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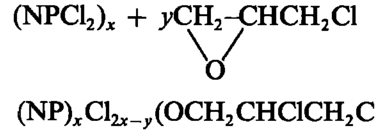
The reaction between poly(dichlorophosphazene) and epoxide compounds using Friedel–Crafts catalysts

M. KAJIWARA, K. SHIOMOTO
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

The reaction between poly(dichlorophosphazene) and epichlorohydrin was carried out in tetrachloroethane using various Friedel–Crafts type catalysts. It was found that ferric chloride, $FeCl_3$, is the most suitable catalyst to transfer chlorine from poly(dichlorophosphazene) to –CH in epoxide compounds. The molecular weight of the prepared product had decreased in comparison with that of poly(dichlorophosphazene); however, the products having the highest molecular weight were prepared with epifluorohydrin or 1,2-epoxy-3,3,3,-trichloropropane.

1. Introduction

Generally, poly(organophosphazenes) have been synthesized by the reaction of poly(dichlorophosphazene) $(NPCl_2)_n$ and nucleophilic reagents such as alkoxides, phenoxides or amines. In this reaction type, chlorine in the poly(dichlorophosphazene) is eliminated as sodium chloride or hydrogen chloride. It is necessary to find a new reaction method without conventional techniques, in which chlorine in poly(chlorophosphazene) could be efficiently used. Laszliewicz and Struszczyk [1] described how hexachlorocyclotriphosphazene, octachlorocyclo-tetrachlorophosphazene or dichlorophosphazene oligomer $(NPCl_2)_m$ can be allowed to react with epichlorohydrin. They believed that the reaction will occur using anhydrous aluminium chloride in tetrachloroethane as shown in Scheme 1 ($x = 3$):



$$(NPCl_2)_x + y\underset{\diagdown O \diagup}{CH_2\text{—}CHCH_2Cl} = (NP)_xCl_{2x-y}(OCH_2CHClCH_2Cl)_y \qquad (1)$$

However, they could not find suitable conditions to transfer chlorine from $-PCl_2$ to the –CH group and did not study the reaction between poly(dichlorophosphazene) and epichlorohydrin.

The object of this report is to explore the satisfactory conditions to transfer chlorine from $-PCl_2$ in poly(dichlorophosphazene) to the –CH group in the epoxide compounds, such as epichlorohydrin, using Friedel–Crafts type catalysts.

2. Experimental procedure

2.1. Preparation of cyclodichlorophosphazene $(NPCl_2)_3$ and poly(dichlorophosphazene) $(NPCl_2)_n$

$(NPCl_2)_3$ was prepared and purified by the method of Saito and Kajiwara [2]. $(NPCl_2)_n$ was synthesized with the solution polymerization as reported by Kajiwara and Shiomoto [3] and is described below.

$(NPCl_2)_3$ (5 g) and sodium dibutyl dithiocarbamate (100 mg) were placed in a three-necked flask equipped with stirrer and condenser, which was then evacuated at 10 torr for 1 h. Then *o*-dichlorobenzene (5 g) was added to the flask, and the mixture was heated to 190° C for 24 h in a flow of dry nitrogen. After the reaction was complete, the method of Allcock and Best [4] was used to separate linear poly(dichlorophosphazene) $(NPCl_2)_n$.

2.2. The reaction of poly(dichlorophosphazene) $(NPCl_2)_n$ with 2,3-dichloro-1-propanol

The reaction of $(NPCl_2)_n$ with 2,3-dichloro-1-propanol, $CH_2ClCHClCH_2OH$, was carried out in tetrahydrofuran (THF) at 60° C for 24 h using triethylamine as a hydrogen chloride acceptor. Since poly(dichlorophosphazene) is hydrolysed, the reaction was carried out in a flow of dried nitrogen gas. After the reaction was over, triethylamine hydrochloride was removed by filtration, and the filtrate was evaporated under reduced pressure. When the condensed solution was added to n-heptane, the dark straw-coloured and viscous liquid was isolated. The product was dried under reduced pressure for 24 h at room temperature.

