

Thermal Degradation Characteristics of Poly[Poly(ethylene glycol)] Phosphates

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SYNOPSIS

Thermal degradation characteristics of some poly[poly(ethylene glycol)] phosphates (PPEGP) based on ethylene glycol (PEGP), an equimolar mixture of ethylene glycol and trigol (PETP), digol (PDGP), and trigol (PTGP) have been studied by combined differential thermal and thermogravimetric analyses (DTA/TGA). It has been shown that, in spite of their structural similarities, the PPEGPs do not conform to any generalized degradation pattern. Local strains in the crosslinked network and the possible intranetwork topographic interferences due to crossovers, entanglements, and varying lengths of polyoxyethylene link units are believed to play a pivotal role in the thermal degradation of individual PPEGPs.

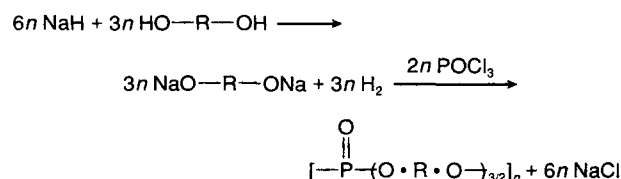
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INTRODUCTION

In an earlier communication,¹ we reported the synthesis and thermal degradation of polydigolphosphate (PDGP). It was shown therein that the technique of a combined DTA–TG analyses could be successfully utilized to establish the purity and the structural identity of the polymer. On the basis of the thermal analytical data, a tentative mechanism of anaerobic thermal degradation of PDGP was also proposed with a projection that the mechanism could be extended to poly (polyethylene glycol) phosphates (PPEGP) in general. In an extension of the above work, we recently synthesized three more PPEGPs and characterized them in respect of their anaerobic thermal degradation. These polymers are based on ethylene glycol (PEGP), trigol (PTGP), and an equimolar mixture of ethylene glycol and trigol (PETP) as the diol components. It will be shown in this article that in spite of structural similarities the PPEGPs do not correspond to any common thermal degradation pattern, although some general characteristics could be observed.

EXPERIMENTAL

Polymers were synthesized by the following procedure reported earlier¹: All materials used for the syntheses were of analytical grades and were subjected to purification by standard procedures. The general scheme of the reaction is represented as follows:



where R = —CH₂CH₂—, —CH₂CH₂·O·CH₂CH₂—, —CH₂CH₂·O·CH₂CH₂·O·CH₂CH₂—, and a 1 : 1 molar mixture of —CH₂CH₂— and —CH₂CH₂·O·CH₂CH₂·O·CH₂CH₂—, respectively, in PEGP, PDGP, PTGP, and PETP.

RESULTS AND DISCUSSION

DTA and TG traces of the polymers PEGP, PETP, and PTGP, respectively, are presented in Figures 1–3. The characteristics of DTA and TG traces of the PPEGP along with those of PDGP are sum-

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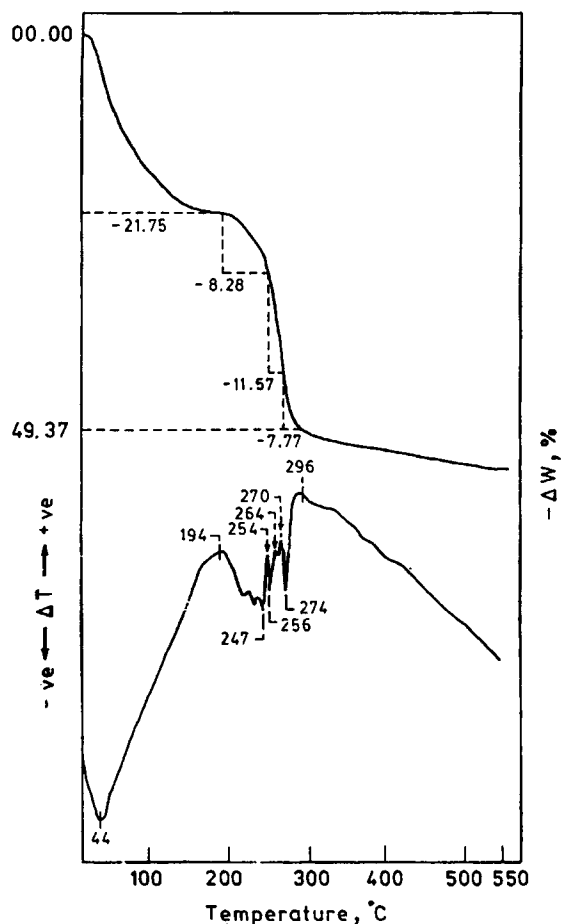


Figure 1 DTA-TG thermograms of PEGP with an argon atmosphere and heating rate of $10^{\circ}\text{C min}^{-1}$. (The numerical data in the figure are the temperature marks on the DT trace and percent weight loss on the TG trace.)

marized in Table I for comparison. In Table II are presented purity of the polymers and the structural identity of the phosphoric acid residues, left after thermal decomposition, which offered the best correlation of the thermal analytical data. In arriving at the listed data, the following considerations were made. The weight loss up to the first plateau in a TG trace (which is complete within 194°C for PEGP, 168°C for PETP, and 165°C for PTGP) represented the loss of moisture. The weight loss between the first and second plateaus in the TG trace represents the volatiles from degradation of polyoxyethylene linkages. The residue after the second plateau accounts for the residual phosphorus (V) oxyacid and the NaCl retained in the polymer.

