that hexadecane is absorbed in the bulk of the polymer at 185°, and that sorption on the polymer surface is dominant at 100°. Below the glass transition temperature the retention volume is linear with $1/T$ (Figure 4). It was also found that at all temperatures below T_g the observed retention volume was independent of the liquid loading. These results strongly indicate that adsorption on the polymer surface dominates at all temperatures below T_g. The transition range between 160 and 130° may then be explained by a nonequilibrium sorption mechanism. Such a mechanism would occur if the diffusion of hexadecane is so slow that only part of the polymer is "available" for this solute. The amount of "available" polymer would decrease with temperature, and the drop in retention volume with a decrease in temperature would be explained. When the glass transition temperature is reached, the hexadecane molecules must diffuse in an essentially frozen polymer structure, most probably characterized with a higher activation energy,[20–22] and adsorption on the polymer surface becomes the dominating sorption mechanism.

It is evident from these experiments that the change in the sign of the slope around T_g occurs for the three substances with the smallest excess free energy of mixing. This may be related to the large size of the hexadecane, naphthalene, and α-chloronaphthalene molecules, and more experiments are needed to clear up this point. It seems likely, however, that acetic acid and *n*-butyl alcohol with their ability to form hydrogen bonds may diffuse in the polymer by another mechanism, and this is why these solutes are able to penetrate the polymers even below the glass transition temperature.

Regardless of what the detailed explanation for the behavior around the glass transition may be, the effect is pronounced and, at least for hexadecane, very sharp and easily detected, and it seems likely that this effect may be a general one for polymer substrates interacting with a "nonsolvent" solute.

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Pyrolysis–Gas Chromatographic Investigation on the Structure of Chlorinated Poly(vinyl chlorides)

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ABSTRACT: The distributions of the chlorine atoms in the chain of chlorinated poly(vinyl chlorides) were studied by means of pyrolysis–gas chromatography over a wide range of degree of chlorination. In addition to vinyl chloride, 1,2-dichloroethylene, and vinylidene chloride units, which up to now were regarded as the only possible microstructures of chlorinated poly(vinyl chloride), the presence of 1,1,2-trichloroethylene units was confirmed. The estimated concentration of the new unit amounted to up to 10% at a high degree of chlorination.

The chemical and physical properties of poly(vinyl chloride) (PVC) vary with the degree of after-chlorination. Chlorinated poly(vinyl chloride) (CPVC) generally shows improved thermal stability. As CPVC is a nonuniform polymer and the distributions of the chlorine atoms along the chain of the polymer are complex, various authors[1–4] have reported conflicting results regarding its molecular structure. Germar[1] has presented ir spectroscopic work on the microstructure of CPVC. He found that chlorination of the methylene groups is favored to form $-CHClCHCl-$ and that $-CH_2CCl_2-$groups are present up to 20% at most. Fredriksen and Crowo,[2] who also used ir spectra, found that the ratio of the chance for chlorination of $-CH_2-$ and $-CHCl-$ is about 2:1. Using nmr spectra of CPVC, Petersen and Rånby[3] and Tho and Berticat[4] determined the concentration of $-CH_2CHCl-$, $-CHClCHCl-$, and $-CH_2CCl_2-$. According to the results, $-CHClCHCl-$ is formed preferentially at the initial stage of chlorination. This is in fairly good agreement with ir results, but the reported high content[3] (up to 34%) of $-CH_2CCl_2-$ rather disagrees with the result (up to 20%) by ir analysis.[1] Generally, the authors[1–4] interpreted the microstructure of CPVC by assuming that only two chlorine atoms could be contained at most in a monomer unit by after-chlorination and that the original PVC has a regular head-to-tail structure. Consequently, only the three units mentioned above were taken into consideration.

