Studies on the reactivity of polymers 2: Chlorination of poly(vinylidene chloride) by sulphuryl chloride in the presence of azobisisobutyronitrile

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Studies of poly(vinylidene chloride) by sulphuryl chloride in the presence of a radical-creating initiator asobisisobutyronitrile are presented. The chlorination rate is defined for a methylene group occurring in the $-CCl_2-CH_2CCl_2-$ sequence.

(Keywords: Chlorination; poly(vinylidene chloride); sulphuryl chloride; micro-structure; kinetics)

INTRODUCTION

Poly(vinylidene chloride) ($PVCl_2$) has a methylene group which is able to undergo chlorination. This group has two neighbouring 1,1-dichloromethyl groups which can cause both inductive and steric effects. These effects greatly influence the reactivity of the methylene group.

Although it is an interesting process, there is no literature information regarding the chlorination of $PVCl_2$. The enrichment of polymers with chlorine could lead to new, interesting technical properties. However, it is of utmost importance to understand the process of chlorination, thus determining the effect of the so called 'neighbour effect' of di-carbon–chloride groups on the reactivity of methylene.

Therefore, the paper presented here provides an interesting model of the chlorination course of $PVCl_2$, polyethylene and other polymers.

EXPERIMENTAL

Synthesis of poly(vinylidene chloride)[1]

Vinylidene chloride (100 g), and ammonium persulphide (3 g) dissolved in water (300 ml), sodium hydroxide (1 g), sodium thiosulphate (1.5 g) and sodium dodecylenebenzenesulphonate were mixed in a three-necked flask (with stirrer, reflux condenser and thermometer). The reaction was carried out for 6 h at 303 K. The addition of saturated NaCl (150 ml) initiated the precipitation of the final product from the emulsion. The product was then washed with water and dried, to form a white powder. (The chloride content in the product was 72.6 wt.%).

$PVCl_2$ chlorination in suspension

Azobisisobutyronitrile (0.1 g), and distilled sulphuryl chloride (30 g) were added to a mixture of poly(vinylidene chloride) (10 g) and chlorobenzene (250 ml). (The latter mixture had been heated to 353 K). Samples of the chlorinated polymer were washed with methanol and dried at 329 K for 24 h.

Characterization of the products

The chlorine content in the chlorinated $PVCl_2$ was determined by the Schröniger method[2]. Infra-red spectra were performed in KBr using a Perkin Elmer Model 621.

RESULTS AND DISCUSSION

In $PVCl_2$ it is possible to replace the two hydrogen atoms of the methylene group with chlorine atoms. *Table 1* shows theoretically possible formulae of constitutional units of $PVCl_2$ subject to chlorination.

It follows from *Figure 1* that, in the presence of a radical-creating initiator (such as azobisisobutyronitrile), chlorination by sulphuryl chloride leads to the production of a maximum chlorine content of 80.9 wt %. Thus the new product contains 3 chlorine atoms in one constitutional unit. This is a summary of the process; since the reaction may be composed of reactions such as: chlorination of methylene with the formation of a chloromethylene group followed by a secondary chlorination with the formation of a dichloromethylene group. Consecutive reactions such as dehydrochlorination, cross-linking or degradation may also occur.

During chlorination with sulphuryl chloride, degradation and dehydrochlorination were not observed. Infra-red absorption bands of poly(vinylidene chloride) during chlorination show characteristic changes. Within the frequency range of 2800–3000 cm^{-1} (corresponding to the stretching vibrations of the $-CH_2-$ and $-CH-$ groups) the intensity of the 3000 cm^{-1}, 2940 cm^{-1} and 2860 cm^{-1} bands (*Figure 3*) decreases as a result of chlorination. In the spectrum of a polymer containing 80.6% chlorine (by weight) the 2860 cm^{-1} band (related to the stretching vibrations of the $-CH_2-$ group) vanishes completely.

