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PRELIMINARY NOTE

Diphosphatetraazacyclooctatetraenes. III. Polymerization Studies

K. J. L. PACIOREK, T. I. ITO AND R. H. KRATZER

Ultrasystems, Inc., 2400 Michelson Drive,
Irvine, California 92715 (U.S.A.)

SUMMARY

Interaction of perfluoroalkylether diamidine with diphenyltrichlorophosphorane failed to give the symmetrical poly(diphosphatetraazacyclooctatetraene); the products isolated were bicyclic compounds of a low thermal stability. The unsymmetrical poly(diphosphatetraazacyclooctatetraene) was readily formed from the reaction of polyimidoylamidine and imido-tetraphenyl-diphosphinic acid trichloride. The thermal and thermal oxidative stabilities were directly comparable to those of the monomeric models [1].

INTRODUCTION

It was of interest to determine whether the low thermal stability found in the monomeric diphosphatetraazacyclooctatetraenes [1] will persist in a polymer environment wherein segment elimination is much more difficult than the liberation of monofunctional species due to the absence of volatile primary products and possible cage effects.

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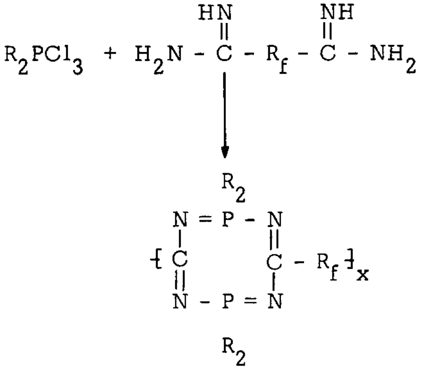
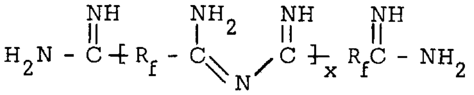
Based on the mechanism of formation of s-diphosphatetraazacyclooctatetraene [2], it was assumed that utilizing a diamidine, a polymeric system should result, i.e.,



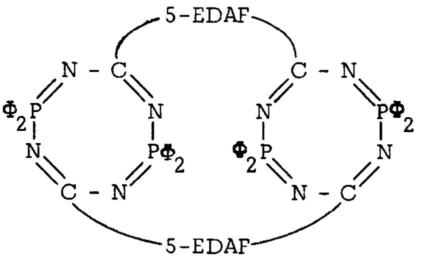
The production of polymeric species should not be prevented by the presence of the unavoidable imidoylamidine linkages in the amidines, i.e.,



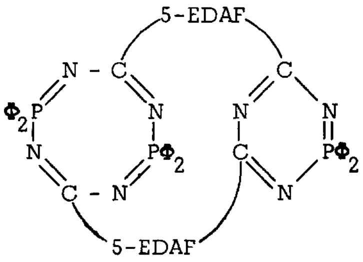
$$H_2N-\overset{NH}{\overset{\|}{C}}\!-\!\left[R_f-\overset{NH_2}{\overset{|}{C}}=N-\overset{NH}{\overset{\|}{C}}\right]_x R_f\overset{NH}{\overset{\|}{C}}-NH_2$$

since in this case instead of poly(diphosphatetraazacyclooctatetraene), a poly(diphosphatetraazacyclooctatetraene-monophospha-s-triazine) would result.

Interaction of the imidoylamidine/amidine mixture derived from 5-EDAF-dinitrile, $N{\equiv}CCF(CF_3)[OCF_2(CF_3)CF]_mO(CF_2)_5O[CF(CF_3)CF_2O]_nCF(CF_3)C{\equiv}N$ (wherein m + n = 3), with diphenyltrichlorophosphorane did not lead to polymerization. Based on elemental analysis, molecular weight determination, and infrared spectral analysis, a mixture of cyclic compounds, depicted by I and II, formed the major portion of the products obtained.



