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Dehydrochlorination of Poly(vinyl Chloride) in Pyridine. I. Effect of Conditions

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ABSTRACT

Poly(vinyl chloride) (PVC) was dehydrochlorinated thermally in pyridine solution under N_2 atmosphere and the effect of variation of reaction time, temperature, and concentration of PVC in pyridine was studied. The extent of dehydrochlorination (or conversion, x%) increases with an increase in reaction time and temperature, and with a decrease in the concentration of PVC. Incomplete precipitation of dehydrochlorinated PVC (DHPVC) occurs by nonsolvent (methanol). During dehydrochlorination there is no HCl evolution as it forms a pyridine hydrochloride complex which is supposed to act as a catalyst for dehydrochlorination. A possible mechanism has been proposed. Chain scission and cross-linking reactions are responsible for the molecular weight changes that take place during the reaction.

INTRODUCTION

Dehydrochlorination of PVC has been carried out either in the solid state or in solution by thermal [1-3], radiation-induced, and photochemical initiation [3]. It has also been carried out by using basic catalyst [4-7]. Pyridine, a weak base, has been used for dehydrochlorination of PVC in a study of free radical initiated grafting of styrene onto the product [8]. However, no detailed study has been reported so far on the dehydrochlorination of PVC in pyridine. In the present investigation, dehydrochlorination in pyridine has been carried out and the effect of various parameters evaluated.

EXPERIMENTAL

Materials

A.R. grade tetrahydrofuran (E. Merck) was purified as follows: Tetrahydrofuran (THF) was refluxed over sodium borohydride until no peroxide could be detected. It was then distilled under nitrogen from metallic sodium [9]. Twice distilled THF was used as the solvent for spectroscopic measurements.

A.R. grade pyridine (BDH) was purified by refluxing it over sodium hydroxide pellets and then distilling with careful exclusion of moisture.

A.R. grade methanol and petroleum ether were distilled once and used as precipitants.

SR-10A grade PVC, supplied by Sri Ram Institute, New Delhi, India, with the following specification was used: $\overline{M}_n$, 43,385.5; $\overline{M}_w$, 96,520.6; H (heterogeneity Index), 2.23; and number of chlorine atoms × 10^3/g PVC, 15.46. $\overline{M}_n$, $\overline{M}_w$, and H all were determined by a Waters Associates GPC instrument. The unit was operated with THF as carrier solvent at 25 ± 3°C using styragel columns with pore sizes of 10^4, 10^3, and 500 Å. Flow rates of 2 mL/min and chart speeds of 0.75 in./min were maintained in all experiments. Approximately 0.4% solution of PVC in THF was prepared.

PVC ($\overline{DP}$ = 1544) was purified as follows: PVC was dissolved in purified THF under vigorous stirring. After being refluxed for 2 h, the solution was passed through 2G glass filter to remove the impurities. MeOH was added to the filtrate and the precipitate was filtered out with 3G glass filter. The purified PVC was dried 24 h in vacuum at room temperature [10].

Method of Dehydrochlorination

Purified PVC in dried and distilled pyridine was refluxed in nitrogen atmosphere to achieve dehydrochlorination [8, 11]. DHPVC was precipitated in methanol, filtered, washed with methanol, and dried in vacuum at 50°C to constant weight. Dehydrochlorinated PVC thus obtained was purified by dissolving it in THF and precipitating by petroleum ether.

Chlorine Estimation

Chlorine estimation of PVC and DHPVC was carried out by Bomb calorimetric method [12].

RESULTS AND DISCUSSION

The dehydrochlorination reaction was carried out in inert atmosphere to avoid the presence of oxygen which leads to less intense discoloration due to short polyene sequences formed and chain scission [13].

The reaction solution changed from colorless to reddish-brown color through yellow, orange, and red as the heating continued. Discoloration of PVC during dehydrochlorination is explained by the development of conjugated double bonds (polyene sequences) in polymeric chains [10].

Though the color became dark, no acidity could be detected in the carrier gas which was passed into water to dissolve any evolved HCl. No evolution of HCl had been detected in a similar reaction using N,N-dimethylformamide (DMF) instead of pyridine, and it was suggested that this is due to DMF-HCl complex formation [7, 14]. Formation of pyridine hydrochloride can similarly take place in the present system, thus accounting for nonevolution of HCl.