The frequency range 1100–700 cm^{-1} is related to

Table 1 Theoretically possible formulas of constitutional units of poly(vinylidene chloride) subject to chlorination

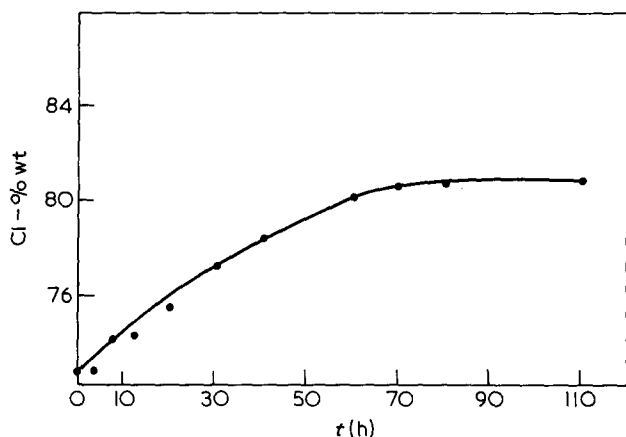| No of constitutional unit	Formula of constitutional unit	Theoretical chlorine content wt%
1	$-CH_2-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-$	73
2	$-\overset{}{\underset{\displaystyle Cl}{C}}H-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-$	80
3	$-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-$	84

Figure 1 Course of chlorination of poly(vinylidene dichloride) by sulphuryl chloride in the presence of azobisisbutyronitrile (AIBN)

skeleton bending vibrations C–C. The intensity of these bands 1070, 1046 and 890 cm^{-1} does not change during chlorination.
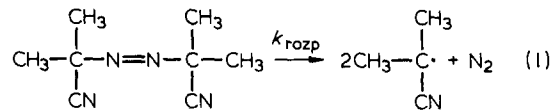
As the content of chlorine increases, the intensity of the 750 cm^{-1} band rises. The above mentioned band corresponds to the stretching bending vibrations C–Cl. This band is also observed in poly(vinyl chloride). At the same time, as a result of chlorination the shifting of the band below 600 cm^{-1} (i.e. the band corresponding to stretching vibrations of $-CCl_2-$) towards lower frequencies is observed (*Figure 3*).

From the analysis it follows that as the process of poly(vinylidene chloride) chlorination proceeds, the intensity of the bands related to methylene groups drops (to the advantage of those bands related to the methylyne groups). This testifies to the fact that during chlorination methylene groups are converted to chloromethylene groups. However, the increase in the content of $-CCl_2-$ groups at the expense of $-CHCl-$ groups is not observed. This is proof that the reaction of introducing the fourth chlorine atom into the constitutional unit does not proceed. So the final product or chlorination is poly-(trichloroethylene) (see *Table 1*, structure 2). Thus this reaction disengages methylene groups: the mechanism of
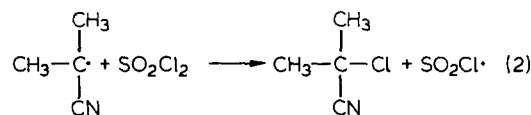
chlorination of methylene groups in PVCl$_2$ can be described by the following reactions:

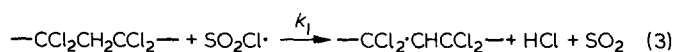*1. Initiation of chlorination*
  (a) Initiator decomposition

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}-N{=}N-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}-CH_3 \xrightarrow{k_{rozp}} 2CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}{\cdot} + N_2 \quad (1)$$

  (b) Chlorosulphonyl radical formation

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}{\cdot} + SO_2Cl_2 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}-Cl + SO_2Cl{\cdot} \quad (2)$$

2. Chlorination of PVCl$_2$
  (a) Polymer radical formation

$$-CCl_2CH_2CCl_2- + SO_2Cl{\cdot} \xrightarrow{k_i} -CCl_2{\cdot}CHCCl_2- + HCl + SO_2 \quad (3)$$