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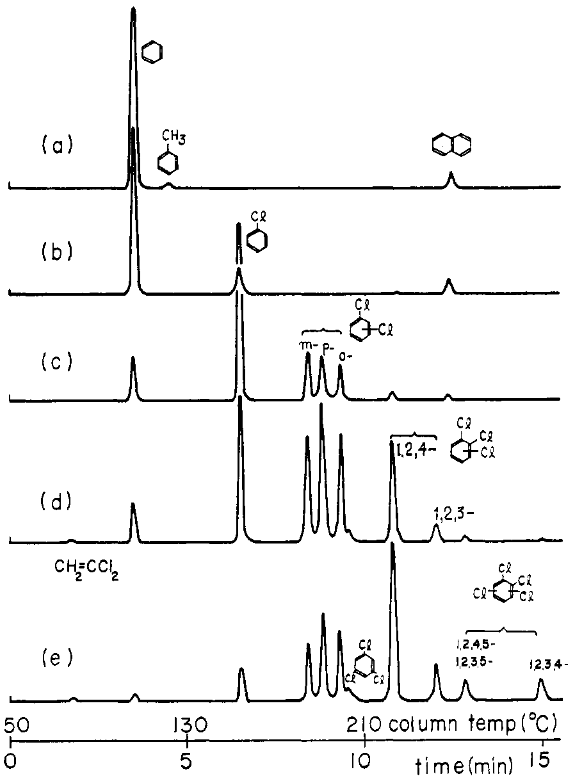

Figure 1. Typical pyrograms of PVC and CPVC at 460°: (a) PVC; (b–e) CPVC, (b) $A = 8.5$, (c) $A = 36.0$, (d) $A = 73.2$, and (e) $A = 92.8$, where A is the degree of chlorination (mole per cent).

In our previous works,[5,6] we have characterized the microstructure of vinylidene chloride–vinyl chloride copolymers[5] and chlorinated polyethylenes[6] by pyrolysis–gas chromatography (PGC). In this report, a pyrolysis–gas chromatographic investigation of CPVC is presented and the chlorine distributions in the chain of the polymer are interpreted by introducing a new concept of 1,1,2-trichloroethylene unit ($-CHClCCl_2-$) in addition to the other three units described above.

Experimental Section

Materials. Commercially available PVC supplied by Mitusi-Chemical Co. Ltd. was used as an original polymer. The chlorination of PVC was made in the following way. PVC powder was dissolved in chloroform and chlorine gas was introduced into the polymer solution with constant stirring at 50°. Seven samples of different chlorine content were prepared during continuous chlorination about 40 hr.

Program Measurements. A furnace-type pyrolyzer described in our previous paper[5,6] was used to decompose the samples. It was directly attached to the inlet port of the Yanagimoto Model GCG-550F gas chromatograph with dual flame ionization detectors. Hydrogen chloride evolved during the thermal decomposition of the polymers was eliminated by precut column[5,6] containing NaOH, which was set in the pyrolyzer unit, and only the aromatic compounds such as benzene and its chlorine-substituted isomers were separated to record pyrograms. Sample size ranging from 0.2 to 0.5 mg was pyrolyzed for 1 min under a flow of carrier gas (N_2) at 460°. The optimum pyrolysis temperature, 460°, was experimentally determined with the intention of obtaining reproducible and characteristic pyrograms. Gas chromatographic conditions and the method of identification of the peaks on the pyrograms were as described in the previous papers.[5,6] Separation columns (3 mm i.d. × 2 m) containing 10 wt % of Carbowax 6000 were used in a programed temperature from 50 to 210° at a rate of 16°/min. Duplicate measurement of the pyrograms agreed to less than 5% from mean.

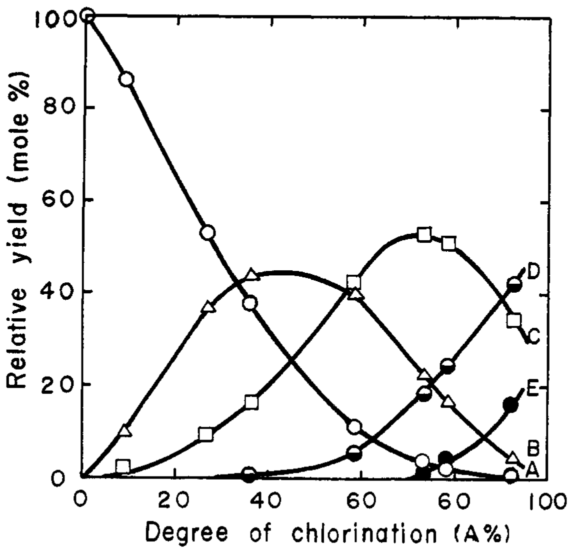

Figure 2. Relationships between the degree of chlorination (A) and the yield of the degradation products from CPVC: A, aromatic hydrocarbons; B, chlorobenzene; C, dichlorobenzenes; D, trichlorobenzenes; and E, tetrachlorobenzenes.

