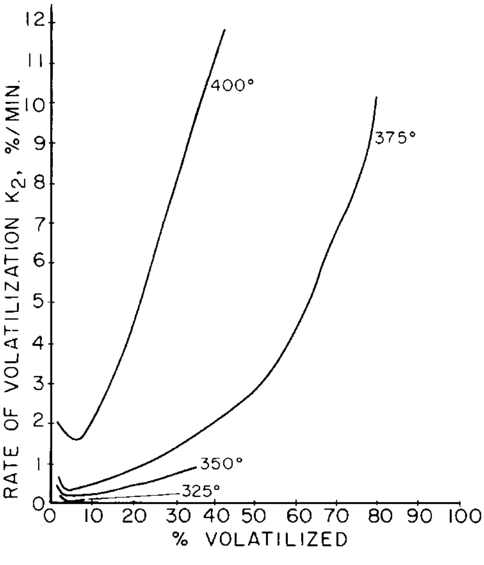


Fig. 9. Rate of degradation as percent of residue in nitrogen.

$$K = A\,e^{-E/RT}$$

in the form

$$-E = 2.3R\,\frac{d(\log K)}{d(1/T)}$$

where the logorithms of the degradation rates K_1 and K_2 are plotted against the reciprocal of absolute temperature, one can obtain the activation energies of the degradation process. These plots for both nitrogen and air atmospheres are shown in Figure 10, with K_2 used as the rate constant.

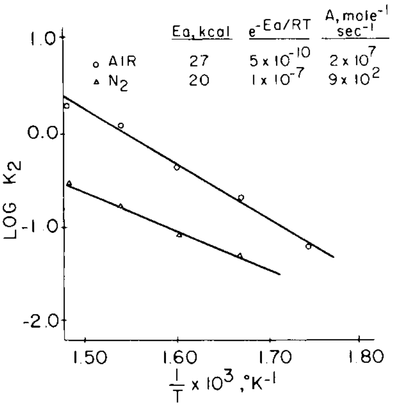


Fig. 10. Arrhenius plot of data in air and nitrogen.

It is cautioned, however, that just as the degradation rates K_1 and K_2 do not represent one particular reaction taking place, so the activation energies obtained here should not be regarded as representing a particular reaction. Rather, the activation energies should be viewed, as pointed out so well by Simha and his co-workers,[14] as a composite value referring to the several reaction mechanisms which may be taking place. It is quite possible that several reactions may be taking place either consecutively or concurrently in this degradation process and that the activation energy values obtained represent the overall process.

The energies of activation obtained with this polymer were 27 and 20 kcal/mole in air and nitrogen, respectively. The term $e^{-E/RT}$ may be viewed as the fraction of the reactant molecules, undergoing collisions at a given instant, that are activated complexes. The term A represents the total frequency of encounters between two reactant molecules, irrespective of whether they possess sufficient energy or not to form the degradation products.[15-17] It is seen from the values of $e^{-E/RT}$ and A, in Figure 10, that the slow step in the two environments is different. In air the number of collisions is much larger than in nitrogen; however, the fraction of activated complex is much lower in air than in nitrogen. The net effect is that the rate of degradation is faster in air than under nitrogen.

MacCollum and Tanner[12] studied the stability of a similar polymer, poly-[bis(trifluoroethoxy)phosphazene], using a thermobalance under vacuum and obtained an activation energy of 56.5 kcal/mole. They used the method of Fuose et al.[18] to determine the rate constants. In this method, the maximum degradation rates are used to calculate the activation energies, and the Fuose method does not necessarily meet the conditions of the same molecular weights and MWSs as is desired.

The question of the order of reaction involved in thermal degradation is of great interest since it may give an insight into the mechanism of degradation. However, when several reactions may be involved, as pointed out by Madorsky,[13] one cannot speak of any given order of reaction, but one can in that case consider the composite reaction which approximates a given order. Figures 11 and 12 show the experimental rate curves at 350°C in air and nitrogen, respectively. The solid lines represent the experimental curves, while the dashed curves represent the theoretical curves calculated from the same initial values of K_1 and K_2 under the assumption that the reaction is quasi-zero order. Comparison of the experimental and theoretical curves indicates that the thermal degradation of this

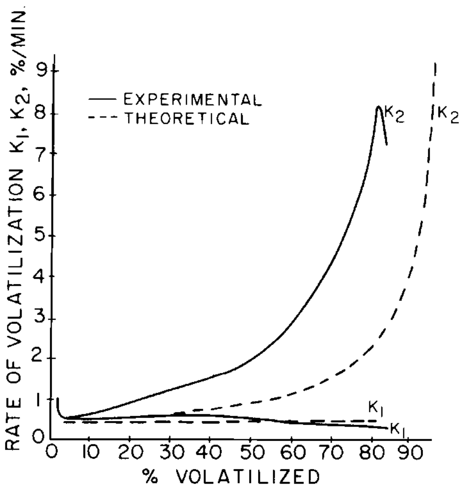


Fig. 11. Rate curves assuming overall zero-order kinetics in air at 350°C.

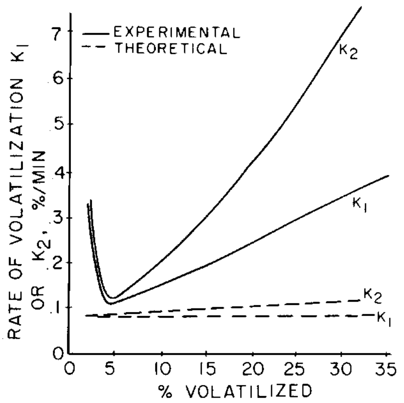


Fig. 12. Rate curves assuming overall zero-order kinetics in nitrogen at 350°C.

polymer in air does indeed approach zero order. The agreement is not near as good under nitrogen atmosphere. However, the zero-order reaction still fits better than a one half-, first-, second-, or third-order reaction. The poorer fit of the theoretical and experimental curves may be an indication that the degradation process is not a single-reaction mechanism but that two or more reactions may be involved.

CONCLUSIONS

This study has indicated that there is a residual amount of trimer present in this polymer. During the early stages of aging, some crosslinking takes place. The primary mode of thermal degradation is through random scission until the polymer is reduced to quite low molecular weight where depolymerization predominates. The rate of degradation is faster in air than in nitrogen. The rates in air approximate the rates in nitrogen at a temperature about 25°C higher than in air. The overall degradation reaction corresponds to quasi-zero-order kinetics. This overall degradation reaction, as determined from initial degradation rates, show energies of activation of 27 and 20 kcal/mole in air and nitrogen, respectively. Previous work[19] with a poly(fluoroalkoxyphosphazene), substituted with about equal mole-% mixtures of the two fluoroalkoxides and aged in air, yielded the same activation energy of 27 kcal/mole when subjected to GPC analysis.

Further studies directed at a better understanding of the degradation of this polymer should take advantage of introducing controlled amounts of such substituants as P—OH, P—Cl, P=O, etc., on the polymer backbone. In this way it may be possible to determine what influence they have on the overall stability of this polymer. In this way, too, it may be possible to realize the full potential stability of this inorganic polymer backbone.

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