

Thermal Degradation of Polydigolphosphate

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SYNOPSIS

A new inherently cross-linked polymer, polydigolphosphate, has been synthesized. The polymer has high affinity for moisture and a tendency to retain sodium chloride, which is produced as a coproduct in the synthesis of the polymer. The purity and, hence, the structural identity of the polymer have been established by combined DTA-TG analyses in an inert atmosphere. Thermal degradation of the polymer has been quantitatively correlated on the basis of a proposed mechanism. The mechanism may serve as a representative one for the degradation of similar polyphosphates of poly(ethylene glycol). © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In an earlier communication,¹ we reported thermal characterization of trimethylol phenol. It was shown therein that thermally induced chemical events of curing and degradation of phenol formaldehyde resin could be established almost quantitatively with the help of combined DTA-TG analyses alone. It was further demonstrated that the occurrence and relative reactivities of various substeps in a particular gross chemical event can also be identified and quantified to ascertain the mechanism of the degradation process. In an extension of this application of the thermal analysis technique, we report here the thermal analytical behavior of another polymer: the condensate of phosphorous oxychloride and diethylene glycol.

The polymer under consideration is itself a new one and has some features that makes it amenable to characterization by thermal analysis only. The polymer is inherently cross-linked and absorbs a considerable amount of moisture at ambient temperature. Further, it retains a substantial amount of sodium chloride that is produced as a coproduct in its synthesis. The retained sodium chloride could be removed only by extraction by hot water repeated for quite a number of times. The individual unspecified amounts of moisture and sodium chloride depend exclusively on the extent of dehydration (by

evacuation), the relative humidity in the ambient atmosphere, and the efficiency of hot water extraction of sodium chloride retained in the polymer. These together offered irreproducible data on elemental analyses, and no definite structure could be assigned to the synthesized polymer. In this particular case, combined differential thermal analysis and thermogravimetry is the only available conventional means to establish the structural identity of the polymer. It is further emphasized that the degradation mechanism reported in this article may be extended to other phosphate-ester polymers in general.

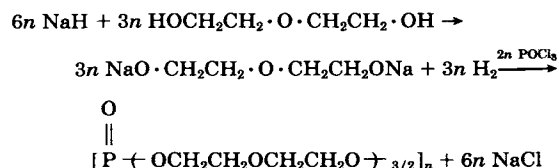
EXPERIMENTAL

Materials

POCl₃ (Johnson Chemicals), diethylene glycol (S.D. Fine Chemicals), tetrahydrofuran (BDH), sodium hydride (E. Merck), and benzene (E. Merck), all of synthesis grade, were used after purification and drying by standard procedures.

Polymer Synthesis

The polymer was synthesized according to the following reaction scheme:



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Eighteen grams of 80% NaH (0.6 mol) washed thoroughly with superdry benzene were reacted with 28.5 mL (0.3 mol) of digol in 50 mL of dry tetrahydrofuran under a blanket of dry nitrogen and with constant stirring until the evolution of hydrogen ceased. The reaction mixture was further stirred under reflux conditions for 1 h to complete the reaction. To this mixture was added 18.5 mL of POCl_3 (0.2 mol) over a period of 30 min under constant stirring. After completion of the reaction, which took about 3 h, the reaction mass was poured into water. The polymer was filtered and purified by repeated washing with hot water, followed by drying under vacuum at 100°C . The polymer obtained was a white solid: yield 90%.

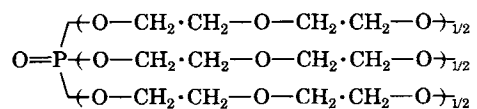
Polymer Characterization

The IR spectrum of the polymer was recorded on a Perkin-Elmer Model 883 spectrophotometer, and DTA and TG analyses were carried out on a Shimadzu DT-40 thermal analyzer unit in argon medium at a heating rate of $15^\circ\text{C min}^{-1}$. Phosphorus content of the polymer was determined by a Schöninger microcombustion apparatus (Heraeus, Germany) following the recommended procedure.²

RESULTS AND DISCUSSION

Structural Identity of the Polymer

On the basis of the reaction scheme and molar ratios of the component monomers used in its synthesis, the product polymer may be assigned the following structure:



with calculated elemental analysis of C, 35.47%; H, 5.91%; and P, 15.27%. The experimental values, however, varied erratically from sample to sample.

