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THERMAL STABILITY OF P–N CONTAINING POLYMERS

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The thermal stability of a number of P–N containing polymers was studied employing softening range, thermogravimetry and differential scanning calorimetry. The products generally exhibited better weight retension than their carbon counterparts showing poor low temperature stability but moderate high temperature (to 1000°) stability. Degradation to about 300° occurs via nonoxidative routes whereas above 300° degradation occurs by oxidative routes in air. Most stability plateaus are kinetically controlled. Other commonalities and possible degradative routes are given.

We have been active in the synthesis of a number of phosphorus polymers [1, 2]. Our reasons for the synthesis of these products is varied and includes the synthesis of thermally stable materials. Here we report on the initial thermal characterization of a number of P–N containing polymers.

Experimental

Products were all synthesized using the interfacial technique. Synthesis and characterizations of products are given in references cited in Table 1.

Viscometry was performed at 30° using a Cannon–Ubbelohde viscometer with serial dilutions. Softening ranges were determined on a Fisher–Johns melting point apparatus at an approximate heating rate of 2 to 10°/min. Elemental and infrared analyses were consistent with that expected and are reported elsewhere and cited in Table 1.

Thermogravimetry was conducted employing a 950 duPont thermobalance. Differential Scanning Calorimetry (DSC) was carried out using a duPont DSC cell fitted on a 900 duPont Thermal Analyzer console employing a linear baseline compensator to insure a constant energy baseline. Gas flows of *ca* 0.3 l/min were employed. A Mettler H20T semimicro balance was employed for the weighing of the DSC samples. DSC measurements were obtained on samples ground to a powder and contained in open aluminum cups to allow the free flow away from the solid of volatilized gas thus more closely simulating the conditions under which TG studies were conducted.

Table 1

A. Properties of products from phenylphosphonic diisocyanate

Nitrogen reactant	Softening range	[η] ml/g (solvent)	Product designation (Ref.)
Piperazine	182—186	12 (DMSO)	1 [24]
1,3-Di-4-piperylpropane[a]	164—168	10 (DMSO)	2 [14]
p-Phenylenediamine	260—280	9 (Formic acid)	3 [3, 4, 7]
m-Phenylenediamine	245—256	5 (Formic acid)	4 [3, 4, 7]
1,6-Hexanediamine	180—193	8 (Formic acid)	5 [3, 4, 7]
Phenylhydrazine	151—156	10 (DMSO)	6 [6]
Hydrazine	145—166	15 (DMSO)	7 [6]
Benzoylhydrazine	147—157	5 (DMSO)	8 [6]
4-Nitrophenylhydrazine	180—200	—	9 [6]
Succinic Acid Dihydrazide	178—180	11 (DMF)	10 [5]
Glutaric Acid Dihydrazide	170—181	4 (DMF)	11 [5]
Azelaic Acid Dihydrazide	162—165	7 (DMF)	12 [5]
B. Properties of products from phenylphosphonic dichloride			
Malonamide	130—140	39 (DMSO)	13 [8]
Urea	294—300	18 (DMSO)	14 [8]
1,6-Hexanediamine	44—83	7 (Formic acid)	15 [9]
1,3-Di-4-piperylpropane[a]	>300	—	16 [9]
p-Phenylenediamine	270—283	6 (Formic acid)	17 [9]
4-Aminomethylpiperidine[a]	262—278	—	18 [9]

[a] Obtained as gifts from Reilly Tar & Chemical Corp., Indianapolis, Ind.

Results and discussion

The thermal stability of P–N products is reported to be considerably less than that of the carbon analogs [10, 11] with most carbon analogs exhibiting almost total weight loss at temperatures less than 400°. Extensive work has been reported on the stabilization of polyurethanes and polyureas [10]. The urea linkage generally undergoes thermal dissociation at *ca* 150 to 200° while the urethane decomposes *ca* 225 to 300°. Polyureas generally begin decomposing about 150 to 200° with almost complete weight loss *ca* 400 to 500° while polyurethanes begin decomposing *ca* 260° with degradation complete *ca* 400°. Stability studies with select P–N products have indicated that certain of these products exhibit markedly better high temperature weight retensions than their carbon counterparts counter to that previously reported [4, 7].