  (b) Polymer chlorination

$$-CCl_2{\cdot}CHCCl_2- + SO_2Cl_2 \xrightarrow{k_2} CCl_2\overset{}{\underset{\displaystyle Cl}{C}}HCCl_2 + SO_2Cl{\cdot} \quad (4)$$
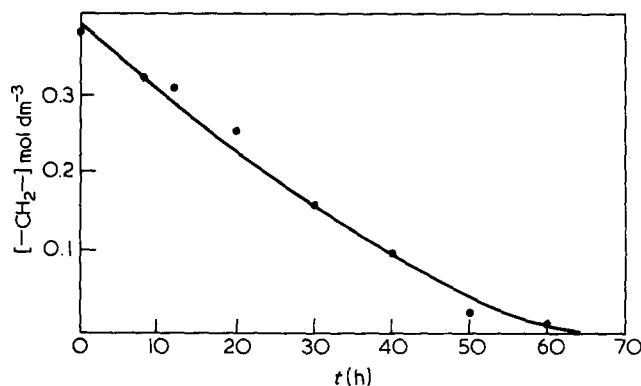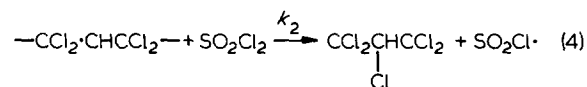

Figure 2 Changes in the concentration of CH$_2$ groups in poly(vinylidene chloride) during chlorination with sulphuryl chloride at 353 K
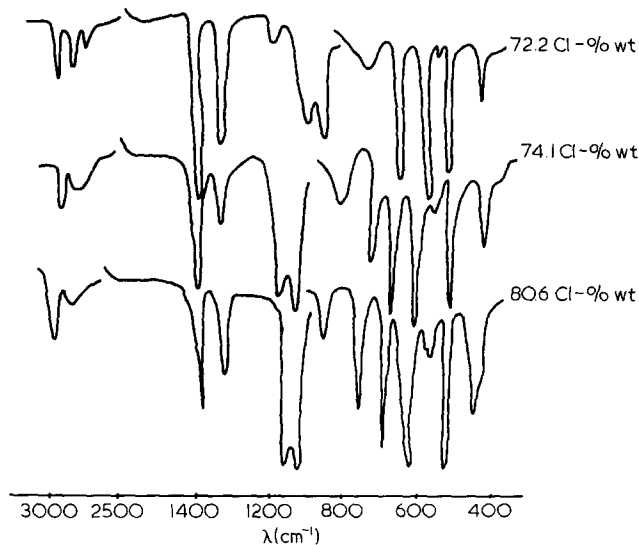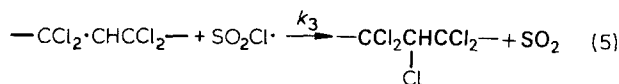

Figure 3 Infra-red spectra of poly(vinylidene chloride) subject to chlorination

3. Termination of chlorination due to the re-combination of polymer radical with the chlorosulphonyl radical

$$-CCl_2 \cdot CHCCl_2 - + SO_2Cl \cdot \xrightarrow{k_3} -CCl_2CHCCl_2 - + SO_2 \quad (5)$$
$$\underset{Cl}{|}$$

By applying a steady state approximation we can obtain the following equation for the formation and decay during the chlorination of the radicals $[SO_2Cl \cdot]$ and $[-C \cdot H-]$:

$$\frac{d[SO_2Cl \cdot]}{dt} = 2 \cdot k_{rozp}[J][SO_2Cl_2] + k_2[-\dot{C}-H-][SO_2Cl_2] \quad (6)$$
$$- k_1[-CH_2-][SO_2Cl \cdot] - k_3[SO_2Cl \cdot][-\dot{C}-H-] = 0$$

$$\frac{d[-CH-]}{dt} = k_1[-CH_2-][SO_2Cl \cdot] - k_2[-\dot{C}-H-][SO_2Cl_2]$$
$$- k_3[SO_2Cl \cdot][-\dot{C}-H] = 0 \quad (7)$$

