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STUDIES OF THE THERMAL STABILITY OF POLY(VINYL CHLORIDE)—I. INFLUENCE OF LIGHT ON THE THERMAL STABILITY OF PVC

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Abstract—The molecular structural defects in four suspension-polymerized poly(vinyl chloride) (PVC) samples and their thermal dehydrochlorination rates in light and dark were determined quantitatively. Based on the influence of light, especially u.v., on the thermal stability of PVC, it is concluded that the rate of thermal dehydrochlorination of PVC in the dark is related to the labile chlorine atoms (particularly internal allylic chlorine atoms), while the rate of photo-thermal dehydrochlorination of PVC in light is related to the carbonyl allylic groups and the double bonds (particularly terminal double bonds). A radical mechanism for the thermal dehydrochlorination (two steps) and the photo-thermal dehydrochlorination (three steps) is proposed.

INTRODUCTION

Poly(vinyl chloride) (PVC) is a thermally unstable polymer. In order to improve the thermal stability, many researchers have determined the structural defects in PVC qualitatively or quantitatively and attempted to establish relationships between the abnormal structures and the rate of dehydrochlorination. In general, the abnormal structures are the internal cause of instability of PVC. It has been reported that the rate of dehydrochlorination may depend on internal double bonds [1], and allylic chlorines located at chain-ends [2–4]. Recent investigations [5–11] have indicated some advances in this area. The chemical factors affecting the thermal stability of PVC are still uncertain.

We now report the results of study of the dehydrochlorination of PVC in the dark (thermal dehydrochlorination) and in light (photo-thermal dehydrochlorination), and propose relationships between abnormal structures and instability of PVC.

EXPERIMENTAL PROCEDURES

Materials

Four suspension-polymerized PVC samples, A-1, B-1, S-1 and C-1, were commercial materials without stabilizers. Chemicals utilized in this work were analytical reagents. Tetrahydrofuran, 1,2-dichloro-ethane and 1,1,2,2-tetrachloro-ethane were treated by the usual methods. Pure nitrogen (99.99%) was further purified to remove traces of oxygen and water.

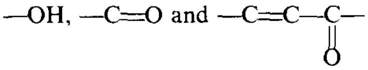
Determination of abnormal structures

The total amount of labile chlorine atoms was determined by phenolysis [12]. The determination of internal allylic chlorine atoms was done by selective reaction with $AgNO_3$ [13] but the reaction took place in the dark. The measurements of total double bonds and internal double bonds were made by the bromine method [14] and the ozonization method [15], respectively. The hydroxyl, carbonyl and carbonyl allylic groups were detected by i.r. (5DXFT-IR) [16], and the conjugated double bonds by u.v. (730-UV) [17]. The rates of dehydrochlorination of PVC samples were obtained in solution using a conductometric system [18, 19]; the process was carried out in the dark and with several light sources under a nitrogen atmosphere.

RESULTS

Structural defects

The amounts of abnormal structures in PVC are given in Table 1. The amount of terminal double bonds in Table 1 was obtained by subtracting the amount of internal double bonds from the total amount [1]. There was a larger amount of the terminal double bonds, and there were no conjugated double bonds in the original PVC samples. The i.r. spectra showed that there were



$$-OH,\ -C{=}O \text{ and } -C{=}C-\underset{\underset{O}{\|}}{C}-$$

groups.

Dehydrochlorination rate

It was shown experimentally that the rate of dehydrochlorination of PVC is extremely dependent on both the temperature and the intensity of the sunlight. We found that at a particular temperature the rate of dehydrochlorination of PVC increases with the intensity of the sunlight.

Since the influence of light on PVC thermal decomposition is significant, we have to consider the light factor when measuring the dehydrochlorination rate. Here, we define the dehydrochlorination in the dark and the dehydrochlorination in light as *thermal dehydrochlorination* and *photo-thermal dehydrochlorination*, respectively.

The experimental results showed the sequence of thermal dehydrochlorination of these four samples

Table 1. Structural defects of PVC samples (1000 v.c.)