Because of varying amounts of moisture absorbed by the polymer, the phosphorus content of the polymer would provide only an idea about the actual polymer content. The sample of the polymer that had been subjected to characterization by thermal analysis in the present investigation has a phosphorus content of 14.2%, indicating a possibility of a substantial amount of moisture and/or NaCl retained by it.

Qualitative information on the structural identity of the polymer was provided by the infrared absorption data. In Table I are presented the observed absorptions and their assignments.³⁻⁶ The data clearly conform to the assigned structure.

Thermal Analytical Characterization

As discussed earlier, a clear understanding of the structural identity of the polymer is likely to be obtained from the thermal analytical data of the polymer. A mechanism of thermal degradation of the polymer is also likely to be provided by the thermograms.

Figure 1 presents the combined DT/TG traces of the polymer in the temperature range $25\text{--}820^\circ\text{C}$ in an inert atmosphere of argon at a heating rate of $15^\circ\text{C min}^{-1}$.

Differential Thermal Analysis

The DTA trace of the polymer shows a clear endothermic event starting at a temperature of about 40°C with a trough at 54°C . The event is identifiable as a physical step involving elimination of absorbed water. Followed by this is a set of multistep exothermic events that starts at around 170°C and is complete at 315°C . This set of multistep events

Table I IR Absorptions of Polydigolphosphate and Their Assignments

Absorption (cm^{-1})	Reported Values (cm^{-1})	Assignments	Remarks
2964	2960	C—H (aliphatic) stretch ³	
1460	1485–1445	P=O stretch ⁵	
1155	1165–1155	P—O—C (aliphatic) ⁶	Distinguishing band for ethoxy ester of phosphoric acid
1070	1150–1060	C—O—C stretch ³ (<i>asym</i>)	Symmetric stretching reportedly too weak to be observed
990	1050–970	P—O—C (aliphatic) ⁶	Asymmetric stretching