In the present study emphasis is given to P–N products which can exhibit double bond character throughout at least a portion of the polymer backbone as illustrated below utilizing resonance structures.

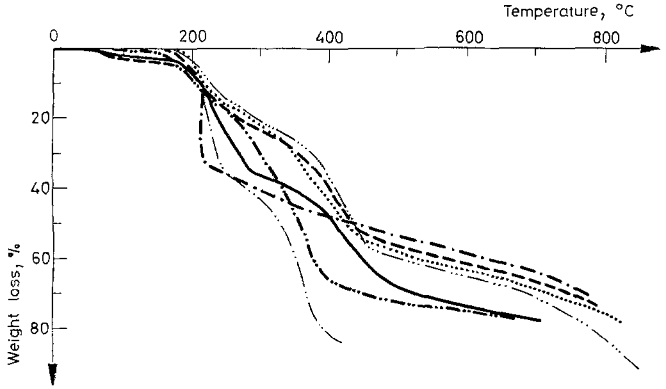


Fig. 1. TG curves of samples from Table 1; heating rate: 30°/min, air flow rate: 0.3 l/min Sample designations (from Table 1 — final column): 6. • • — • • ; 7. ——— ; 8. — · · — ; 9. — · — ; 10. · · · · · ; 11. — — — ; and 12. · · · — · · · —

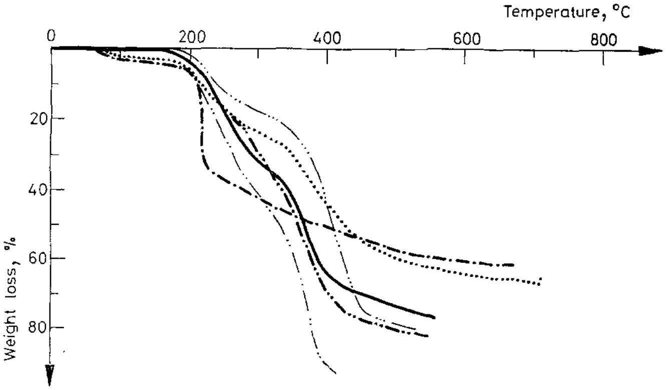


Fig. 2. TG curves of samples in Fig. 1 in N_2 atmosphere

Such "double bond character" could enhance the thermal stability of the chains. For the present study the phosphorus-containing moiety(Ø-P = O) was held constant.

Product structures are straight forward and are of form I for products from phenylphosphonic dichloride and of form II for products from phenylphosphonic diisocyanate.

Attempts to trap degradation products utilizing dry ice, acetone and liquid nitrogen traps proved largely unsuccessful with the only product collected (in

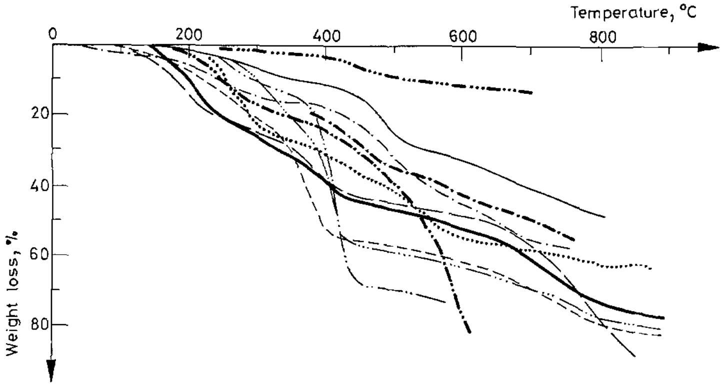


Fig. 3. TG curves in air atmosphere for following samples (from Table 1): 1. - - -; 2.— · · —; 3. ———; 4. — — —; 5. · · · · - · · ·; 13. · · — · ·; 14. · · · — · · ·; 15. · · · ·; 16. ———; 17.— · —; 18. — · —