Sample	BD[a]	IDB[a]	TDB[a]	CDB[a]	LC[a]	IAC[a]	—OH[b]	—C═O[b]	—C═C—C═O[b]
C-1	2.76	0.180	2.58	0	0.30	0.24	0.4079	0.3823	0.5322
S-1	3.34	0.137	3.20	0	0.69	0.41	0.3739	0.3500	0.5881
B-1	3.07	0.158	2.91	0	0.52	0.44	0.4502	0.4278	0.6091
A-1	3.09	0.148	2.95	0	0.92	0.69	0.3839	0.3929	0.5576

[a] DB, total double bonds; IDB, internal double bonds; TDB, terminal double bonds; CDB, conjugated double bonds; LC, total labile chlorines; IAC, internal allylic chlorines.

[b] The amounts of hydroxyl, carbonyl and carbonyl allylic groups are expressed in A/l (mm^{-1}), where $A/l = \epsilon C$.

Table 2. Data of dehydrochlorination of PVC samples[a]

Decomposition	Sample	Induction period (min)	dHCl/dt × 10^2 (%/min)
Thermal	A-1	16	1.9
	B-1	20	1.5
	S-1	27	1.4
	C-1	32	0.9
Photo-thermal	A-1	4	6.4
	B-1	4	6.1
	S-1	3	7.3
	C-1	6	5.2

[a] $T = 453$ K; N_2; light source: white light (intensity: 2500 lx).

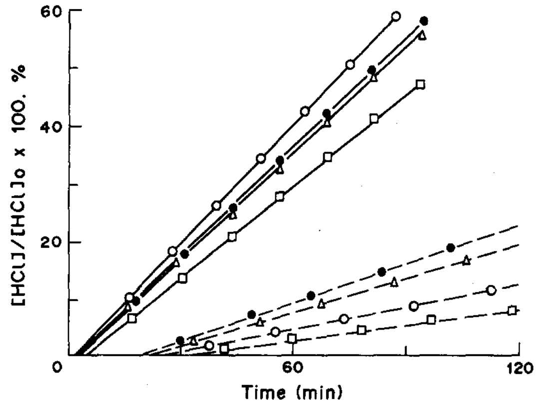


Fig. 1. Curves of the thermal dehydrochlorination and the photo-thermal dehydrochlorination. ●, A-1; △, B-1; □, C-1; ○, S-1; $T = 453$ K; (——) in white light (intensity: 2500 lx); (----) in the dark.

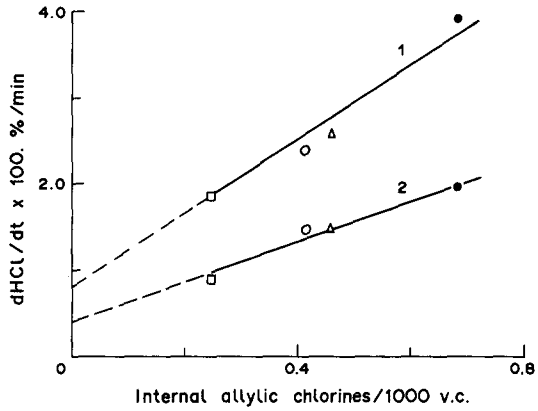


Fig. 3. Relationship between the internal allylic chlorines and the thermal dehydrochlorination. ●, A-1; △, B-1; □, C-1; ○, S-1; curve 1: 463 K; curve 2: 453 K; in the dark.

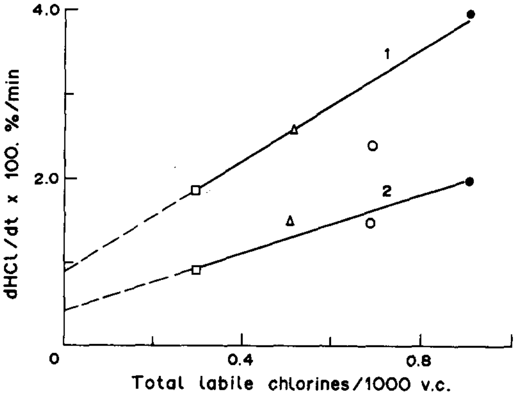


Fig. 2. Relationship between the total labile chlorines and the thermal dehydrochlorination. ●, A-1; △, B-1; □, C-1; ○, S-1; curve 1: 463 K; curve 2: 453 K; in the dark.