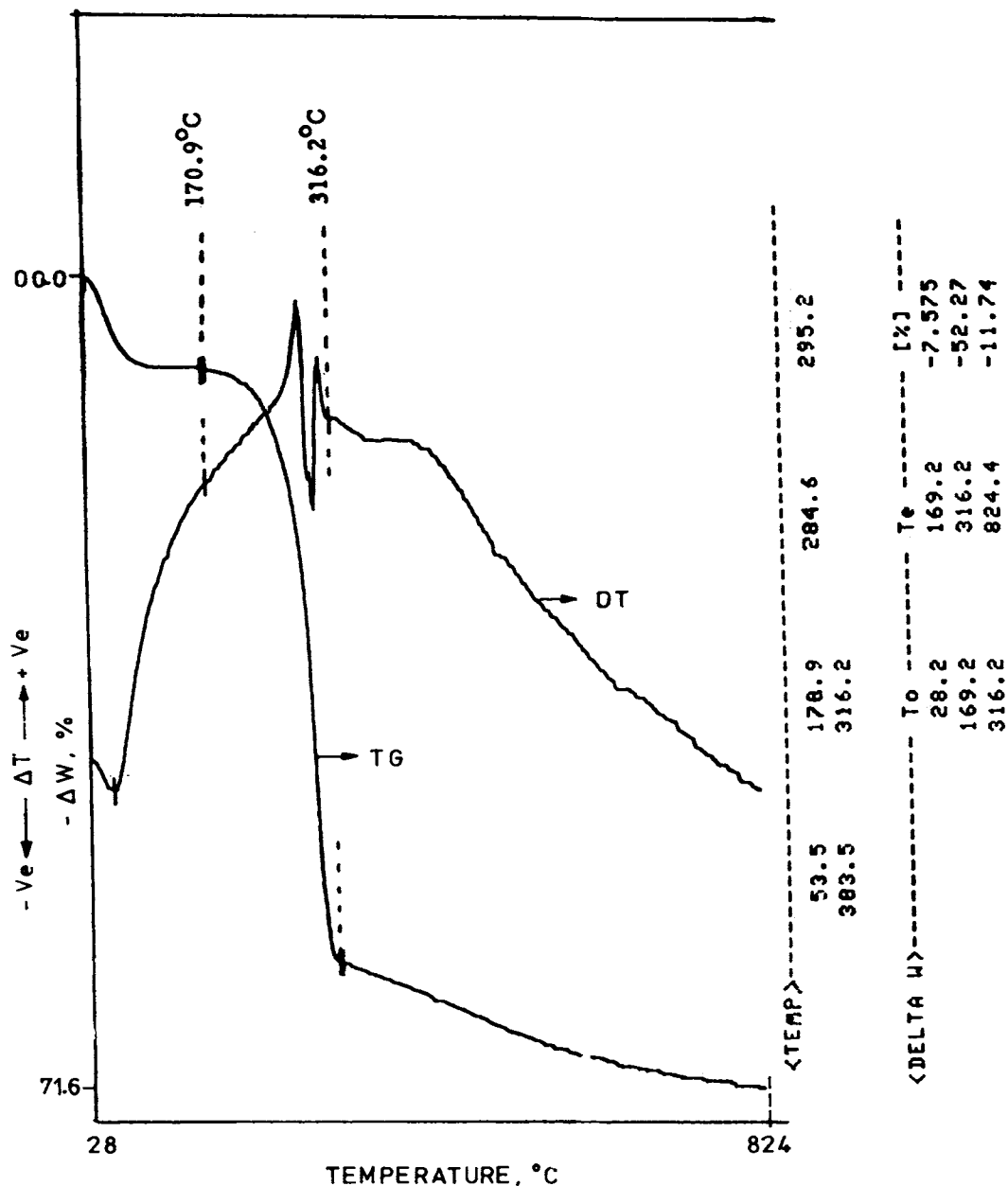


Figure 1 DT-TG thermograms of polydigolphosphate in the temperature range 25–820°C; argon atmosphere; heating rate 15°C min⁻¹. (The numerical data on the side of the figure relate to temperature marks on the DT trace and percent weight loss on the TG trace between the initial temperature, T_0 , and the end temperature, T_e .)

is nothing but the structural degradation of the polymer. An enlarged DTA trace of the polymer in the temperature range 170–400°C is presented in Figure 2 together with the accompanying TG trace. It is clear from Figure 2 that there are three distinct substeps, all of which are exothermic and occur in the temperature ranges 170–285.7 (peak)–290.4°C; 290.4–293.1 (peak)–295.9°C; and

295.9–303.5 (peak)–316.2°C. The DTA trace beyond this temperature is essentially featureless, indicating that the principal degradation process is almost complete at 316°C.

Specific changes taking place in each of the substeps and justification of their exothermicity can, however, be ascertained only after an analysis of the corresponding TG trace.