2.3. The reaction of poly(dichlorophosphazene) $(NPCl_2)_n$ with epichlorohydrin and other epoxide compounds in tetrachloroethane

Tetrachloroethane including 5 wt % of poly(dichlorophosphazene) and catalysts such as $AlCl_3$ or $FeCl_3$ were kept in the three-necked flask (mole ratio of catalyst to $NPCl_2$: 0.5) and the reaction mixture was vigorously stirred at 80° C for 1 h. Then, 3 mol epichlorohydrin or other epoxide compounds were put into the flask and the reaction temperature was raised slowly to 100° C. The reaction was carried out for 24 h at the same temperature, and then tetrachloroethane was evaporated under vacuum. The obtained product

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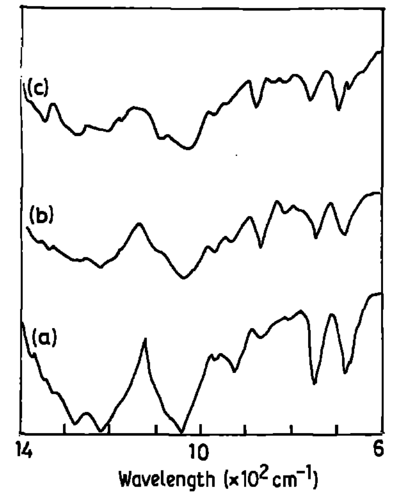

Figure 1 Infrared absorption spectra of the products: (a) $[NP(OCH_2CHClCH_2Cl)_2]_n$, (b) Product I, (c) Product II prepared using $FeCl_3$ and epichlorohydrin.

was dissolved in carbon tetrachloride and was washed successively with dilute hydrogen chloride, sodium carbonate aqueous solution, and water. The carbon tetrachloride solution dehydrated by anhydrous sodium sulphate was refluxed overnight with activated charcoal powder. When the decoloured carbon tetrachloride solution was added to n-hepatane, Product I was precipitated. The product which was insoluble in carbon tetrachloride was extracted with THF. After treatment with activated charcoal it was added to n-heptane. The precipitated Product II was removed by filtration. Also styrene oxide, butylene oxide and epifluorohydrin were used.

2.4. Analysis

The products were analysed by infrared absorption spectra, ^1H-nuclear magnetic (NMR), gel permeation chromatography (GPC), differential calorimetry (DTA) and thermal analysis (TG). The instruments used in this study were Shimazu IR-450, JNM PMY-60, Toso 60B, and Shimazu microthermal analyser DF-20B, SC-20, respectively.

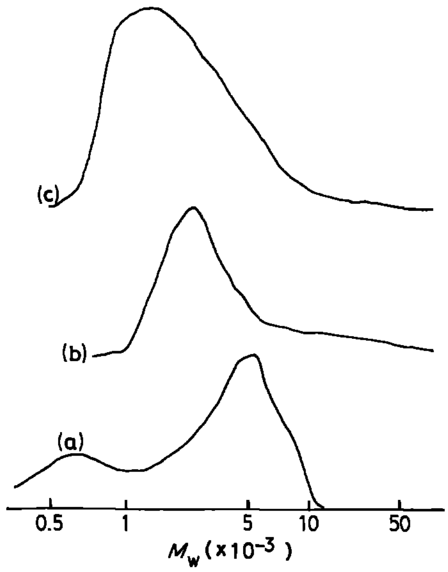

Figure 2 GPC curves of the products: (a) $[NP(OCH_2CHClCH_2Cl)_2]_n$, (b) Product I prepared using $FeCl_3$ and epichlorohydrin, (c) Product II prepared using $FeCl_3$ and epichlorohydrin.

3. Results and discussion

3.1. Reaction of poly(dichlorophosphazene) with 2,3-dichloro-1-propanol

The product is a dark straw-coloured and viscous liquid. Density and refractive index of the product are 1.4 to 1.46 g cm^{-3}, and 1.498 to 1.529, respectively. The IR absorption spectra of the product are shown in Fig. 1a. (i) 1230 cm^{-1} or 870 cm^{-1}, (ii) 1380 cm^{-1} and 740 cm^{-1}, (iii) 1290 cm^{-1}, (iv) 1060 cm^{-1} and (v) 680 cm^{-1} are attributed to P–N, $-CH_2$, $-CH_2Cl$, P–OC and C–Cl, respectively.

The molecular weight distribution curve of the product using THF is given in Fig. 2a and the weight- or number-average molecular weight of the product estimated from the curve is summarized in Table I. The product formed in this study has low molecular weight in comparison with the high molecular weight of poly(dichlorophosphazene) and other poly(organophosphazenes) prepared under the same experimental conditions [3].