During precipitation of DHPVC from the reaction solution by methanol, a major part was precipitated out, leaving a small amount in solution. On removal of methanol and pyridine by careful evaporation of this solution, the remaining DHPVC could be recovered. The sum of two portions was of practically the same weight as that of the original PVC used for the reaction. Thus, during the reaction, no gaseous or liquid product was formed.

The degree of dehydrochlorination or conversion, x% was calculated as the ratio between the chlorine atoms lost from PVC and total available amount per g of PVC [15].

Effect of Reaction Temperature on Dehydrochlorination

PVC was dehydrochlorinated in pyridine solution at a concentration of 41.7 g/L for 135 min at different temperatures. The results are presented in Table 1 and Fig. 1.

From Table 1 it can be seen that with an increase in temperature, there is an increase in the amount of DHPVC. This continuous increase in the precipitated material clearly indicates the formation of an increasing amount of high molecular weight product. At higher temperature the very high molecular weight product separates from the reaction mixture [15]. The increasing amount of this highly

TABLE 1. DHPVC Yield (%) and Conversion X (%) as Functions of the Reaction Temperature for a Solution of PVC in Pyridine (41.7 g/L), Dehydrochlorinated for 135 min

Dehydrochlorination temperature (°C)	Total yield (%) (MeOH precipitated + cross-linked)	Total yield (%)		No. of chlorine atoms × 10^3/g DHPVC	Conversion X (%)
		Methanol-precipitated DHPVC yield (%)	Cross-linked product (separated in reaction) yield (%)		
120	89.6	89.6	0	14.90	3.62
125	91.2	91.2	0	14.87	3.82
135	95.2	68.4	26.8	14.82	4.14
150	95.6	66.4	29.2	14.59	5.63

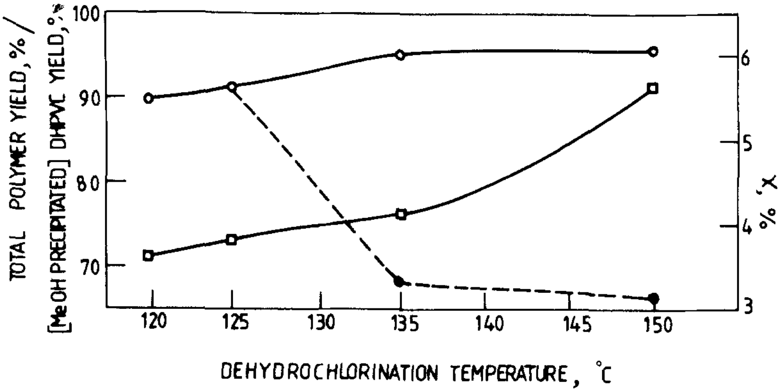


FIG. 1. Change in total polymer yield, [MeOH precipitated] DHPVC yield, and conversion x as a function of reaction temperature. (○) Total polymer yield, %. (●) [MeOH precipitated] DHPVC yield, %. (□) Conversion x, %.

insoluble product (Table 1) can only take place if intermolecular reactions (leading to cross-linking) occur in a considerable amount. With an increase in reaction temperature, there is an increase in % conversion (Fig. 1). This was also observed by Tishuchida et al. [6] in dehydrochlorination of PVC by alkali amide in liquid ammonia. With an increase in % conversion there will be more chance of polyene formation which at higher temperature can easily undergo cross-linking reactions. As the proportion of this cross-linked product increases with an increase in temperature, there is a corresponding decrease in the amount of DHPVC (Fig. 1).

Effect of PVC Concentration on Dehydrochlorination

PVC was dehydrochlorinated in pyridine solution at 120°C for 135 min in N_2 atmosphere using various concentrations of PVC in pyridine. The results are presented in Table 2 and Fig. 2.

From Table 2 it can be clearly seen that with an increase in the concentration of PVC in the reaction mixture, there is an increase in the precipitated amount of DHPVC. This indicates a tendency toward more chain scission (thus producing an increasing amount of low molecular weight product) with a decrease in concentration. Similar results were obtained by Shindo and Hirai [10] in a dehydrochlorination reaction between THF solution of PVC and alcoholic KOH. However, % conversion decreases initially at a faster rate and then becomes almost constant with an increase in the concentration of PVC as observed in the base-catalyzed dehydrochlorination of PVC [6].