was not exactly the same as that for photo-thermal dehydrochlorination. The two sequences are represented thus:

thermal dehydrochlorination rates:

$$A-1 > B-1 > S-1 > C-1,$$

photo-thermal dehydrochlorination rates:

$$S-1 > A-1 > B-1 > C-1.$$

Table 2 and Fig. 1 show the parameters and kinetic curves for the samples.

DISCUSSION

Relationships between abnormal structures and thermal dehydrochlorination

By plotting the abnormal structural contents vs the thermal dehydrochlorination rate, we found that the thermal dehydrochlorination rate of PVC is related primarily to the amount of labile chlorine atoms, especially to internal allylic chlorines (see Figs 2 and 3) and is almost independent of other abnormal

Table 3. Test of dehydrochlorination in different light sources[a]

Light source	Induction period (min)	dHCl/dt × 10^2 (%/min)
Ultraviolet	13	12.19
White	32	2.57
Infrared	43	1.42
Dark	56	1.02

[a] Sample: A-1; $T = 443$ K; N_2: intensity: 1500 lx.

structures. At the given temperatures (453 or 463 K), the PVC dehydrochlorination rate increased with increase of the amount of labile chlorine atoms.

The labile chlorines in PVC include internal allylic chlorines, allylic chlorines at chain-ends, tertiary chlorines and carbonyl allylic chlorines. In general, tertiary chlorines do not occur in PVC [8]. The labile chlorines consist, therefore, of various kinds of allylic chlorines [2]. Since the allylic chlorine atoms are more active, the abnormal carbon–chlorine bonds require less energy for splitting than normal carbon–chlorine bonds. From Figs 2 and 3, we cannot exclude other factors since some dehydrochlorination was observed even when labile chlorine atoms were absent. Therefore, the labile chlorines are not the only cause of thermal decomposition of PVC.

Relationships between abnormal structures and photo-thermal dehydrochlorination

As mentioned above, because of both light and heat affecting PVC, the rate of photo-thermal dehydrochlorination is much higher than that of thermal dehydrochlorination. Preliminary experiments on the influence of various light sources on PVC decomposition were carried out. For u.v. light, the photo-thermal decomposition was fastest, being approximately 12-times faster than the thermal decomposition (Table 3). Clearly, certain groups in PVC must be sensitive to u.v. light. By plotting the amount of structural defects vs the dehydrochlorination rate, we found that both the carbonyl allylic groups and double bonds in PVC are related to the rates of photo-thermal dehydrochlorination (Figs 4–6). Since the amounts of internal double bonds and carbonyl allylic groups are small compared with that of terminal double bonds, the terminal double bonds are considered as the main factor affecting the photo-thermal dehydrochlorination of PVC. This may be because, when PVC is heated to decompose under light and heat conditions, first the double bonds become initiation sites to release hydrogen chloride and then form conjugated double bonds. The higher the amount of the original double bonds, the greater the possibility of formation of conjugated double bonds, which can easily absorb more energy to accelerate the decomposition of PVC. An experimental result given in Table 4 refers to 35% chlorinated polyethylene (CPE) without double bonds; it showed that the rate of thermal dehydrochlorination of CPE is exactly the same as that of the photo-thermal process of CPE.

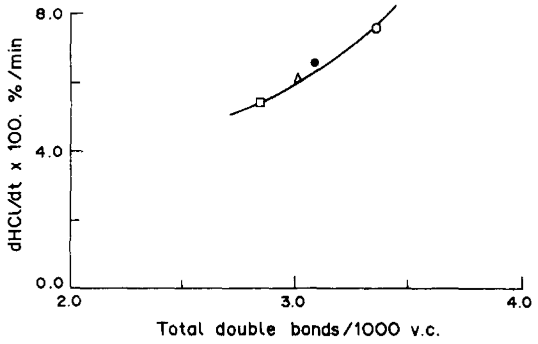


Fig. 4. Relationship between the total double bonds and the photo-thermal dehydrochlorination. ●, A-1; △, B-1; □, C-1; ○, S-1; $T = 453$ K; in white light (intensity: 2500 lx).