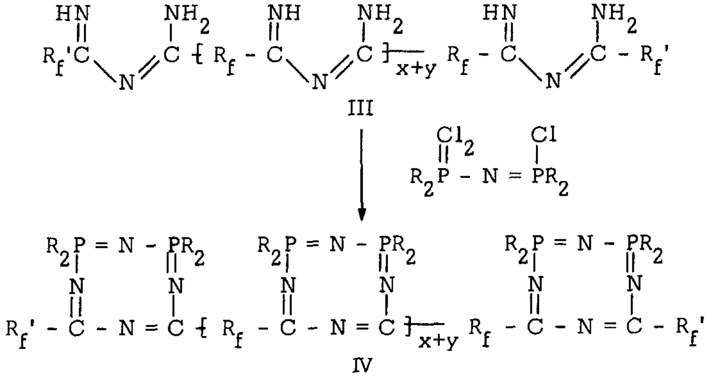
I



II

It is thus obvious that this process does not lend itself to polymer synthesis. The thermal and thermal oxidative stability of the materials containing the s-diphosphatetraazacyclooctatetraene unit, Table 1, was even lower than that of the pure monomeric compounds [1]. After exposure to 235°C in air, based on infrared analysis, all the octatetraene rings were destroyed, not transformed into diphospha-s-triazines. These results show clearly that the involatile nature of the components not only does not prevent degradation, but also alters the decomposition path leading to a more extensive breakdown.

Studies performed on the monocyclic octatetraenes have shown unsymmetrical isomers to be substantially more thermally stable than the symmetrical analogues [1]. The corresponding unsymmetrical polymers, IV, were synthesized from polyimidoylamidines, III, i.e.



$R_f = CF(CF_3)[OCF_2CF(CF_3)]_mO(CF_2)_5O[CF(CF_3)CF_2O]_nCF(CF_3)$, $m + n = 3$
The abbreviation used for this segment is 5-EDAF.
$R_f' = C_3F_7OCF(CF_3)$

The poly-u-diphosphatetraazacyclooctatetraene thus obtained exhibited thermal and thermal oxidative behavior directly comparable to that of the corresponding monocyclic compounds. At 235°C, the oxygen uptake and volatile production were minimal and molecular weight lowering was below 20% showing a low degree of degradation. However, at 316°C a drastic drop in molecular weight took place and, as shown by infrared spectral examination, all the octatetraene rings were transformed into monophospha-s-triazine moieties, via elimination of $(C_6H_5)_2PN$ units, in agreement with the results obtained for the monocyclic analogues.

TABLE 1

Degradation of symmetrical and unsymmetrical polydiphosphatetraazacyclooctatetraenes[a]

Compound	Temp °C	Atm	Starting material		Residue	Oxygen consumed		Volatiles	
			mg	MW	MW	mg	%[b]	mg	%[c]
s-poly$\{$5-EDAF-$C_2N_4P_2\Phi_4\}$	235	Air	445.6	3050	2030	6.1	86.1	23.9	5.4
s-poly$\{$5-EDAF-$C_2N_4P_2\Phi_4\}$	316	N_2	468.8	3050	n.d.[d]	n.a.[e]	n.a.	116.4	24.8
s-poly$\{$5-EDAF-$C_2N_4P_2\Phi_4\}$	316	Air	459.6	3050	n.d.	7.0	95.0	104.8	22.8
u-poly$\{$5-EDAF-$C_2N_4P_2\Phi_4\}$	235	Air	481.5	8700	7150	0.0	0.0	0.5	0.1
u-poly$\{$5-EDAF-$C_2N_4P_2\Phi_4\}$	316	N_2	467.6	8700	2450	n.a.	n.a.	15.4	3.3

a) All the tests were performed over a period of 24 hr. b) Percent of oxygen available. c) Weight percent of starting material. d) Not determined. e) Not applicable.

