Polymer Bulletin 6, 535–539 (1982)

Polymer Bulletin

Solution Polymerization of Phosphonitrilic Chloride Trimer in Chlorobenzene

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SUMMARY

The solution polymerization of phosphonitrilic chloride trimer has been studied by using 50% by weight monomer in chlorobenzene. Polymerization reactions were conducted at temperatures between 198° and 240°C, and reaction times ranged from 12 to 96 h. Mostly soluble polymer was obtained up to a conversion of 30%; insoluble product was detected only above 240°C and 72 h. of reaction time. Polymers were characterised by intrinsic viscosity and weight average molecular weight, Mw, by light scattering (Zimm plot).

INTRODUCTION

Thermal polymerization of phosphonitrilic chloride trimer, $(PNCl_2)_3$ has been studied extensively (Allcock et al. 1964, 1965) leading to high molecular weight open-chain polydichlorophosphazene. Temperatures in bulk polymerization usually ranged from 245 to 270°C (Allcock et al. 1965) and a mixture of soluble and crosslinked products has been obtained.

Solution polymerization, on the other hand, has received little attention. Solvents like carbon tetrachloride and benzene have been studied in connection with polymerization of $(PNCl_2)_3$, but low molecular weight are reported (Patat 1951). Recently, the effect of several solvents on polymerization of phosphonitrilic chloride trimer was reported. (Retuert et al. 1979). The monomer concentration seems to have an important role in the yield of soluble polymers. In this report, we describe the results of solution polymerization of $(PNCl_2)_3$ in chlorobenzene (50 wt.% monomer) at temperatures from 198 to 240°C and reaction times ranging from 12 h. to 96 h.

EXPERIMENTAL

Phosphonitrilic chloride trimer was sublimed twice under vacuum (10^{-3} mmHg) at 50°C and recrystallized from n-heptane. Solvents were purified according to conventional methods.

The polymerization reactions were carried out in glass ampoules sealed under vacumm (10^{-4} mm Hg). A known amount of chlorobenzene was distilled through the vacuum line into a glass ampoule containing the weighed trimer (in order to have a 50% monomer). The whole system was evacuated and, repeated freeze-thawing cycles were applied. Finally the tubes were sealed under vacuum and placed into a constant-temperature bath.

0170-0839/82/0006/0535/$ 01.00

After a suitable reaction time, the glass ampoules were opened and the content poured into dry benzene and precipitated into a large excess of n-heptane (yields were calculated from unreacted trimer and soluble polymer).

Toluene solutions of polymer were prepared for weight average molecular weight measurements. $\bar{M}w$ was determined by light scattering (Brice-Phoenix apparatus, Model 2000, λ = 436nm.) Intrinsic viscosities were measured by a Ubbelohde viscometer at 25°C ± 0.02 in toluene solution.

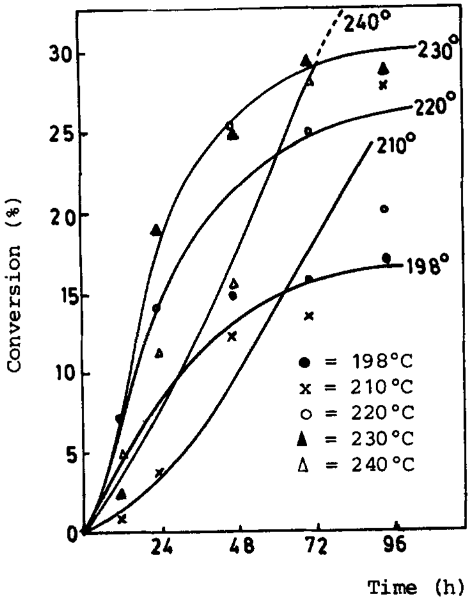
RESULTS AND DISCUSSION

Results of polymerizations are shown in Figures 1 and 2. Table 1 gives intrinsic viscosity and molecular weight data determined by Zimm method. Figure 3 shows a typical Zimm plot obtained for the 96 h. polymerization of $(PNCl_2)_3$ at 210°C.

The dependence of polymer yield upon reaction time at different temperatures is shown in Figure 1. It is important to point out that this yield corresponds to soluble material; since crosslinked polymer was almost undetectable. The yields have a tendency to reach a maximun and then decrease.

Polymerization reactions carried out at 240°C and above 72 h. showed the appearance of insoluble material. In this case conversion over 90% was attained. In fig. 2 the dependence of polymer yield with reaction temperature is reported. Increasing yields are observable, reaching a maximun around 230°C. The results can be interpreted similar to bulk polymerization and taking into account that the solvent influences the reaction rate. Conductance data show that $(PNCl_2)_3$ conductivity begins to increase at 202°C and becomes strong around 220°C (Allcock 1964). This phenomenon suggests an ionic mechanism and would explain the yield maximun obtained at a given temperature. With temperatures under 240°C, the chlorobenzene would provide an adequate medium for propagation. In this way chain-to-chain interaction may be avoided and mostly soluble and high molecular weight polymer is obtained. The appearance of crosslinked material after 72 h. at 240°C may be interpreted as follows : at 240°C the number of ionized $(PNCl_2)_3$ molecules has increased notably. These ionized molecules may initiate chain-propagation toward high molecular weight polymers or displace the monomer-chain equilibrium toward the monomer by cyclization. This latter phenomenon has been observed in bulk polymerization (Allcock 1966). Up to 72 h. of reaction time the second alternative is the more probable since low yield of soluble polymer is obtained. At reaction times greater than 72 h., where soluble polymer yields are significant (30%), because many ionized $(PNCl_2)_3$ molecules still remain, the system presumably would move toward high conversions of crosslinked polymer.