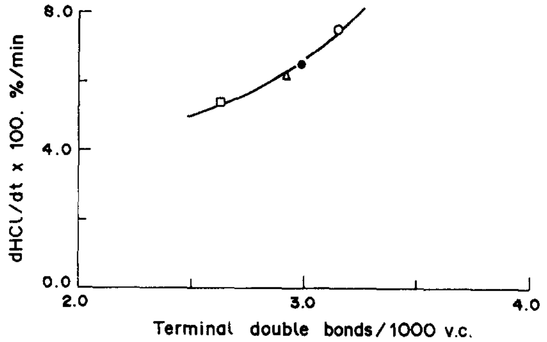


Fig. 5. Relationship between the terminal double bonds and the photo-thermal dehydrochlorination. ●, A-1; △, B-1; □, C-1; ○, S-1; $T = 453$ K; in white light (intensity: 2500 lx).

Exploration of PVC decomposition mechanism

As discussed above, the thermal decomposition and the photo-thermal decomposition of PVC have constant rates corresponding to the radical mechanism of PVC dehydrochlorination [21]. However, it should be noted that none of the proposed mecha-

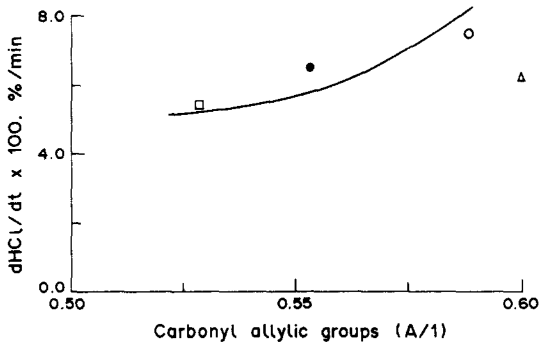


Fig. 6. Relationship between the carbonyl allylic groups and the photo-thermal dehydrochlorination. ●, A-1; △, B-1; □, C-1; ○, S-1; $T = 453$ K; in white light (intensity: 2500 lx).

Table 4. Data of dehydrochlorination of CPE[a]

Decomposition type	Induction period (min)	dHCl/dt × 10^2 (%/min)
Thermal	35	0.01
Photo-thermal	35	0.01

[a] $T = 453$ K; N_2; light source; white light (intensity: 1500 lx).

Table 5. Differences between thermal and photo-thermal decompositions of PVC

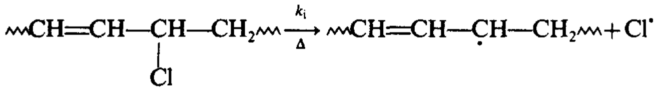
Decomposition type	Mechanism	Decomposition rate	Initiation site	Molecular weight effect[a]
Thermal	Radical (two steps)	Slow (constant)	Labile chlorines	Small
Photo-thermal	Radical (three steps)	Fast (constant)	Double bonds	Large

[a]See Ref. [23].

nisms dealt with two problems. One is the difference between the thermal and photo-thermal decompositions of PVC; another is the influences of abnormal structures on the thermal and photo-thermal decompositions of PVC. Obviously, the thermal dehydrochlorination is quite different from the photo-thermal process. Here, we make proposals about these two processes.