It is thus apparent that the polymer environment does not enhance the stability of the octatetraene materials. In the case of the symmetrical isomers, although no polymers were formed, the absence of potential monofunctional nitrile unit resulted in what appeared to be an altered degradation path.

EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air-sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means. Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 1330. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Stability Studies

The degradations were performed in sealed ampoules of ~ 50 ml volume over a period of 24 hr at the specified temperatures. The media studied were nitrogen and air; the gas pressures used were ~ 350 mm Hg at room temperature. The samples were introduced into the ampoules as Freon-113 solutions. The solvent was removed in vacuo and the sample dried at 50°C or above. At the conclusion of the experiment, the ampoules were cooled in liquid nitrogen and opened into the vacuum system and the volatiles measured and analyzed. The involatile residues were handled in an inert atmosphere enclosure to avoid any interferences from subsequent hydrolysis or oxidations in the case of purely thermal degradations. The residue itself was weighed and subjected to infrared spectral analyses and molecular weight determination.

Reaction of 5-EDAF-Bisamidine with Diphenyltrichlorophosphorane

A solution of the amidine, $H_2N(HN=)C\text{-5-EDAF}[(H_2N-)C=N-C(=NH)\text{-5-EDAF}]_{x<1}C(=NH)NH_2$ [3], (MW, 1600; 2.80 g, 1.73 mmol) and triethylamine (3.8 ml, 27.28 mmol) in Freon-113 (40 ml) was added over a period of 1.2 hr to a solution of diphenyltrichlorophosphorane (2.41 g, 8.27 mmol) in benzene (10 ml) at 50°C. The mixture was then stirred and heated at 50°C for 115.5 hr. Upon cooling, the solids were removed by filtration and washed with Freon-113. The filtrate was concentrated then filtered through a 1.5 x 5 cm column of Woelm neutral alumina to give, after solvent removal, a product (2.41 g, 60.3% yield); MW, 3050. Anal. Calcd. for di-octatetraene, $C_{88}H_{40}F_{72}N_8O_{10}P_4$: C, 36.94; H, 1.41; F, 47.81; N, 3.91; O, 5.59; P, 4.33; MW, 2861.05. Anal. Calcd. for octatetraene-phosphatriazine, $C_{76}H_{30}F_{72}N_7O_{10}P_3$: C, 34.29; H, 1.14; F, 51.39; N, 3.68; O, 6.01; P, 3.49; MW, 2661.86. Found: C, 38.19; H, 2.13; F, 48.02; N, 3.06; P, 4.22; MW, 3050.

Reaction of Poly-5-EDAF-Imidoylamidine with Imido-Tetraphenyl-Diphosphinic Acid Trichloride

A solution of the poly(polyimidoylamidine), $C_3F_7OCF(CF_3)[C(NH_2)=N-C(=NH)5\text{-EDAF}]_xC(=NH)N=C(NH_2)CF(CF_3)OC_3F_7$, (3.78 g, 0.60 mmol; MW, 6300 [3]) and triethylamine (1.7 ml, 12.19 mmol) in Freon-113 (12 ml) was added over a period of 1 hr to a solution of imido-tetraphenyldiphosphinic acid trichloride (2.28 g, 4.65 mmol) in acetonitrile (40 ml) at 50°C. The mixture was stirred and heated at 50°C for 70 hr. After cooling and solvent removal, the solid residue was tritiated with Freon-113 and the extracts filtered through a 1.5 x 4 cm column of Woelm neutral alumina resulting in a white solid (5.15 g, 98.1% yield), MW, 8700. Anal. Calcd. for $C_{273.16}H_{127.8}F_{216.04}O_{28.95}P_{12.78}$: C, 37.58; H, 1.48; F, 47.01; N, 4.10; O, 5.30; P, 4.53; MW, 8731.11. Found: C, 37.01; H, 1.55; F, 48.51; N, 4.11; P, 4.37.

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