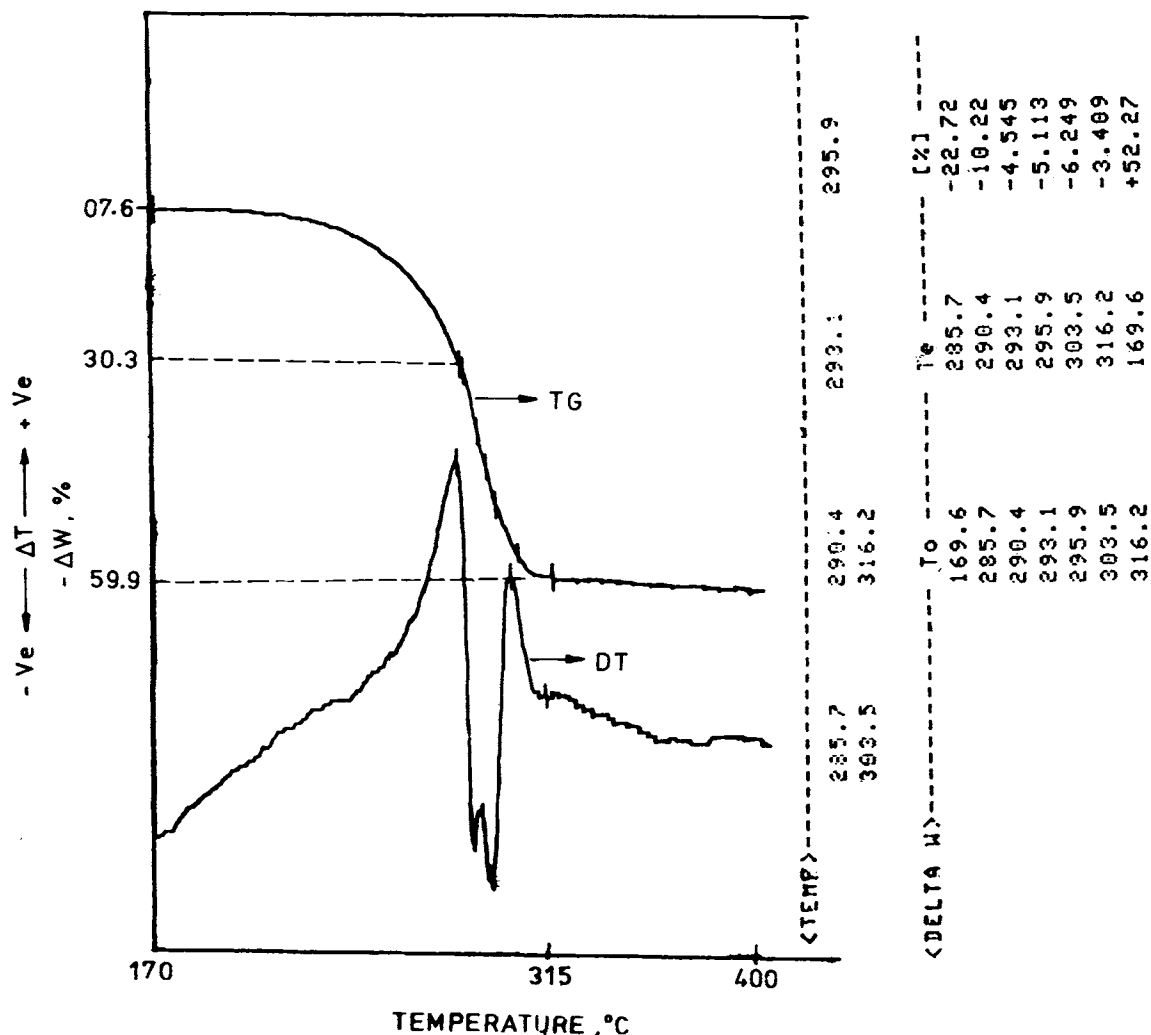


Figure 2 Enlarged DT-TG thermograms of polydigolphosphate in the temperature range 170–420°C (other conditions same as in Figure 1).

Thermogravimetric Analysis

The TG trace in Figure 1 shows an initial mass loss of 7.575% up to 102°C, which corresponds to the first endothermic event in the DTA and is due to the elimination of absorbed water. With the assumption that the polymer retained no NaCl in it, phosphorus content is calculated to be $15.27 \times (100 - 7.575)/100$, i.e., 14.113%. This value agrees excellently with the observed phosphorus content of 14.2% and suggests a possibility that the polymer has been freed from NaCl by repeated hot water extractions.

The TG trace shows a plateau region in the temperature range 102–170°C, indicating a thermal stability of the polymer up to 170°C under the experimental dynamic thermal stress conditions. Beyond 170°C, there is a sharp and drastic exponential

weight loss up to 316°C, followed by a slow and continuous weight loss even up to 820°C. Unlike three distinct substeps identifiable in the DTA trace, the first derivative TG trace (not shown here) offered no evidence of any substeps in mass loss in the temperature range 175–315°C, indicating that the consecutive exothermic substeps overlap each other.