by comparing equations (6) and (7) it follows that

$$[SO_2Cl \cdot] = \frac{k_{rozp}}{k_3} \frac{[J][SO_2Cl_2]}{[-\dot{C}-H-]} \quad (8)$$

and from equations (7) and (8) we obtain

$$\frac{k_{rozp} \cdot k_1}{k_3} \frac{[J][SO_2Cl_2][-CH_2-]}{[-C \cdot H-]} \left(1 - \frac{k_3 \cdot [-\dot{C}-H-]}{k_1 \cdot [-CH_2-]}\right)$$
$$= k_2[-\dot{C}-H-][SO_2Cl_2] \quad (9)$$

$$\frac{k_3 \cdot [-\dot{C}-H-]}{k_1 \cdot [-CH_2-]} = 0 \quad (10)$$

$$[-\dot{C}-H-] = \left(\frac{k_{roz}k_1}{k_2 \cdot k_3}[-CH_2-]\right)^{1/2}$$

The rate equation for chlorination takes the following form:

$$w = \frac{-d[CH_2]}{dt} \cong \frac{d[-CHCl-]}{dt}$$

$$= \left(\frac{k_2 \cdot k_1}{k_3} \cdot k_{roz} \cdot [J]\right)^{1/2} \cdot [-CH_2-][SO_2Cl_2] \quad (11)$$

$$w = k_{2'}[-CH_2-]^{1/2}[SO_2Cl_2]$$

$$k_{2'} = k_{2'_{cf}}(k_{rozp} \cdot [J])^{1/2}$$

Table 2 Rates and rate constants of $PVCl_2$ chlorination with sulphuryl chloride at 353 K in presence of AIBN

Concentration (mol . dm^{-3})			Chlorination rate (mol dm^{-3} s^{-1})	Chlorination rate constant (mol$^{-1/2}$ dm$^{3/2}$ s^{-1})	Chlorination effect rate mol^{-1} s$^{-1/2}$ dm^3
Initiator	SO$_2$Cl$_2$	-CH$_2$-			
2.275 x 10^{-3}	0.8292	0.384	1.9 x 10^{-6}	3.69 x 10^{-7}	7.2 x 10^{-4}

where: k_{rozp} is the decay rate constant of the initiator, $k_{2'}$ is the rate constants of $PVCl_2$ chlorination, $[J]$ is the initiator concentration, $[SO_2Cl_2]$ is the concentration of sulphonyl chloride and $[-CH_2-]$ is the concentration of methylene groups in $PVCl_2$.

Figure 2 shows the changes in the concentration of the methylene groups during chlorination and the values of the rates and rate constants of chlorination with sulphuryl chloride at 353 K are shown in *Table 2*.

The rate of chlorination of methylene groups in the sequence $-CCl_2CH_2CCl_2-$ is much lower than the rate for methylene groups in the sequences $-CHClCH_2CHCl-$ (in polyvinylchloride). The ratio of the two rates is $1:56$. The chlorination rate constants are also much lower. Thus it is evident that both the 'neighbour' and steric effects greatly affect the reactivity of the methylene group.

CONCLUSION

The methylene group in poly(vinylidene chloride) can be chlorinated with sulphuryl chloride. As a result of this reaction a polymer is formed containing 80.9% chlorine (by weight) which corresponds to 3 chlorine atoms in its constitutional unit. Under these conditions the chloromethylene groups in chlorinated $PVCl_2$ remain inactive. When the methylene group has dichloromethylene groups on either side, instead of monochloromethylene groups, the reaction with sulphuryl chloride is 54 times slower. Chlorination of poly(vinylidene chloride) provides a model of the reactivity of the $-CCl_2-CH_2-CCl_2-$ sequence with sulphuryl chloride for many other polymer arrangements and, in particular, for chlorinated PE and PVC.

REFERENCES

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2 Schroniger W. *Mikrochim. Acta.* 1954, 74