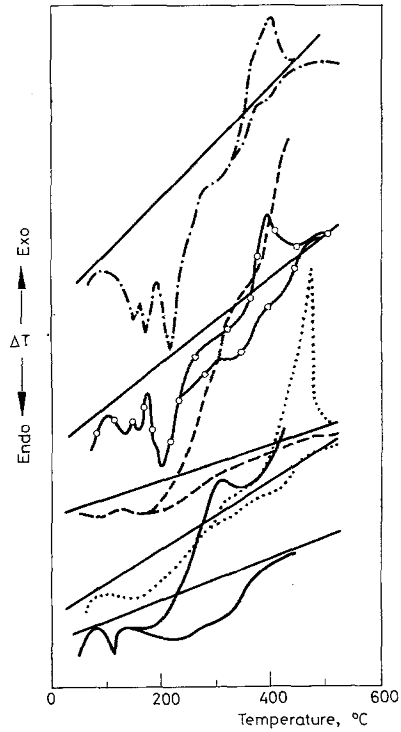
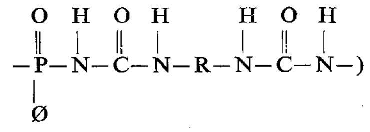
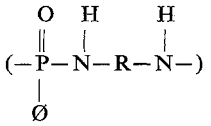
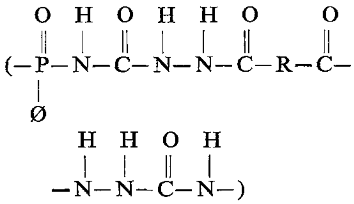
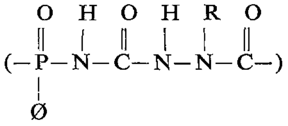
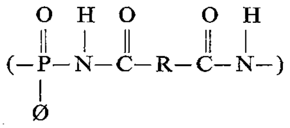


Fig. 4. DSC curve of samples from Table 1; heating rate: 30°/min in air (lower portion of couple) and nitrogen (upper portion of couple when the curves split); flow rate: 0.3 l/min; gas "Y"-axis sensitivity: 0.2°/in (0.008 millivolt/in); the $\Delta T = 0$ line is the straight solid line. Samples (from Table 1) 7. — · — ·; 8. o o o; 13. — — —; 14. · · · · ·; 16. ———

every instance) being water. Most systems emitted (presumably nitrogen containing) volatile mixtures exhibiting pH's from *ca* 7 to 11. Several products from the diisocyanate emitted degradation products which were odoriferous, irritating and possibly toxic since we experienced on several occasions headaches after being exposed to the fumes.

Table 2

Results as a function of backbone structure

Family	Designation	Backbone structure	Initin	30%	50%
			deg.		
Polyphosphonyl-ureas	PPU	 $-\underset{\underset{\varnothing}{\vert}}{\overset{\text{O}}{\overset{\parallel}{\text{P}}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\text{R}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-)$	50	350	450
Polyphosphon-amides	PPOA	 $(-\underset{\underset{\varnothing}{\vert}}{\overset{\text{O}}{\overset{\parallel}{\text{P}}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\text{R}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-)$	175	400	700
Polyphonyl-hydrazides	PPHD	 $(-\underset{\underset{\varnothing}{\vert}}{\overset{\text{O}}{\overset{\parallel}{\text{P}}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{R}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$ $-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-)$	50	350	425
Polyphonyl-hydrazines	PPHN	 $(-\underset{\underset{\varnothing}{\vert}}{\overset{\text{O}}{\overset{\parallel}{\text{P}}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{R}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-)$	175	250	350
Polyphosphonyl-amides	PPA	 $(-\underset{\underset{\varnothing}{\vert}}{\overset{\text{O}}{\overset{\parallel}{\text{P}}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{R}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\overset{\text{H}}{\overset{\vert}{\text{N}}}-)$	150	400	600

a) Temperatures are average and given to 25°

b) Initial degradation temperature order PPHN ≅ PPOA > PPA > PPHB ≅ PPU (lowest)

c) Overall high temperature stability PPOA > PPA ≅ PPU ≅ PPHD > PPHN

Because of the inability to collect and identify degradation products and the belief that degradation is occurring by complex, often several concurring pathways, only generalizations will be presented.