DTA-TG Correlation

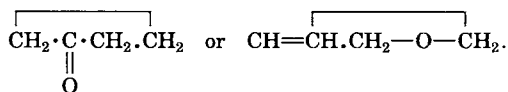
Although the exothermic substeps of degradation overlap each other, the weight loss corresponding to each of the substeps has been found to offer valuable information on the fragment mass of the liberated species. Table II summarizes the stepwise mass loss pattern and the possible fragments that could account for it.

The data in Table II are self-explanatory and correlation between the stepwise mass loss and the volatiles produced is excellent, barring a slight discrepancy between the theoretical and observed fragment weights in each substep, which may be rationalized on the basis of overlapping temperature zones of the consecutive substeps. The observed overall mass loss of 56.54% excellently compares with the calculated mass loss of 56.16%. The data also clearly establish that the polymer is almost completely free of NaCl.

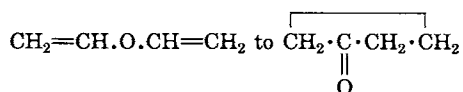
Mechanism of Degradation

On the basis of the available data and the deliberations made so far, a mechanism of degradation of the polymer may be proposed as in Scheme 1.

In substep I, the thermicity of the process per unit of phosphate group is the sum total of the heat effects due to the breaking of two O—C and two C—H bonds and formation of two O—H bonds and two C=C bonds at the cost of two C—C bonds. Coupled with this will be an additional heat effect associated with the secondary transformation of the leaving moiety, $\text{CH}_2=\text{CH}-\text{O}-\text{CH}=\text{CH}_2$, to, say, cyclobutanone



The heat effect in the primary process of degradation in substep I will be endothermic by an amount of 16 kcal per mol of the phosphate moiety. This value has been calculated on the basis of an average bond dissociation enthalpy⁷ of 83, 147, 99, 84 and 111 kcal mol⁻¹ for C—C, C=C, C—H, C—O, and O—H bonds, respectively. Coupled with this, there would be an additional exothermic heat effect of 40 kcal due to secondary transformation of



or 19 kcal for transformation to a species like



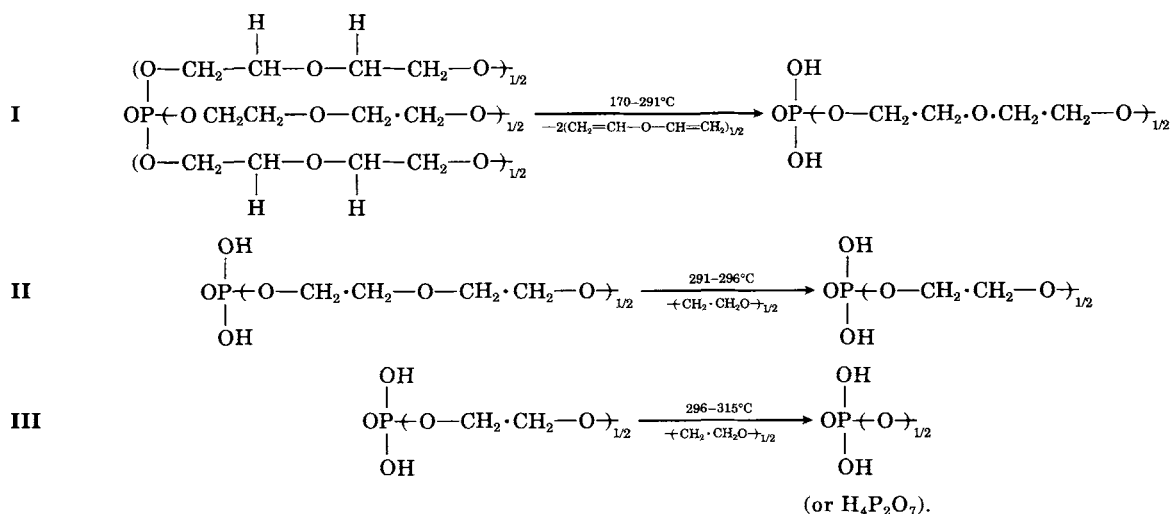
Both of these would account for a net exothermic effect of 24 or 3 kcal, respectively, for substep I.