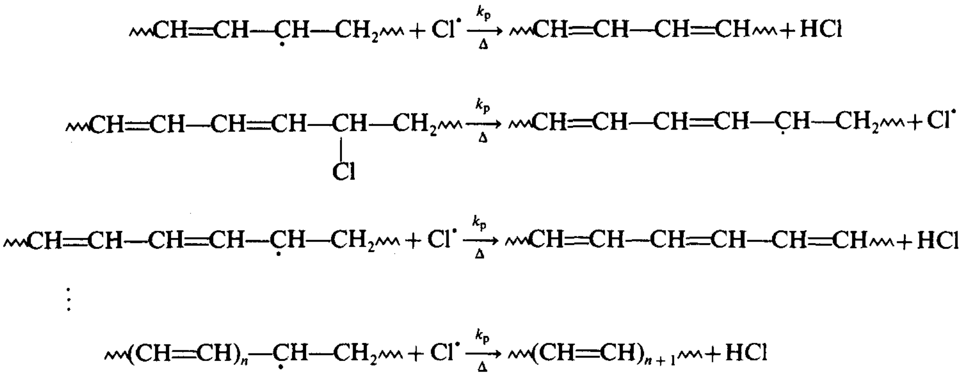
(*A*) *Process of thermal dehydrochlorination.* The thermal dehydrochlorination of PVC starts with the releasing of allylic chlorine atoms and then conjugated double bonds are produced rapidly. Therefore, the process may consist of the following two steps:

(*i*) *Initiation*



$$\sim\!\mathrm{CH{=}CH{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2}\!\sim \xrightarrow[\Delta]{k_i} \sim\!\mathrm{CH{=}CH{-}\underset{\bullet}{C}H{-}CH_2}\!\sim+\mathrm{Cl}^\bullet$$

(*ii*) *Propagation*



$$\sim\!\mathrm{CH{=}CH{-}\underset{\bullet}{C}H{-}CH_2}\!\sim+\mathrm{Cl}^\bullet \xrightarrow[\Delta]{k_p} \sim\!\mathrm{CH{=}CH{-}CH{=}CH}\!\sim+\mathrm{HCl}$$

$$\sim\!\mathrm{CH{=}CH{-}CH{=}CH{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2}\!\sim \xrightarrow[\Delta]{k_p} \sim\!\mathrm{CH{=}CH{-}CH{=}CH{-}\underset{\bullet}{C}H{-}CH_2}\!\sim+\mathrm{Cl}^\bullet$$

$$\sim\!\mathrm{CH{=}CH{-}CH{=}CH{-}\underset{\bullet}{C}H{-}CH_2}\!\sim+\mathrm{Cl}^\bullet \xrightarrow[\Delta]{k_p} \sim\!\mathrm{CH{=}CH{-}CH{=}CH{-}CH{=}CH}\!\sim+\mathrm{HCl}$$

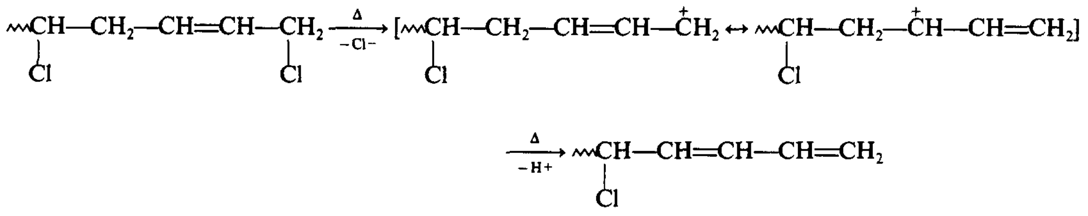
$$\vdots$$

$$\sim\!\mathrm{(CH{=}CH)_n{-}\underset{\bullet}{C}H{-}CH_2}\!\sim+\mathrm{Cl}^\bullet \xrightarrow[\Delta]{k_p} \sim\!\mathrm{(CH{=}CH)_{n+1}}\!\sim+\mathrm{HCl}$$

(*B*) *Process of photo-thermal dehydrochlorination.* The terminal double bonds are the primary initiation sites. Generally, the terminal double bonds in PVC are primarily composed of 1-chloro-2-alkene structure ($\mathrm{Cl{-}CH_2{-}CH{=}CH{-}}$). Therefore, the process of photo-thermal dehydrochlorination may consist of the following three steps:

