not just compressed or expanded along the Γ axis with changing c, but changes its shape. Thus the particular average of the distribution function which is determined by either of the two methods ($\bar{\Gamma}_z$ or $\bar{\Gamma}$) will change with concentration. Clearly this case requires further study.

Acknowledgement

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Polymerization of hexachlorocyclotriphosphazene by sulphur and selenium

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The thermal bulk polymerization of hexachlorocyclotriphosphazine is described. The possibility of obtaining soluble polymer using sulphur and selenium as catalysts was investigated. It was found that the catalytic activity of selenium was much lower than that of sulphur. Monomeric sulphur may be acting as a chlorine-attractive agent for hexachlorocyclotriphosphazine.

Keywords Polymerization; bulk thermal; catalysis; sulphur; selenium; hexachlorocyclotriphosphazine

Introduction

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ polymerizes rapidly without gel formation, in glass or stainless steel reactors at 220°–290°C using catalysts[1] such as $AlCl_3$, $Et_3Al_2Cl_3$, Et_3Al, Et_2AlOEt, Br_3B, Al, B, Cr, Ni, Mg, Cu, Mn, Co or Fe. The polymerization of $(NPCl_2)_3$ in different solvents was reported by Retuert[2]. The present work describes the thermal bulk polymerization of $(NPCl_2)_3$ and the possibility of obtaining soluble polymer using sulphur and selenium as catalysts.

Experimental

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was prepared by reaction of phosphorus pentachloride with ammonium chloride in tetrachloroethane[3]. (M.pt. of pure trimer, 112°C.)

A mixture of hexachlorocyclotriphosphazene (2.5 g) and small amount of sylphur or selenium was placed in a pyrex tube (200 × 40 mm) which was then evacuated to 10 mm for 1 h, sealed and heated in an oven just below 300°C. When the polymerization was complete the product was treated with benzene and the polymer precipitated by addition of n-heptane using the method of Allcock[4]. Unreacted trimer was recovered by vacuum distillation. As the precipitated polydichlorophosphazene was unstable in water, chlorine in the polymer was substituted with a nucleophilic reagent by refluxing in benzene for 24 h. After the water was added to remove aniline hydrochloride formed during the reaction, the benzene solution was dried over anhydrous sodium sulphate.

The M_n and M_w of polydianilinophosphazene were determined by gel permeation chromatography using THF as the solvent.

Results and Discussion

The relation between yields of linear and crosslinked polymer or oligomer and reaction time at 250°C when 100 mg of sulphur was added is shown in *Figure 1*.

It is found that the maximum yield of linear polydianilinophosphazene occurs with a reaction time of 15 h, the recovered product is mostly hexachlorocyclotriphosphazene and crosslinked polymer is formed after 23 h. Yield of linear polydianilinophosphazene is shown in *Figure 2* when the amount of sulphur is changed and the reaction temperature and time are kept constant.

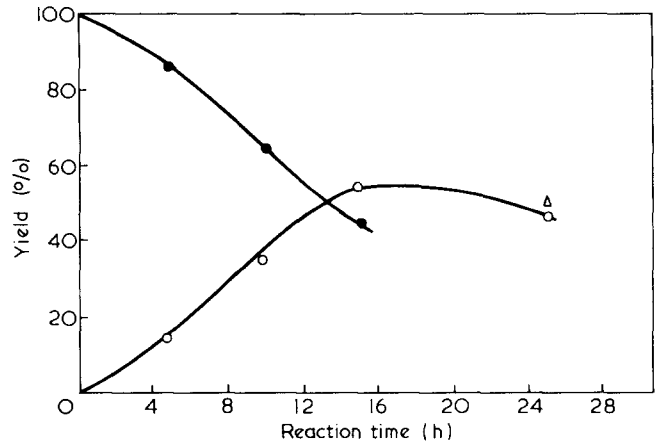

Figure 1 Relation between reaction time and oligomer (●), linear (○) or crosslinked polymer (△) using sulphur at 250°C. Linear polymer: $[NP(HNC_6H_5)_2]_n$