The identity of the residual phosphorus (V) oxyacids was ascertained from the overall phosphorus content and the weight loss suffered by the polymer

up to the end of second stage of degradation. The amount of NaCl originally retained in the polymer was determined by the difference. Overall phosphorus content in the polymer was determined following the Schoniger microcombustion method.

The DTA traces of the polymers PEGP, PETP, and PTGP show clear endothermic events starting at a temperature as low as about 30°C with a trough at 44 , 47 , and 41°C , respectively. These endothermic events are identifiable as physical steps involving elimination of absorbed water. It is to be noted that all the polymers including PDGP have the characteristic property of retaining a substantial amount of water. Followed by these endotherms are sets of multistep exothermic and/or endothermic events that start at around 170°C and are complete at around 300°C , representing the structural degradation of the polymers. But no generalized mechanism or structure-property correlation could be established because of distinctly different thermal degradation patterns of the polymers.

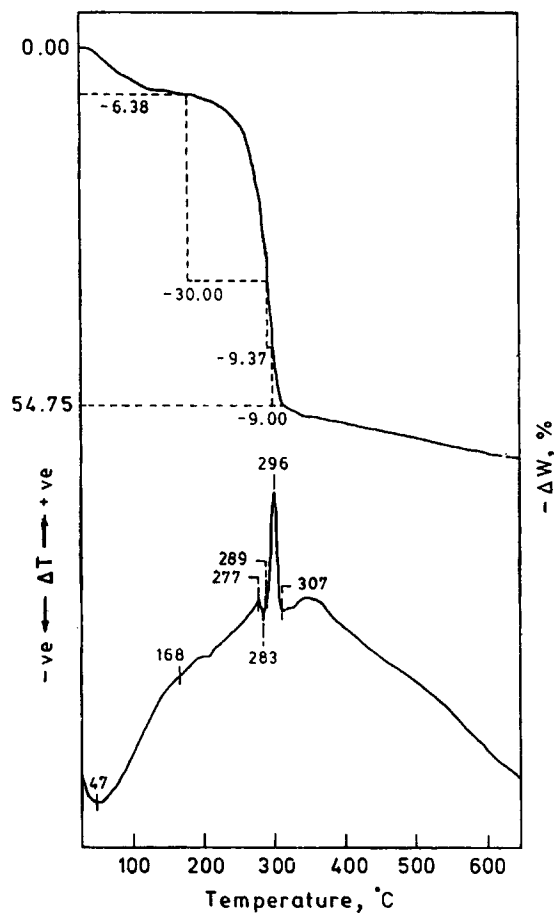


Figure 2 DTA-TG thermograms of PETP (other conditions are the same as in Fig. 1).

Table I Summary of the DTA and TG Characteristics of PPEGPs^a

							Total Wt Loss (%)				
PEGP	Ambient	44	194	254	(264)	270	296				
	TG wt loss (%)	←	21.75	→	8.28	→	11.57	→	7.77	→	49.37
		←	Stage 1	→	Stage 2	→	Stage 3	→	Stage 4	→	
PETP	Ambient	47	168	277	(287)	289	296	307			
	TG wt loss (%)	←	6.38	→	30.00	→	9.37	→	9.00	→	54.75
		←	Stage 1	→	Stage 2	→	Stage 3	→	Stage 4	→	
PTGP	Ambient	41	165	278	284	280	293				
	TG wt loss (%)	←	4.38	→	49.56	→	9.21	→		63.15	
		←	Stage 1	→	Stage 2	→	Stage 3	→			
PDGP ^b	Ambient	54	170	286	293	290	296	304	316		
	TG wt loss (%)	←	7.58	→	32.94	→	9.66	→	9.66	→	59.84
		←	Stage 1	→	Stage 2	→	Stage 3	→	Stage 4	→	

^a Numerals appearing above and below the line in each polymer correspond to the peak and trough temperatures, respectively. Numerals on the line against each polymer are the temperature at which an inflection, but neither peak nor a trough can be identified. Numerals in parentheses are temperatures where the peaks and trough are identifiable but very less prominent. Numerals with an underline are the temperatures of very sharp peaks.

^b Data reproduced from Ref. 1.