TABLE 2. DHPVC Yield (%) and Conversion X (%) as a Function of PVC Concentration in Dehydrochlorination Reaction at 120°C for 135 min

PVC concentration in pyridine (g/L)	DHPVC (precipitated by methanol) yield (%)	No. of chlorine atoms × 10^3/g DHPVC	Conversion X (%)
25.0	15.2	14.68	5.10
28.0	54.8	14.79	4.34
31.3	64.0	14.87	3.82
41.7	89.6	14.90	3.62

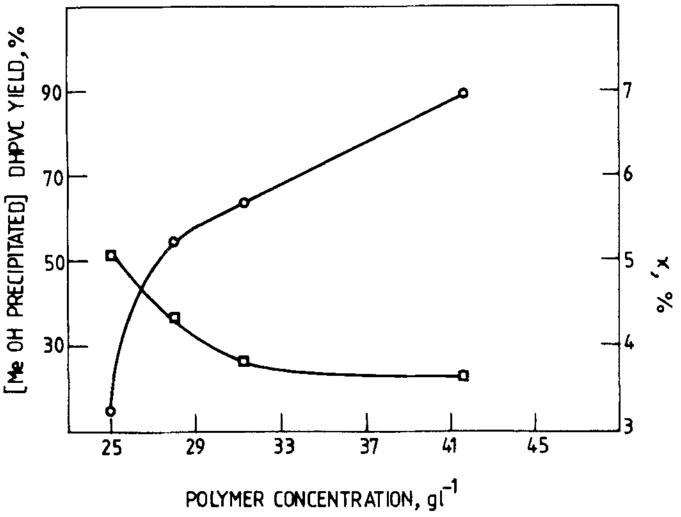


FIG. 2. Change in [MeOH precipitated] DHPVC yield and conversion x as a function of PVC concentration in dehydrochlorination reaction. (○) [MeOH precipitated] DHPVC yield, %. (□) Conversion x, %.

TABLE 3. DHPVC Yield (%) and Conversion X (%) as a Function of Heating Time for a Solution of PVC in Pyridine (41.7 g/L) Dehydrochlorinated at 120° C

Dehydro-chlorination, time (min)	DHPVC (precipitated by methanol) yield (%)	No. of chlorine atoms $\times 10^3$/g DHPVC	Conversion X (%)
45	90.5	15.13	2.13
90	88.0	14.93	3.42
135	89.6	14.90	3.62
180	90.0	14.76	4.53

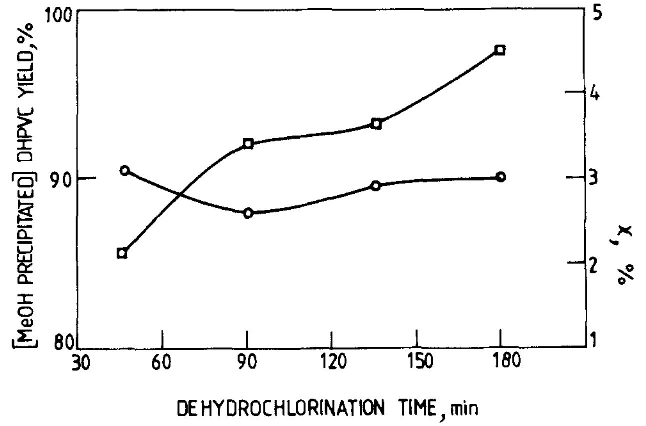


FIG. 3. Change in [MeOH precipitated] DHPVC yield and conversion x as a function of reaction time. (○) [MeOH precipitated] DHPVC yield, %. (□) Conversion x, %.

Effect of Reaction Time on Dehydrochlorination

PVC was dehydrochlorinated in pyridine solution using a PVC concentration of 41.7 g/L at 120°C in an N_2 atmosphere for different time periods and the results are presented in Table 3 and Fig. 3.

It can be seen from Table 3 that the precipitated amount of DHPVC is approximately 90%, irrespective of reaction time. However, % conversion increases continuously with an increase in reaction time (Fig. 3). Similar results were observed by Tsuchida et al. [6] in the base-catalyzed dehydrochlorination of PVC.