DSC and TG curves are identical to about 300° in air and nitrogen indicating initial degradation is occurring *via* identical, nonoxidative routes. This is unexpected since the analogous nonphosphorus polyurethanes and polyureas undergo degradation *via* oxidative routes throughout their entire degradation in air [10]. Above about 300° there is a wide variance in the thermal curves obtained in air and nitrogen with curves in air consistent with degradation occurring by oxidative modes. Physically most products melt before or while undergoing initial degradation, being solid and colored (from light gray to black) after about 500°. The stability plateaus are usual for products containing grossly different bond energies between atoms in the polymer backbone [for instance 2, 12, 13]. Most plateaus are kinetically controlled and when studied at constant time result in additional weight loss — the amount and rate characteristic of the product and temperature. For instance the product from phenylphosphonic diisocyanate and 4-nitrophenylhydrazine at 800° still retains ca 25% of its original weight. Holding at 800° for 30 mins results in an additional 21% weight loss. There appears no marked difference in the high temperature weight retension in air or nitrogen. This is in marked contrast with most organometallic and "usual" carbon based polymers where weight retension in nitrogen is greater than that in air.

Degradation patterns are apparent when considering each family of polymers. General results appear in Table 2. Thus weight retension appears independent of the nature of "R" (Table 2) to a first approximation. This indicates that the critical bonds involved in the chain stability are not included in the N-R-N moiety. This is substantiated by the absence of added thermal stability for condensations with "piperyl" derivatives compared to those involving primary amines.

There appears no direct relationship between the temperature where initial degradation occurs and the product's higher temperature stability.

The product from phenylphosphonic diisocyanate and urea deserves special comment because of its exceptional stability retaining over 80% weight at 800° in both air and nitrogen. This product exhibits the (supposed) greatest polar character within its backbone. Whether this polar character is the major feature contributing to its overall better weight retension is yet to be determined.

While it is obvious that the present products exhibit better higher temperature stability than their carbon analogs, some are favorable when compared to other products mentioned as exhibiting moderately to good weight retension (c.f. for instance Figure 5).

Reports on the actual sequence of bond breakage (and formation) for the thermal degradation of condensation type polymers are just beginning to emerge. For select products we attempted such a study utilizing comparisons of infrared spectra of products at different stages in their degradation. Trends to *ca* 400 to 500° appear somewhat common in air and nitrogen. There was a general decrease in the size of bands about *ca* 685, 740—760 and 1420—1445 (all bands listed in cm^{-1})

all bands associated with the P-phenyl moiety suggesting that the P-phenyl moiety (derived from the phenylphosphonic dichloride or phenylphosphonic diisocyanate reactant) is one of the initial bonds to degrade. The band about 1680, characteristic of the carbonyl groups in ureas and urethanes [14, 15], also decreases. It is possible that the carbonyl group is split out giving carbon monoxide in nitrogen and/or carbon dioxide in air.

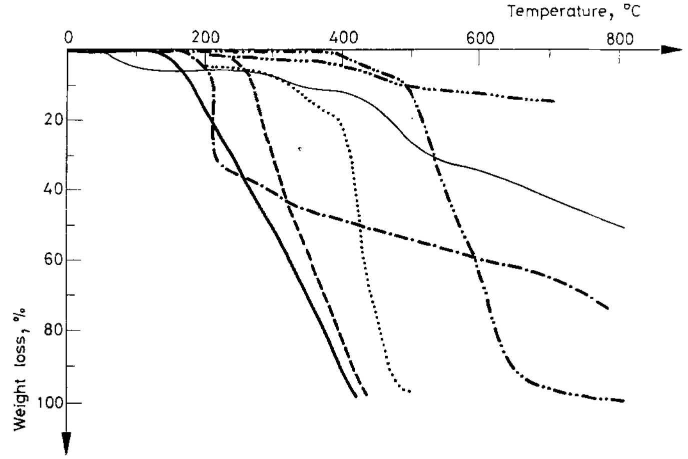
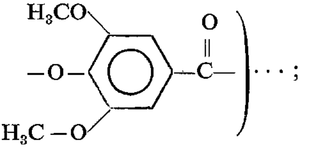


Fig. 5. TG curves: phosphorus 9. · — · —; 14. — · · · —; 16. ———; nonphosphorus — polycarbonate