TABLE I The yield or weight- and number-average molecular weight of the Proucts I and II

R in $(NPR_2)_n$	Reaction		$(NPCl_2)_n$ (g)	Catalyst	Product I			Product II		
	°C	h			Yield (g)	$\bar{M}_w$ (×10^{-3})	$\bar{M}_n$ (×10^{-3})	Yield (g)	$\bar{M}_w$ (×10^{-3})	$\bar{M}_n$ (×10^{-3})
2,3-Dichloro-1-propanol	40	72	2.6	–	3.8	–	–	–	9.5	4.1
	60	72	1.8	–	2.8	–	–	–	4.3	3.1
Epichlorohydrin	100	24	1.7	$SnCl_4$	1.8	2.6	0.95	2.0	6.3	1.7
			2.4	$TeCl_4$	0.5	–	–	1.0	3.6	1.8
			3.5	$TiCl_4$	0.3	–	–	–	19.6	2.2
			2.2	$BiCl_3$	0.1	–	–	–	–	–
			4.6	AlF_3	–	–	–	0.9	1.9	1.4
			4.2	$AlCl_3$	4.7	1.3	0.8	–	–	–
			5.4	$AlBr_3$	2.8	–	–	0.9	2.2	1.7
			5.8	$FeCl_3$	2.3	7.5	1.6	7.8	11.8	2.1
			2.1	$MgCl_2$	0.3	–	–	–	–	–
			2.6	$CuCl_2$	0.3	2.6	1.5	3.1	3.7	1.7

TABLE II The yield or weight- and number-average molecular weights of Products I and II

R in $(NPR_2)_n$	Reaction		$(NPCl_2)_n$ (g)	Product I			Product II		
	°C	h		Yield (g)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_n$ ($\times 10^{-3}$)	Yield (g)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_n$ ($\times 10^{-3}$)
Styrene oxide	100	24	6.0	2.7	2.4	1.9	1.4	3.3	2.0
Butylene oxide	100	24	4.8	1.9	–	–	2.4	5.0	2.2
Epifluorohydrin	100	24	1.7	1.3	21.3	0.4	0.9	29.5	0.4
1,2-epoxy-3,3,3-trichloropropane	100	24	2.2	0.4	37.6	1.3	1.1	39.4	0.8

^{1}H-NMR of the product was determined. The $-CH_2Cl$ signal appears at 3.7 p.p.m., the $-CHCl$ at 3.9 p.p.m. and the $-CH_2$ at 4.0 p.p.m., respectively. The ratio of the protons in $-CH_2Cl$, $-CHCl$ and $-CH_2$ is 2 : 1 : 2. Consequently, in the reaction of poly(dichlorophosphazene) with 2,3-dichloro-1-propanol, poly(2,3-dichloro-1-propoxyphosphazene) is prepared as shown in Scheme 2:

$$(NPCl_2)_n + nCH_2ClCHClCH_2OH \xrightarrow[nEt_3N]{THF} [NP(OCH_2CHClCH_2Cl)_2]_n \qquad (2)$$

3.2. Reaction of poly(dichlorophosphazene) with epichlorohydrin

The reaction of poly(dichlorophosphazene) with epichlorohydrin was carried out in the presence of $FeCl_3$, $AlCl_3$, $SnCl_4$, $TeCl_4$, $TiCl_4$, $BiCl_3$, AlF_3, $AlBr_3$, $MgCl_2$ and $CuCl_2$ under the same experimental conditions as given in Table I. This was done for selecting the most effective catalyst, so that the same reaction as shown in Scheme 1 will occur. The yields of Products I and II are shown in Table I.

It is found that Product I is not formed when AlF_3 was used. Product I is a black-coloured and highly viscous liquid. Also, the refractive index and the density of the product is similar to that of $[NP(OCH_2CHClCH_2Cl)_2]_n$. However, the molecular weight of Product I is below 1000 when $TeCl_4$, $TiCl_4$, $BiCl_3$ and $MgCl_2$ are used. Product II is not obtained using $AlCl_3$, $BiCl_3$ and $MgCl_2$. Also, Product II which was prepared using $SnCl_4$, $FeCl_3$, and $CuCl_2$ has a higher molecular weight compared with that of Product I prepared under the same conditions, and the values of the refractive index and density of the product are close to those of $[NP(OCH_2CHClCH_2Cl)_2]_n$. Further, the use of $FeCl_2$ provides a good yield of Products I and II. On the other hand, Product I prepared with $FeCl_3$ has the highest molecular weight.

Infrared absorption spectra of Products I and II formed in the latter case were determined. It is observed that the vibrations of the P–N bond occur at 1230 cm^{-1} and 970 cm^{-1}, that of the P–O–C bond at 1060 cm^{-1}, and that of the C–Cl bond at 680 cm^{-1}. These peak positions are consistent with the peak positions in the case of $[NP(OCH_2CHClCH_2Cl)_2]_n$.