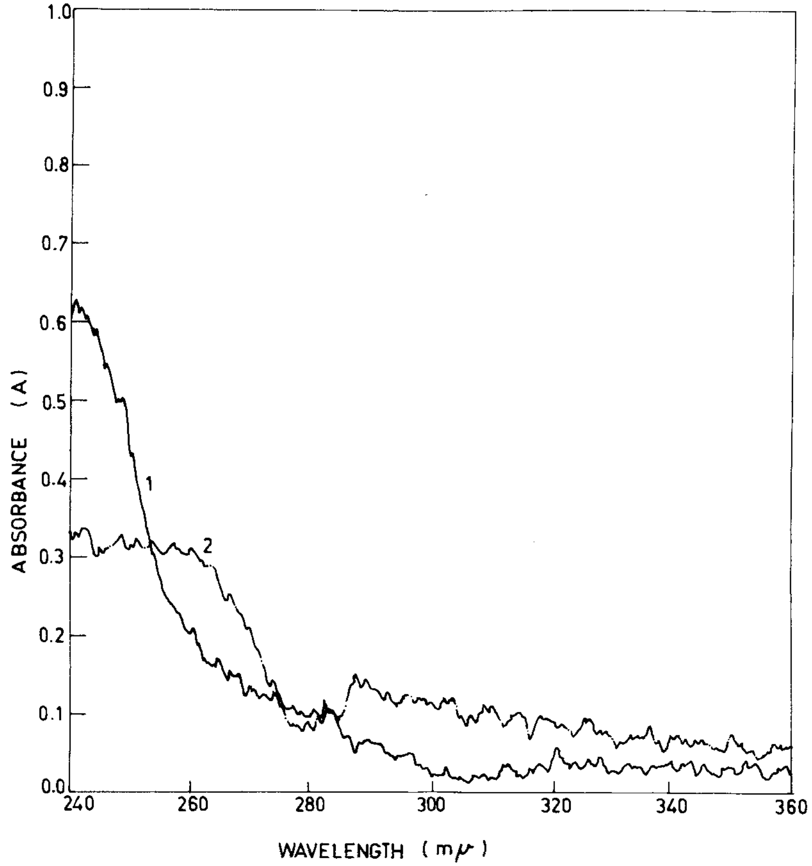


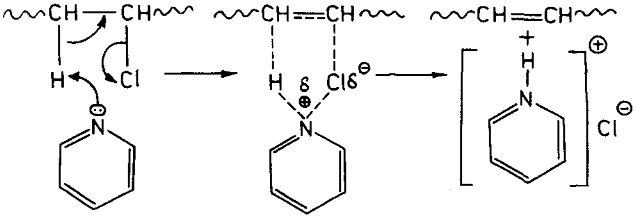
FIG. 4. Ultraviolet absorption spectra for DHPVC prepared in DMF and pyridine under identical conditions. Time = 90 min. Temperature = 120° C. PVC concentration in pyridine or DMF = 41.7 g/L. (1) UV spectra for DHPVC prepared in DMF. (2) UV spectra for DHPVC prepared in pyridine.

The mechanism of dehydrochlorination of PVC is a well-studied phenomenon but nevertheless it has not been conclusively established. It has been reported earlier that dehydrochlorination is accompanied by chain scission and cross-linking reactions [13]. These are the subsequent processes which are set in by the loss of HCl from PVC and are responsible for the molecular weight changes in the reaction. For the formation of polyene sequences in inert atmosphere, several mechanisms such as radical [16-18], ionic [17, 19], and unimolecular [17, 20] have been proposed.

However, Bengough and Grant [14], in a study of thermal dehydrochlorination of PVC in DMF solution, found that dehydrochlorination was very fast in DMF as compared to other solvents. This was due to solvent-polymer interaction due to basicity of the solvent. A DMF-HCl complex was formed which catalyzed the reaction. Pyridine, due to its basic character, acts in a similar way. This was found to be the case by the similarity in the UV spectra of dehydrochlorinated PVC prepared in pyridine and DMF under identical conditions: time = 90 min, temperature = 120°C, PVC concentration in pyridine or DMF = 41.7 g/L (Fig. 4).

Although the solubility parameters of PVC and pyridine are not very close (9.4 and 10.7, respectively), PVC is readily soluble in pyridine. It is possible only if there is some interaction between PVC and pyridine. The solution of PVC in DMF as observed by Bengough and Grant [14] is similar.

It was concluded from the above results that due to the interaction between pyridine and polymer, an intermediate was formed which facilitated the elimination of HCl. The latter was eliminated as pyridine hydrochloride rather than as the free acid:



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