First, as evident from their DTA thermograms, the polymers, in general, degrade in three steps. But PTGP shows only two steps in its total degradation. Second, all the PPEGPs produced acetylene on isothermal heating in an inert medium in the temperature range 194–300°C, but PDGP did not. Third, the final residue is pyrophosphoric acid from PDGP and PEGP, whereas it is orthophosphoric acid from PETP and PTGP. Fourth, regarding the thermici-

ties of the steps of degradation (Table I), some discrepancies are notable. In the case of PDGP, the observed thermicities and the reactions taking place in various stages of degradation were fairly well correlated.¹ In the cases of other PPEGPs, however, such an exercise was preempted in the absence of any authentic information on the identities of the degradation products. The steps of the degradations of the polymers span a small temperature range of

Table II Purity of PPEGPs and Structural Identity of the Residual Phosphoric Acid After Degradation

Polymer	F.W. ^a per Single P Atom	Structural Identity of Residual Phosphoric Acid	Total F.W. ^a of Volatiles	Inherent Moisture (%)	Volatiles (%)	Inherent NaCl (%)	Net Polymers Content (%)
PEGP	137	H ₄ P ₂ O ₇	48	21.75	27.62	1.03	77.12
PETP	203	H ₃ PO ₄	105	6.38	48.37	0.10	93.52
PTGP	269	H ₃ PO ₄	171	4.38	58.77	3.17	92.45
PDGP ^b	203	H ₄ P ₂ O ₇	114	7.78	52.26	0.00	92.22

^a F.W. = formula weight, calculated on the basis of the structure O=P(—O·R·O—)_{3/2}.

^b Data reproduced from Ref. 1.

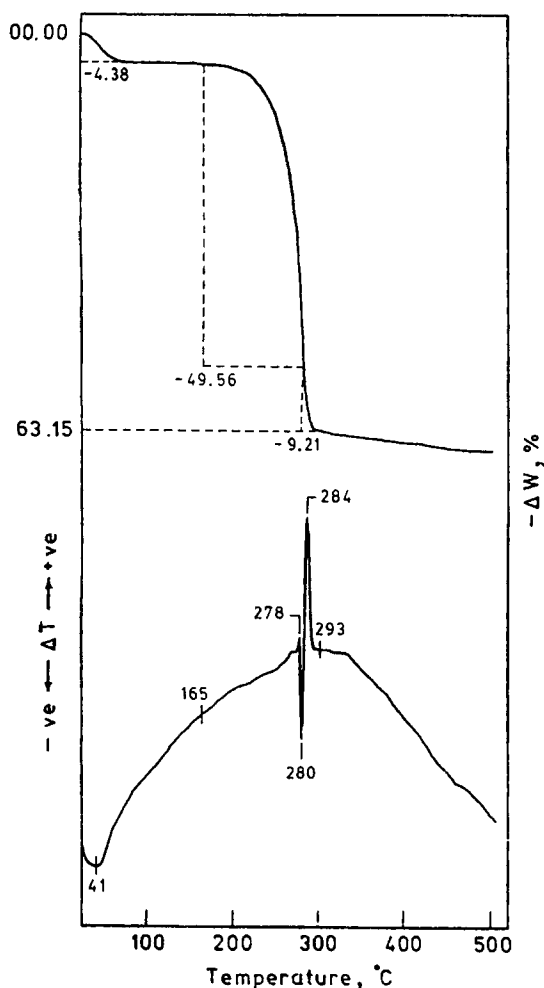


Figure 3 DTA-TG thermograms of PTGP (other conditions are the same as in Fig. 1).

10–20°C. A very close control of temperature in such a narrow range to monitor the degradation products is, however, quite difficult in practice.

Nevertheless, in an attempt to rationalize the apparent discrepancies in thermicities at various stages of degradation, some notable factors inherent to any crosslinked network are worth mentioning. The local strains depending upon the oxyethylene link lengths may profoundly influence the thermicity of the steps both in magnitude and in sign and also the temperature ranges in which the degradation takes place. An apparent discrepancy in the identity of the residual phosphorus (V) oxyacids may also owe their origin to these complex factors in PPEGP network polymers. The role of substituted phosphoric acids in effecting secondary transformation of acetylene, the diolefins, or other radical species (which are most likely to be the primary off gases) to more stable molecular moieties also cannot be ruled out.

In conclusion, the PPEGP are thermally unstable and differ widely in their thermal degradation patterns. Crossovers, entanglements, lengths of link units, and nonuniformity in the network structure possibly give rise to intranetwork topographic interferences which largely influence the degradation pattern and thermicities of individual degradation steps.

The study also shows that with some supporting data on the phosphorus content the technique of combined DTA/TG analyses can be very successfully employed to establish the purity and structural identity of the PPEGP network polymers.

REFERENCES

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