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 CCl₄ at the same temperature a soluble polymer having a molecular weight not greater than 130000 is obtained. Konceny 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 it 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
convenient time for the polymerization was found to be 48 hours, be-
cause 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 cyclo-
hexane. Influence of trimer
concentration on cross-linked
polymer yield.

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