Substeps II and III in the degradation scheme involves a net cleavage of one-half of a C—O bond

Table II Stepwise Mass Loss in the Temperature Range 175–315°C

Step	Substep	Temp Range	Thermicity	Percent Mass Loss		Fragment Weight ^a	Fragment Identity	Theoretical Fragment Weight	Residue Identity
				Loss	Residue at 175°C				
1	—	30–102	Endo	7.575	—	—	—	—	—
2	I	170–290.4	Exo	32.940	35.64	72.35	$2(\text{CH}_2=\text{CH} \cdot \text{O} \cdot \text{CH}=\text{CH}_2)_{1/2}$	70	$(\text{HO})_2(\text{PO})-(\text{OCH}_2\text{CH}_2\text{O} \cdot \text{CH}_2\text{CH}_2\text{O})_{-1/2}$
	II	290.4–295.9	Exo	9.658	10.45	21.21	$-(\text{CH}_2\text{CH}_2\text{O})_{-1/2}$	22	$(\text{HO})_2(\text{PO})-(\text{OCH}_2\text{CH}_2\text{O})_{-1/2}$
	III	295.9–316.2	Exo	9.658	10.45	21.21	$-(\text{CH}_2\text{CH}_2\text{O})_{-1/2}$	22	$(\text{HO})_2(\text{PO})-(\text{O})_{-1/2}$
	[Total]	[170–316.2]	—	[52.256]	[56.54]	[114.77]	—	[114]	$[\text{H}_4\text{P}_2\text{O}_7]$ (Pyrophosphoric acid)

^a Based on the structure $(\text{PO})-(\text{O} \cdot \text{CH}_2\text{CH}_2\text{O} \cdot \text{CH}_2\text{CH}_2\text{O})_{-3/2}$. Formula weight = 203.



Scheme 1

with an endothermicity of $\frac{1}{2} \times 84 = 42 \text{ kcal mol}^{-1}$. The secondary heat effect associated with the isomerization of $\frac{1}{2}(\text{CH}_2\cdot\text{CH}_2\cdot\text{O})$ to $\frac{1}{2}(\text{CH}_3\text{CHO})$ calculated on the basis of a bond dissociation enthalpy of $170 \text{ kcal mol}^{-1}$ for the C—O bond, however, works out to be an evolution of 43 kcal. The net heat effect in both the substeps is, therefore, only very slightly exothermic. The overall exothermicity of all the three substeps is therefore well justifiable, although as a rule of thumb, degradation, in general, should be an endothermic process.

There are some striking differences in the degradation pattern between substep I and substeps II and III. First, in I, the link unit between two phosphorus atoms is split off in a single spell. In II and III, it is split in two spells. Second, in case of I, there is dehydration of the bulk unit, leaving the P—OH group in the residue; in II and III, however, no dehydration of the link unit takes place.

These apparent discrepancies in the proposed mechanism can be rationalized on the basis of a marked difference in the temperature range of the individual substep. Further, local strain on the link units, which would be more acute in substep I due to inherently cross-linked nature of the polymer, may be responsible for such behavior.

A subsequent loss of weight in the TG trace beyond 315°C may therefore be attributed to slow evaporation of pyrophosphoric acid and/or to its dehydration to polyphosphoric acid. In fact, a substantial residue in the form of a glassy scale can be recovered after thermal analysis that dissolves in water and tests for acid and phosphate.

The proposed mechanism of degradation is based exclusively on the correlation of DTA/TG data on a quantitative scale. A confirmation to this mechanism could have been obtained by GC or evolved gas analysis by GC-MS, which could not be undertaken due to lack of facilities.

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