Results and Discussion

In the following, vinyl chloride ($-CH_2CHCl-$), 1,2-dichloroethylene ($-CHClCHCl-$), vinylidene chloride ($-CH_2CCl_2-$), and 1,1,2-trichloroethylene ($-CHClCCl_2-$) units are briefly denoted by V, D_{12}, D_{11}, and T_{112}, respectively. The degree of chlorination (A) of CPVC is defined as the percentage number of monomer unit containing two chlorine atoms as follows: $A = 6.10 \times (\text{Cl wt } \% - 56.8)$.

Figure 1 shows typical pyrograms of original PVC and CPVC at the pyrolysis temperature of 460°. Every degradation product except toluene (C_7) and naphthalene (C_{10}) contains six carbone atoms (an aromatic ring), that is, a triad of C_2 units. For simplicity, the small amounts of toluene and naphthalene observed with lower chlorine containing CPVC were converted into benzene in the calculation and added to the observed yield of benzene. As shown in Figure 1, the most conspicuous product from PVC is benzene, whereas with increasing degree of chlorination (A), various chlorine-substituted aromatics are observed.

Figure 2 shows the relationships between degree of chlorination (A) and the observed yield of the degradation products from CPVC. The relative yield was calculated from the relative peak area appearing on the pyrograms making molar sensitivity corrections for the flame ionization detector.

According to the degree of chlorination, where pronounced changes are observed as shown in Figure 2, we can summarize as follows.

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[5] S. Tsuge, T. Okumoto, and T. Takeuchi, *Makromol. Chem.*, in press.

[6] S. Tsuge, T. Okumoto, and T. Takeuchi, *Macromolecules*, **2**, 200 (1969).

TABLE I
ESTIMATION OF T_{112} FRACTION

Sample no.[a]	Mol % of trichlorobenzenes				Mol % of tetrachlorobenzenes (D)	Mol % of T_{112}	
	1,2,3- (A)	1,2,4- (B)	1,3,5- (C)	Total		$^1/_3$(A + D)	$^1/_3$(2A + D)
3		0.6		0.6			
4	0.8	4.9		5.7		0.3	0.5
5	3.3	15.4	Trace	18.7	1.6	1.6	2.7
6	4.6	19.5	0.2	24.3	4.7	3.1	4.6
7	8.5	32.8	0.9	42.2	16.3	8.3	11.1

[a] The numbers are the same as those in Table III.

