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The Solution Polymerization of Hexachlorocyclotriphosphazene

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Summary

The polymerization of hexachlorocyclotriphosphazene (trimer) is studied in different solvents. A soluble low molecular weight polymer is obtained when benzene is the solvent, a highly cross-linked polymer when cyclohexane is the solvent, and a mixture of soluble and insoluble polymers results when the solvent is chlorobenzene. The conversion-concentration curve for the trimer shows a dependence of the amount of soluble and insoluble polymer formed on the trimer concentration. No polymerization took place when the solvent was toluene, nitrobenzene or THF, but a reaction between solvent and trimer was detected.

Introduction

Hexachlorocyclotriphosphazene (trimer) has been used to prepare polydichlorophosphazene. The bulk and solution polymerization of this trimer have been reported in the literature, but the former has been studied more extensively and is the method currently used for the preparation of the polymers. The data on the conditions and mechanisms of polymerization are not yet well defined, except for the conditions reported by ALLCOCK et al.(1965,1966) for bulk polymerization.

The studies of solution polymerization are scarce.PATAT and KOLLINSKY (1951), working with different solvents, found that protonated solvents react with the trimer at 300°C to produce substituted oligomers of low molecular weight, and that in CCl_4 at the same temperature a soluble polymer having a molecular weight not greater than 130000 is obtained. KONECNY et al.(1960) studied the effect of catalysts on the polymerization of trimer in benzene at 210°C and did not observe any solvent effect. None of these papers discuss the possibility of any solvent effect on the polymerization process. This paper reports the results of some studies on the effect of solvents and concentration on the polymerization of trimer, and on the possibility of obtaining soluble polymers.

Results and discussion

Polymerizations were carried out in benzene, toluene, nitrobenzene, THF, and cyclohexane, with trimer concentrations varying between 20 and 80%. Since is known that water has a notorious catalytic effect on the bulk polymerization of the trimer (ALLCOCK et al.1966) special care in the dried of the solvents and the reactor vessel was necessary as is described in the experimental part. The most

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convenient time for the polymerization was found to be 48 hours, because some of the solutions would stop flowing if the process was allowed to continue for a longer time. A reaction temperature of 210°C was chosen in order to prevent the occurrence of substitution reactions between the solvent and the trimer.

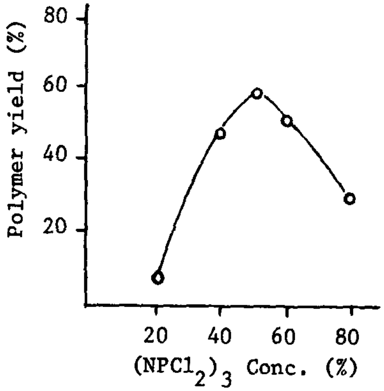

Fig.1 Polymerization in benzene. Influence of trimer concentration on soluble polymer yield.

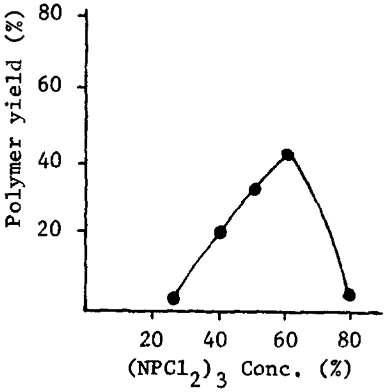

Fig.2 Polymerization in cyclohexane. Influence of trimer concentration on cross-linked polymer yield.

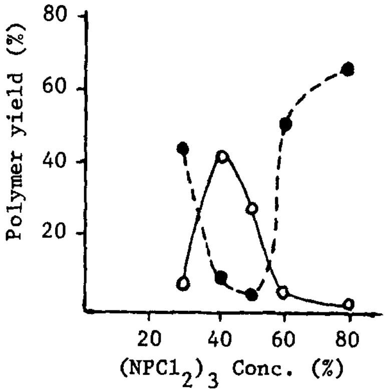

Fig.3 Polymerization in chlorobenzene. Influence of trimer concentration on the yield of soluble (o) and cross-linked polymer (●).

Toluene and nitrobenzene reacted considerably with the trimer, giving colored products of low molecular weight. No polymerization ocurred with THF. In cyclohexane, benzene and chlorobenzene there was no pressure build up and no evidence of solvent reaction with the trimer. Colorless polymers in which there was no incorporation of carbon and hydrogen were obtained by precipitation.

Polymerization in benzene. The polymerization of trimer at different concentration in benzene (Fig.1) produced only soluble polymers of low molecular weight (<10000) as determined from viscosity measurements.

Polymerization in cyclohexane. Fig. 2 shows the yield of polymer at different trimer concentrations. Only cross-linked polymers were obtained, even when the reaction time was reduced to twelve hours. The yield in this case was 11% for a 50% trimer concentration.