(*i*) *Rearrangement of 1-chloro-2-alkene structure*

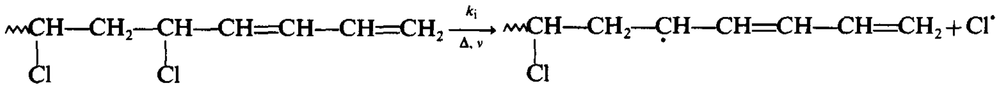
The rearrangement takes place by an ionic mechanism [2, 22]:



$$\sim\!\mathrm{\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}CH{=}CH{-}\underset{\underset{Cl}{|}}{CH_2}} \xrightarrow[-\mathrm{Cl}^-]{\Delta} [\sim\!\mathrm{\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}CH{=}CH{-}\overset{+}{C}H_2} \leftrightarrow \sim\!\mathrm{\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}\overset{+}{C}H{-}CH{=}CH_2}]$$

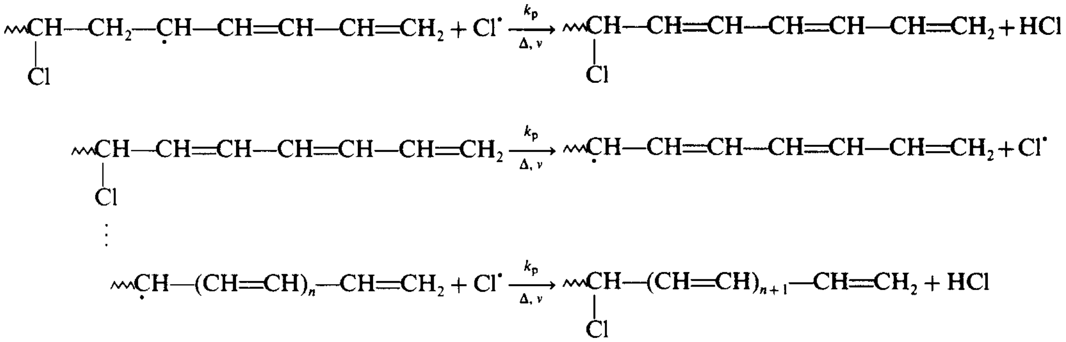
$$\xrightarrow[-\mathrm{H}^+]{\Delta} \sim\!\mathrm{\underset{\underset{Cl}{|}}{CH}{-}CH{=}CH{-}CH{=}CH_2}$$

(*ii*) *Initiation*



$$\sim\!\mathrm{\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}\underset{\underset{Cl}{|}}{CH}{-}CH{=}CH{-}CH{=}CH_2} \xrightarrow[\Delta,\,\nu]{k_i} \sim\!\mathrm{\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}\underset{\bullet}{C}H{-}CH{=}CH{-}CH{=}CH_2}+\mathrm{Cl}^\bullet$$

(iii) Propagation



$$\sim\underset{\substack{|\\ Cl}}{C}H-CH_2-\underset{\bullet}{C}H-CH=CH-CH=CH_2 + Cl^{\bullet} \xrightarrow[\Delta,\,\nu]{k_p} \sim\underset{\substack{|\\ Cl}}{C}H-CH=CH-CH=CH-CH=CH_2 + HCl$$

$$\sim\underset{\substack{|\\ Cl}}{C}H-CH=CH-CH=CH-CH=CH_2 \xrightarrow[\Delta,\,\nu]{k_p} \sim\underset{\bullet}{C}H-CH=CH-CH=CH-CH=CH_2 + Cl^{\bullet}$$

$$\vdots$$

$$\sim\underset{\bullet}{C}H-(CH=CH)_n-CH=CH_2 + Cl^{\bullet} \xrightarrow[\Delta,\,\nu]{k_p} \sim\underset{\substack{|\\ Cl}}{C}H-(CH=CH)_{n+1}-CH=CH_2 + HCl$$

The first step is very important to the process. Without it, light would not have a significant effect on the dehydrochlorination. Obviously, under the influence of light and heat, PVC can absorb more energy to produce more chlorine radicals, so that the rate of photo-thermal dehydrochlorination of PVC is much higher than that of thermal dehydrochlorination. The differences between these two processes are summarized in Table 5.

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