The ^{1}H-NMR spectrum of Product I was determined. The peaks at 3.7, 3.9 and 4.0 p.p.m. are assigned to the CH_2Cl, the $CHCl$ and the CH_2 groups, respectively, but they slightly shift to high field in comparison to those of $[NP(OCH_2CHClCH_2Cl)_2]_n$. The ratio of the protons in them is 2 : 1 : 2. On the other hand, NMR spectra could not be obtained for Product II because it is insoluble in $CDCl_3$. Generally, it was concluded that the epoxide ring was cleaved by catalysts such as $ZnCl_4$, $TiCl_4$, $SnCl_4$, $FeCl_3$, BCl_3, BF_3, $BeCl_3$, etc. The order of the activity for Friedel–Crafts type catalysts reported was as follows: $AlCl_3 > FeCl_3 > SnCl_3 > TiCl_3\ TeCl_4 > BiCl_3$. The results presented suggest that the most suitable catalyst to get the reaction as shown in Scheme 1 is $FeCl_3$.

3.3. Reaction of poly(dichlorophosphazene) with other epoxide compounds

Poly(dichlorophosphazene) was allowed to react with other epoxide compounds such as styrene oxide, butylene oxide, 1-2-epoxy-3,3,3-trichloropropane and epifluorohydrin instead of epichlorohydrin. This reaction was carried out using $FeCl_3$. After the reaction was over, the molecular weight and IR absorption spectra and the separated and purified products were determined with GPC and IR, respectively.

It is found that the frequencies of the P = N stretching vibration in the product prepared using styrene oxide and butylene oxide were not observed in the infrared absorption spectra. Consequently, it seems that the reaction given in Scheme 1 does not proceed with styrene and butylene oxides. On the other hand, using epifluorohydrin and 1,2-epoxy-3,3,3-trichlorpropane, the frequencies of the P = N streching vibration of the product are observed in the IR absorption spectra.

The yield and the weight- and number-average molecular weights of Product I and II estimated from GPC curves are summarized in Table II. It is found that the product having the highest molecular weight in comparison with other epoxide compounds is prepared with epifluorohydrin and 1,2-epxoxy-3,3,3-trichloropropane. It is suggested that the electron-attracting fluorine or chlorine atoms provide an easy reaction with poly(dichlorophosphazene). The product II prepared in the reaction of epichlorohydrin and poly(dichlorophosphazene) using $FeCl_3$ was identified by elemental analysis and the results are given in Table III. It is found that the analytical value is in good agreement with the theoretical value.

The thermal properties of Product II were determined with DTA and TG, and the results are shown

TABLE III Elemental analysis of Product II with the reaction of epichlorohydrin and polydichlorophosphazene

	Composition (wt %)				
	C	H	P	N	Cl
Calculated*	23.9	3.3	10.3	4.7	47.1
Found	23.3	3.9	11.6	4.6	47.9

*For $[NP(OCH_2CHClCH_2Cl)_2]_n$.

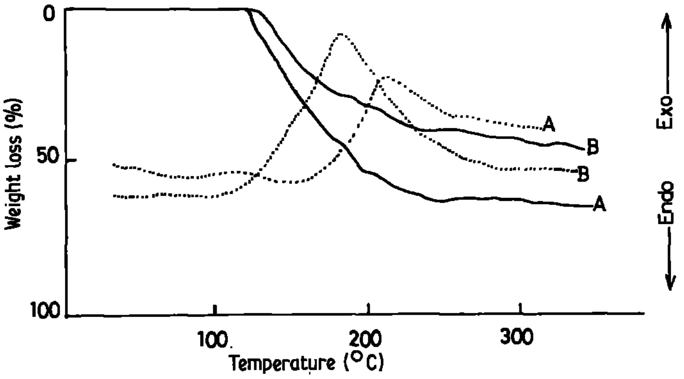

Figure 3 DTA and TG curves of (A) product II and (B) $[NP(OCH_2CHClCH_2Cl)_2]_n$. (——) TG, (···) DTA.

in Fig. 3. The thermal decomposition temperature of the products appear at 170 or 200° C. It seems that both products are not very stable for heating. Also, the glass transition temperature of Product II was observed to be at about −37° C, and the value is similar to that of $[NP(OCH_2CHClCH_2Cl)_2]_n$.

4. Conclusions

The transfer of chlorine from poly(dichlorophosphazene) to the CH group in epoxide compounds has been investigated by the use of various Friedel–Crafts type catalysts. It is found that the transfer of chlorine occurs in such reactions; however, the molecular weight of the product prepared has decreased in this reaction compared with that of poly(dichlorophosphazene) and 2,3-dichloro-1-propanpol.

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