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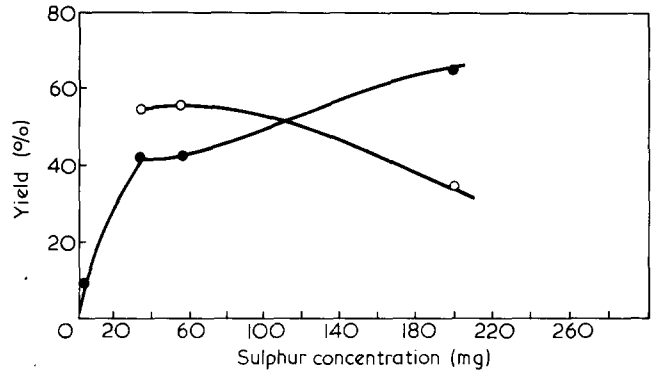

Figure 2 Relation between the concentration of sulphur and oligomer (○) or linear polymer (●) yield at 250°C for 7 h. Linear polymer: $[NP(HNC_6H_5)_2]_n$

Table 1 Yield of oligomer, linear and crosslinked polymers formed under various experimental conditions

Reaction temperature (°C)	Time (h)	Additive (mg)	Yield (%) (1)	(2)	(3)
290	1/3	S 100	42	58	0
	1	100	12	88	0
190	30	Se 100	100	0	0
	5	100	100	0	0
	1	100	40	15	46
	5/4	1	67	33	0
	8/3	5.7	74	27	0
	5	6.1	20	33	47
	5/4	10	73	27	0

(1) Oligomer (2) Linear polymer (3) Crosslinked polymer
Linear polymer; $[NP(HNC_6H_5)_2]_n$

It is clear that yield of linear polydianilinophosphazene is increased with the increased amount of sulphur. Also, the polymerization reaction is run for 1/3 or 1 h at 290°C using 100 mg of sulphur, and the results are summarized in *Table 1*.

The optimum conditions for the preparation of a linear polydianilinophosphazene is reaction at 290°C for 1 h using 100 mg sulphur with hexachlorocyclotriphosphazene (2.5 g). As selenium falls within the sulphur group of the periodic table, the polymerization of hexachlorocyclotriphosphazene may be accelerated. The yields of polydianilinophosphazene under various experimental conditions are summarized in *Table 1*.

It is found that the catalytic activity of selenium is much lower than that of sulphur.

The molecular weight distribution of the polymer is determined by gel permeation chromatography, and the results are shown in *Figure 3*. The polymer prepared with the addition of sulphur has a high molecular weight and is of the same order of magnitude as other polymers formed by thermal bulk polymerization.

The polymerization of $(NPCl_2)_3$ was reported by Allcock[5], where he also added sulphur to $(NPCl_2)_3$ which accelerated the polymerization but linear and crosslinked polydichlorophosphazene occurred together in the product. Generally it was recognized that sulphur was polymerized at temperatures above 115°C and the polymeric sulphur thus formed was depolymerized above 200°C. Monomeric sulphur formed by the depolymerization may be acting as chlorine-attractive agents for hexachlorocyclotriphosphazene.

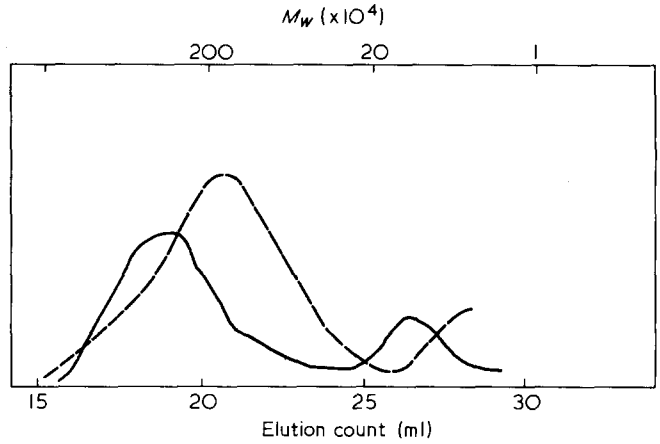

Figure 3 Molecular weight distribution curves of the polymer prepared using sulphur (——) and without additive (— — —). Linear polymer: $[NP(HNC_6H_5)_2]_n$

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