TABLE II
STRUCTURES OF THE TRIADS IN CPVC AND THE DEGRADATION PRODUCTS FROM THE TRIADS

No. of Cl atoms introduced in a triad by after-chlorination	Combination of three units[a]	Structures of the triads in CPVC	Degradation products from the triads[b]
0	V, V, V	VVV	B
1	V, V, D_{11}	VVD_{11}, $VD_{11}V$, $D_{11}VV$	CB
	V, V, D_{12}	VVD_{12}, $VD_{12}V$, $D_{12}VV$	CB
2	V, V, T_{112}	VVT_{112}, $VT_{112}V$, $T_{112}VV$	*o*-
	V, D_{11}, D_{11}	$VD_{11}D_{11}$, $D_{11}VD_{11}$, $D_{11}D_{11}V$	*m*-
	V, D_{11}, D_{12}	$VD_{11}D_{12}$, $D_{11}D_{12}V$, $D_{12}VD_{11}$ $VD_{12}D_{11}$, $D_{11}VD_{12}$, $D_{12}D_{11}V$	*m*- or *p*- *o*- or *m*-
	V, D_{12}, D_{12}	$VD_{12}D_{12}$, $D_{12}VD_{12}$, $D_{12}D_{12}V$	*o*-, *m*-, or *p*-
3	V, D_{11}, T_{112}	$VD_{11}T_{112}$, $D_{11}T_{112}V$, $T_{112}VD_{11}$ $VT_{112}D_{11}$, $D_{11}VT_{112}$, $T_{112}D_{11}V$	1,2,3- 1,2,4-
	V, D_{12}, T_{112}	$VD_{12}T_{112}$, $VT_{112}D_{12}$, $D_{12}VT_{112}$ $D_{12}T_{112}V$, $T_{112}VD_{12}$, $T_{112}D_{12}V$	1,2,3- or 1,2,4-
	D_{11}, D_{12}, D_{12}	$D_{11}D_{11}D_{12}$, $D_{11}D_{12}D_{11}$, $D_{12}D_{11}D_{11}$	1,2,4- or 1,3,5-
	D_{11}, D_{12}, D_{12}	$D_{11}D_{12}D_{12}$, $D_{12}D_{11}D_{12}$, $D_{12}D_{12}D_{11}$	1,2,4- or 1,3,5-
	D_{11}, D_{11}, D_{11}	$D_{11}D_{11}D_{11}$	1,3,5-
	D_{12}, D_{12}, D_{12}	$D_{12}D_{12}D_{12}$	1,2,4- or 1,3,5-
4	V, T_{112}, T_{112}	$VT_{112}T_{112}$, $T_{112}VT_{112}$, $T_{112}T_{112}V$	1,2,3,4-
	D_{11}, D_{11}, T_{112}	$D_{11}D_{11}T_{112}$, $D_{11}T_{112}D_{11}$, $T_{112}D_{11}D_{11}$	1,2,3,5-
	D_{11}, D_{12}, T_{112}	$D_{11}D_{12}T_{112}$, $D_{12}T_{112}D_{11}$, $T_{112}D_{11}D_{12}$ $D_{11}T_{112}D_{12}$, $D_{12}D_{11}T_{112}$, $T_{112}D_{12}D_{11}$	1,2,3,4- or 1,2,3,5- 1,2,4,5- or 1,2,3,5-
	D_{12}, D_{12}, T_{112}	$D_{12}D_{12}T_{112}$, $D_{12}T_{112}D_{12}$, $T_{112}D_{12}D_{12}$	1,2,3,4-, 1,2,3,5- or 1,2,4,5-

[a] V = $-CH_2CHCl-$, D_{11} = $-CH_2CCl_2-$, D_{12} = $-CHClCHCl$, and T_{112} = $-CHClCCl_2-$. [b] B = benzene; CB = chlorobenzene; *o*-, *m*-, and *p*- = dichlorobenzenes; 1,2,3-, 1,2,4-, and 1,3,5- = trichlorobenzenes and 1,2,3,4-, 1,2,3,5-, and 1,2,4,5- = tetrachlorobenzenes.

1. $A \leqq$ **35%.** Because the sequence length of the successive V becomes shorter with increasing the degree of chlorination (A), the yield of aromatic hydrocarbons (mainly benzene) decreases with the rise of A, whereas increasing amounts of chlorobenzene and dichlorobenzenes are observed. The yields of *o*-, *m*-, and *p*-dichlorobenzenes are nearly equal each other.

2. 35% $\leqq A \leqq$ **75%.** Trichlorobenzenes, which first appear on the pyrogram of CPVC with A = 36.0%, increase in quantity with the rise of A, whereas the yield of chlorobenzene shows a maximum (45 mol %) near A = 40% and begins to decrease with the increase of A. As shown in Table I, among trichlorobenzenes, the amount of 1,2,4 isomer is largest and that of 1,3,5 isomer is very small.

3. 75% $\leqq A$. The yield of tetrachlorobenzenes, which are first observed with CPVC (A = 73.2%), increases with the rise of A, whereas that of dichlorobenzenes begins to decrease through a maximum (53 mol %) near A = 70%. Finally, above A = 90%, the yield of aromatic hydrocarbons and chlorobenzene is below 5 mol %, while that of trichlorobenzenes and tetrachlorobenzenes becomes about 40 and 15 mol %, respectively.

These observed degradation products, which are formed mainly by dehydrochlorination reaction of the polymers followed by subsequent cyclization under the atmosphere of nitrogen at the high temperature, are closely related to the triads between V, D_{12}, D_{11}, and T_{112}. Table II shows the possible structures of the triads in CPVC and the degradation products anticipated to be yielded from the corresponding triads. In this case, it is assumed that the original PVC chains have a regular head-to-tail structure and that the dehydrochlorination reaction must occur to form conjugated polyene structure along the chain of the polymer, otherwise random chain scissions might participate to yield other compounds than aromatic derivatives.