Results of intrinsic viscosities and molecular weights of different experiments are collected in Table 1. A tendency is observed to obtain relatively higher viscosity values with increasing reaction time and temperature. By considering a linear model of polymer chain, this increase in viscosity should correspond to an increase in molecular weight, however, this relation was not found, as is observed in Table 1. This fact may be due to a high degree of branching in the polymer chain or to gel formation involving the hydrolytically unstable P-Cl bonds. Zimm plots can be obtained for molecular weight determinations as is shown in Fig. 3



--- = Crosslinked polymer

Fig. 1. Conversion versus reaction times for soluble polydichlorophosphazene, obtained from thermal polymerization of $(PNCl_2)_3$ in chlorobenzene (50 wt%)

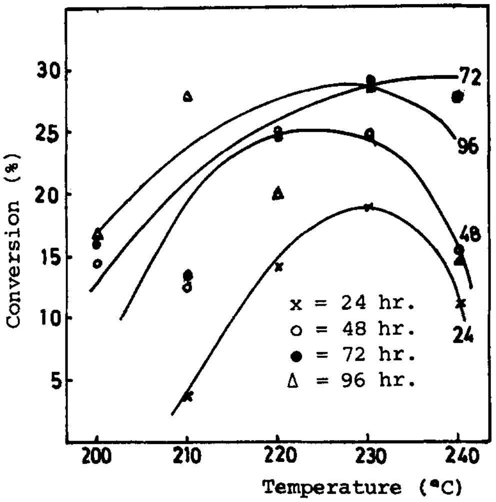


Fig. 2. Conversion versus temperature for soluble polydichlorophosphazene, obtained from thermal polymerization of $(PNCl_2)_3$ in chlorobenzene

TABLE 1

Characterization of $(PNCl_2)_n$ samples

Exp. N°	Temperature	Time (hours)	$[\eta]^a$ dl/g	Mw x 10^{-6}
10	198°C	48	0.135	-----
11		72	0.215	-----
12		96	0.140	-----
13	210°C	12	-----	-----
14		24	0.133	-----
15		48	0.221	0.915
16		72	0.315	0.435
17		96	0.531	1.550
18	220°C	48	0.453	3.029
19		72	0.375	3.887
20		96	0.444	-----
21	230°C	24	0.185	2.570
22		48	0.297	1.590
23		72	0.474	0.960
24		96	0.484	0.930
25	240°C	24	0.360	4.710
26		48	0.400	4.730
27		72	0.550	2.770
28		96	0.450	9.420

a : Toluene, 25°C

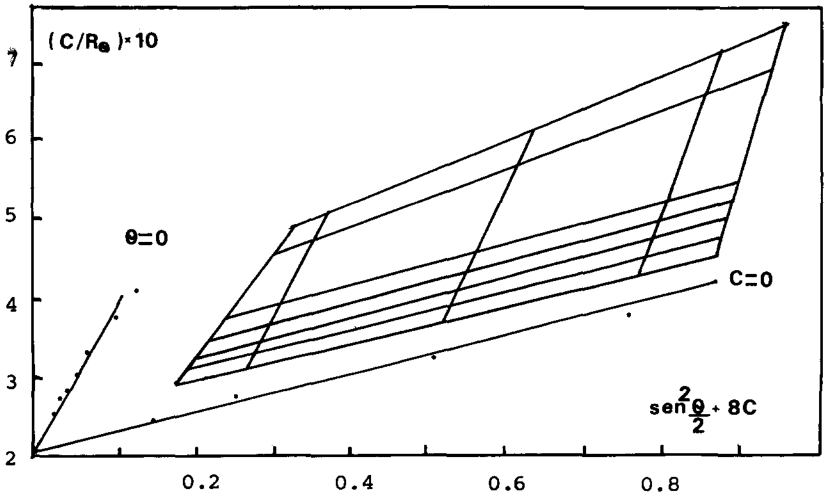


Fig. 3. Zimm plot for polydichloro phosphazene obtained from thermal polymerization of $(PNCl_2)_3$ in chlorobenzene (50 wt%) at 210°C and 96 h. ($\bar{M}w$ = 1.53 x 10^6, $[\eta]$ = 0.53 (dl/g) in toluene 25°C)

(experiment N°17) provided the polymer concentration is less than 1 wt %. Since molecular weight measurements were possible nearly in all cases and also broad molecular weight distribution have been reported in phosphazene derivatives (Singler et al. 1974, Allen et al. 1970), we think that branched polymer, and obviously broad molecular weight distributions are responsible for the relative low intrinsic viscosity values and for the lack of correlation between η and molecular weight.

ACKNOWLEDGMENTS.

This research was supported in part by the Servicio de Desarrollo Científico y Creación Artística de la Universidad de Chile. Authors are indebted to Dr. Deodato Radic for dn/dc determinations.

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Accepted February 3, 1982

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