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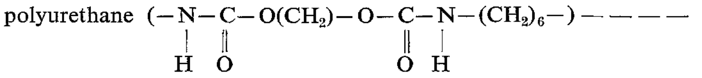
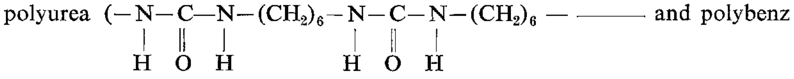


polyurethane $(-\underset{\substack{| \\ \mathrm{H}}}{\mathrm{N}}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\mathrm{O(CH_2)}-\mathrm{O}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\underset{\substack{| \\ \mathrm{H}}}{\mathrm{N}}-(\mathrm{CH_2})_6-)$ — — — —



polyurea $(-\underset{\substack{| \\ \mathrm{H}}}{\mathrm{N}}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\underset{\substack{| \\ \mathrm{H}}}{\mathrm{N}}-(\mathrm{CH_2})_6-\underset{\substack{| \\ \mathrm{H}}}{\mathrm{N}}-\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}-\underset{\substack{| \\ \mathrm{H}}}{\mathrm{N}}-(\mathrm{CH_2})_6$ — ——— and polybenz imidazole · · — · · —

There is a general shifting of the maximum band density from *ca* 3300 to *ca* 3100 characteristic of the formation of amine moieties from amide units. A new band about 1400 (possibly due to primary amide formation – 1420 to 1400 [15] or N=N formation – 1455–1400 [15, 16]) generally appears.

Several moieties can be tentatively eliminated. The O=P–OH moiety exhibits a band about 2700 to 2550 [15]. No new band appears in this region in spectra of the degradation products. The P=N moiety is eliminated due to the absence of several new or growing bands in the 1300–1100 region [15, 17]. Isocyanate formation is eliminated by the absence of new bands in the 2400 to 2300 region [15].

Studies as presented above must be considered tentative at best since only the most important changes will be detected. Additionally band identifications are also tentative.

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RÉSUMÉ — Etude de la stabilité thermique dans le domaine du ramollissement de plusieurs polymères contenant P et N, par thermogravimétrie et par analyse calorimétrique différentielle (DSC). Les produits conservent généralement d'autant mieux leur stabilité pondérale que leurs équivalents carbonés possèdent une faible stabilité thermique à basse température mais une stabilité modérée à haute température (jusqu'à 1000°C). Jusqu'à 300°C, la dégradation se produit par un processus non oxydant alors qu'au-dessus de cette température et dans l'air, la dégradation s'effectue par le biais de l'oxydation. La plupart des paliers thermogravimétriques sont contrôlés cinétiquement. D'autres voies de dégradation possibles sont également signalées.

ZUSAMMENFASSUNG — Die thermische Stabilität einer Anzahl P—N-haltiger Polymere wurde durch die Untersuchung des Erweichungsbereichs, die thermogravimetrische Analyse und die Differential-Abtastkalorimetrie geprüft. Die Produkte erwiesen im Allgemeinen eine bessere Konstanz des Gewichts als ihre kohlenstoffhaltigen Analoge mit geringer Stabilität bei niedrigen, doch mäßiger Stabilität bei hohen Temperaturen (bis zu 1000°C). Die Zersetzung bis zu 300°C erfolgt auf nicht-oxidativem Wege, während bei Temperaturen über 300°C die Zersetzung in Luft sich auf oxidativem Wege vollzieht. Die meisten Stabilitätsplateaus sind kinetisch bedingt. Andere Einzelheiten und mögliche Zersetzungswege werden angeführt.

Резюме — Изучена термическая стабильность ряда P—N содержащих полимеров, используя облась размягчения, термический гравиметрический анализ и дифференциальную сканирующую калориметрию. Эти продукты, в общем, показывают лучшую удерживаемость веса и умеренно высокую температурную (до 1000°С) стабильность, чем их углеродные аналоги, показывающие плохую низкую температурную стабильность. Деградация до 300°С протекает через безокислительную стадию, в то время как выше 300°С — окислением на воздухе. Большинство стабильных плат кинетически контролировались. Даны другие обобщения и возможные стадии деградации.