Polymerization in chlorobenzene. Mixtures of soluble and cross-linked polymers were obtained at all trimer concentrations in the proportions shown in Fig.3. The highest yield of soluble polymer, and the lowest of cross-linked polymer, was obtained when the concentration of trimer was in the range of 40% to 60%. In several experiments performed with a trimer concentration of 50% it was not possible to detect any cross-linked polymer. The soluble polymers were stable in toluene for relatively long periods (two or three days) and were of high molecular weight ($M_v = 2.6 \times 10^6$), in contrast to those obtained in benzene.

Bulk polymerization. Experiments performed in bulk showed that polymerization took place very slowly at 210°C, five or six days being required for yields of about 30%.

These results show that solvents such as benzene, chlorobenzene and cyclohexane do not react with the trimer at 210°C, but they do exert a definite influence on the course of the polymerization which is evidenced by an increase in the conversion dependent on the initial concentration of trimer.

KONECNY et.al.(1960) studied the polymerization in a 23% benzene solution of trimer at 210°C and did not detect any solvent effect. This may be due to the fact that under these conditions the presence of polymer is almost undetectable with reaction times of less than 25 hours. It is also quite clear that the solvent determines the type of polymer formed; only cross-linked product in cyclohexane and soluble product in benzene and chlorobenzene.

The effect of the solvent on the polymerization of trimer observed in the results of this work can be compared with the observations of PATAT and KOLLINSKY (1951) using CCl_4 as the solvent. Polymerization at 300°C with different trimer concentrations resulted in higher total yields than those obtained in bulk polymerizations under similar conditions of time and temperature. Soluble polymers with maximum molecular weights of 130000 were obtained in variable proportions.

The soluble polymers obtained in chlorobenzene have high molecular weights comparable to those of the products of bulk polymerization. This solvent effect would be in agreement with the assumption that the process is ionic (ALLCOCK and BEST 1964), (KONECNY and DOUGLAS 1959), and therefore a rather electrophilic solvent such as chlorobenzene should have a different effect on the polymerization than

a less electrophilic solvent like benzene or an inert one like cyclohexane. Cyclohexane may be considered to have a dilution effect with no interaction with the growing chains,thereby allowing crosslinking to take place.
The optimum trimer concentration in both benzene and cyclohexane falls within the range between 50% and 60%, which corresponds to one mole of trimer to every three or four moles of solvent. At these concentrations the probability that open or ionized trimer molecules can close again may be assumed to be low, thus favoring the initiation and propagation steps.

Experimental.

Preparation of hexachlorocyclotriphosphazene. A mixture of 104 g (0.5 mol) PCl_5, 27 g (0.5 mol) NH_4Cl and 7.5 g $POCl_3$ in 1 l.of 1,1,2,2-tetrachloroethane was heated under reflux for three hours. The resulting solution was cooled, filtered to remove unchanged NH_4Cl, and the solvent evaporated in a rotary vacuum evaporator. The product was extracted with light petroleum ether (b.p. 40-60°C), leaving behind insoluble materials and phosphonitrilic chlorides; the solution was filtered and the solvent evaporated in a rotary vacuum evaporator. Cyclic phosphonitrilic chlorides were composed of aproximately 80% trimer and 20% tetramer which were separated by vacuum sublimation at 50°C. The more volatile fraction of crude trimer was recrystallized from n-heptane, and finally sublimed again. The pure compound, m.p. 113°C, was stored under vacuum until used. The products were identified by their ^{31}P-NMR spectra, obtained on a Varian XL-100 spectrometer.
Polymerization. The solvents (E.Merck, reagent grade) were kept 24 hours over sodium, then refluxed over sodium for ten hours, fractionally distilled twice, and stored over calcium hydride until used. Polymerization was carried out in 10 ml sealed tubes that were kept 10 hours at 250°C and 10^{-4} Torr prior to being used. One gram of trimer was then placed in the tube and the system evacuated to 10^{-4} Torr for two hours. The tube was then immersed in liquid nitrogen and the required amount of solvent distilled into it, and then it was evacuated for one hour and sealed under vacuum. The tubes were kept in an oven at 210°C for the required time. When polymerization was completed (after about 48 hours) the contents of the tubes were treated with benzene and the polymers precipitated by adding an excess of n-heptane (ALLCOCK et al, 1966). The unreacted trimer was recovered by vacuum distillation.
Intrinsic viscosity. Measurements were made on toluene solutions at 26.5 ± 0.05 °C in an Ubbelohde viscometer having a flow time of 206.9 seconds for this solvent. Molecular weights were determined from the intrinsic viscosity by means of the equation (PATAT and KOLLINSKY 1951), $\eta = 1.65 \times 10^{-5} M_n^{0.69}$

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