From the classification in Table II, it can be pre-

TABLE III
MOLE FRACTION OF V, D_{11} + D_{12}, and T_{112}

Sample No.[a]	Degree of chlorination,[a] mol %	Mole fraction (mol %) V	Mole fraction (mol %) D_{11} + D_{12}	Mole fraction (mol %) T_{112}
1	8.5	91.5	8.5	
2	26.8	73.2	26.8	
3	36.0	64.0	36.0	
4	58.5	41.5,[b] 42.0[c]	58.2,[b] 57.5[c]	0.3,[b] 0.5[c]
5	73.2	28.6, 28.0	69.8, 69.3	1.6, 2.7
6	78.7	22.7, 23.2	74.2, 72.2	3.1, 4.6
7	92.8	11.0, 12.2	80.7, 76.7	8.3, 11.1

[a] The numbers and the values are the same as those in Table I. [b] Calculated from $T_{112} = {}^1/_3(A + D)$ in Table I. [c] Calculated from $T_{112} = {}^1/_3(2A + D)$ in Table I.

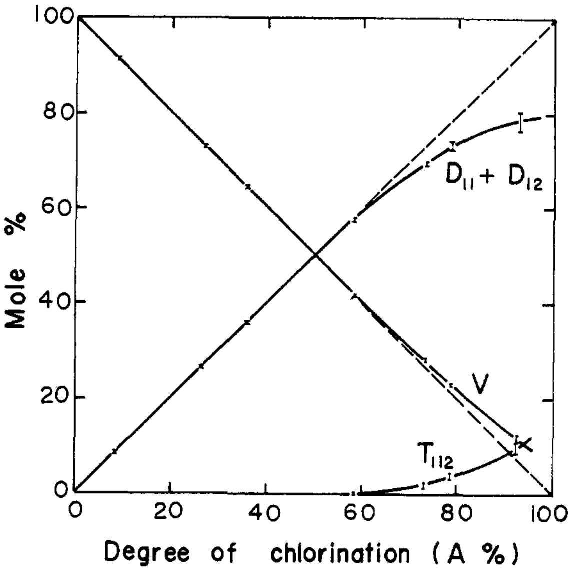

Figure 3. Relationships between the degree of chlorination (*A*) and the concentration of V, D_{11} + D_{12}, and T_{112}.

sumed that the triad, from which 1,2,3-trichlorobenzene or tetrachlorobenzenes are formed, must contain at least one T_{112}. Assuming that the triads, which consist of V, D_{11}, and T_{112}, or V, D_{12}, and T_{112}, form 1,2,3- and 1,2,4-trichlorobenzenes with equal probability, these triads exist up to twice the observed molar fraction of 1,2,3-trichlorobenzene. Considering these conditions and assuming that the triads which contain two T_{112} are rare, we can estimate the concentration of T_{112} from the yield of 1,2,3-trichlorobenzene and total tetrachlorobenzenes as shown in Table I. The concentration of T_{112} amounts about 10 mol % with CPVC (A = 92.8).

Table III shows the concentrations of V and D_{11} + D_{12} calculated from the value of the concentration of T_{112} and the chlorine content of the corresponding CPVC. As might be expected from Table II, it is difficult to distinguish D_{11} from D_{12} by degradation products alone. However, the yield of vinylidene chloride and 1,3,5-trichlorobenzene, which are closely associated with the successive D_{11} structure,[5] are observed in small amounts first with CPVC (A = 73.2%). Consequently, it is presumed that D_{12} has a tendency to be formed in larger amount than D_{11} at the earlier stage of chlorination.

The relationships between the concentration of V, D_{11} + D_{12}, and T_{112} and the degree of chlorination are shown in Figure 3. If the presence of T_{112} were neglected, the relationships should obey the broken diagonal lines.

In this paper, we have characterized the chlorine distributions in the chain of CPVC by analyzing the degradation products, and the presence of T_{112} structure, which contains three chlorine atoms, has been confirmed. Considering the results obtained by PGC, we are currently reinvestigating the nmr and ir data of the same CPVC.