lated.[1a,12] Polyenyl free radicals may undergo chain transfer to poly(vinyl chloride) to yield polyenes and polymeric radicals. As the conjugated sequence length of a polyenyl free radical increases, the radical is increasingly stabilized and transfer is less likely.

The effect of a reactive additive present during irradiation is indicated in films prepared from tetrahydrofuran solutions. The presence of a small concentration (0.75 wt %) of hydroxytoluene effectively suppresses conjugated unsaturation on irradiation. This protective effect is also indicated in electron spin resonance spectra in which the singlet associated with polyenyl free radicals is absent.

Conclusions

Electron irradiation of poly(vinyl chloride) induces a radical chain dehydrochlorination reaction, which, under vacuum, yields stable polyenyl free radicals with sequences of conjugated double bonds. Delocalization of the electron in polyenyl free radicals produces a singlet in electron spin resonance. At high enough values of the sequence length, the optical absorption spectra may converge. The presence of reactive additives or chemical inhomogeneities in the polymer chain suppresses the formation of polyenyl radicals and optical absorption.

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Structural Investigation of Chlorinated Polyethylenes by Pyrolysis–Gas Chromatography

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ABSTRACT: The distributions of chlorinated polyethylenes with various chlorine–carbon ratios were studied by use of direct pyrolysis–gas chromatography. The experimentally obtained results, in which the conception of random terpolymer between ethylene ($-CH_2CH_2-$), vinyl chloride ($-CH_2CHCl$), and 1,2-dichloroethylene ($-CHClCHCl-$) was adopted, were in fairly good agreement with those reported by ir.

Chlorinated polyethylenes (CPE) are formed by a simple chemical substitution reaction of hydrogens in polyethylene (PE) with chlorines. The resultant polymers range widely in properties from elastomers to resins. Some work on the characterization of the polymers has been reported[1,2] by the use of ir. Nambu[1] has interpreted ir data of CPE formed by the CCl_4 solution method at 70° and concluded that $-CH_2CHCl-$ and $-CHClCHCl-$ units are formed, but that the formation of $-CCl_2-$ does not occur during the chlorination of PE up to 68.1 wt % chlorine. Oswald and Kubu[2] have developed the ir investigation of CPE and discussed the concentration of the following three structures, $-CH_2CH_2CH_2-$, $-CH_2CH_2CHCl-$ and $-CHClCH_2CHCl-$, determined from the characteristic absorption bands of the δ (CH_2) mode between 1396 and 1470 cm^{-1}. However, the ir method has some disadvantages in the troublesome preparation of transparent film, KBr disk or solutions in addition to poor resolution of the ir spectra in these regions.

Recently we have characterized the sequence distributions of triads of vinylidene chloride–vinyl chloride copolymers by pyrolysis–gas chromatography (PGC).[3] In the present report a pyrolysis–gas chromatographic study of CPE is presented, and the distributions of chlorine in the chain of the polymers are discussed.

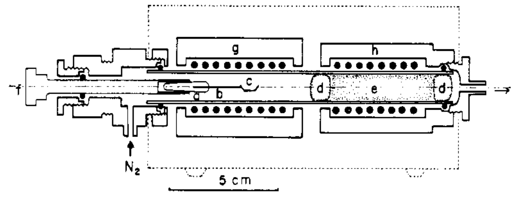

Figure 1. Pyrolyzer: a, glass rod; b, needle; c, sample dish (Ag); d, glass wool; e, NaOH coated on Diasolid H; f, sample charging rod; g, pyrolysis heater; h, precut heater.

Experimental Section

Materials. The series of CPE samples used in this work was obtained by chlorination of low-density PE using the CCl_4 solution method proposed by Campbell and Lyman,[4] and by suspension-chlorination of high-density PE (the latter samples were supplied by Showadenko Co. Ltd.). Chlorine contents of the samples were determined by the usual chemical method and are listed in Table I.

Pyrolysis–Gas Chromatographic Conditions. Figure 1 shows the furnace-type pyrolyzer used in this study. It was directly attached to the inlet port of the Yanagimoto Model GCG-550F gas chromatograph with double flame ionization detectors. The precut column in the pyrolyzer contained 25 wt % NaOH coated on Diasolid H (30–60 mesh) to adsorb hydrogen chloride evolved during the degradation of the polymers.

Samples ranging in size from 0.1 to 0.3 mg were pyrolyzed

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TABLE I

RELATIVE YIELD OF DEGRADATION PRODUCTS OF CPE

			Relative yield, wt %							
Sample no.[a]	Chlorine content, wt %	Chlorine-carbon ratio R	Benzene (A)	Toluene (B)	Styrene (C)	Naphthalene (D)	Aromatic hydrocarbons (A + B + C + D)	Chlorobenzene	Dichlorobenzenes	Others[b]
1-S	10.9	0.05	5.6	2.8	2.0		10.4			89.6
2-S	20.0	0.10	7.4	3.5	1.9		12.8			87.2
3-A	28.8	0.16	13.6	6.9	3.6	2.7	26.8			73.2
4-A	35.8	0.22	16.0	8.4	4.3	3.8	32.5			67.5
5-C	42.9	0.29	13.1	6.1	3.9	3.5	26.6	1.2		72.2
6-A	58.1	0.53	22.7	11.1	5.2	5.8	44.8	2.9	Trace	52.3
7-A	66.8	0.74	23.2	10.9	4.5	5.8	44.4	14.5	4.1	37.0

[a] S, chlroinated by solution method; A, C, chlorinated by suspension method (A, amorphous sample; C, crystalline samples).
[b] Others are mainly C_1–C_3 hydrocarbons.

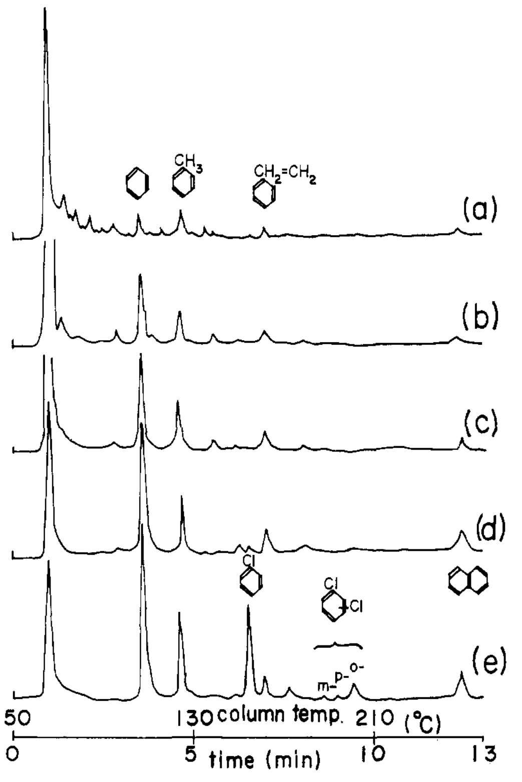

Figure 2. Typical pyrograms at 660° under a flow of nitrogen: (A): CPE, a, R = 0.05; b, R = 0.16; c, R = 0.22; d, R = 0.53; e, R = 0.74.

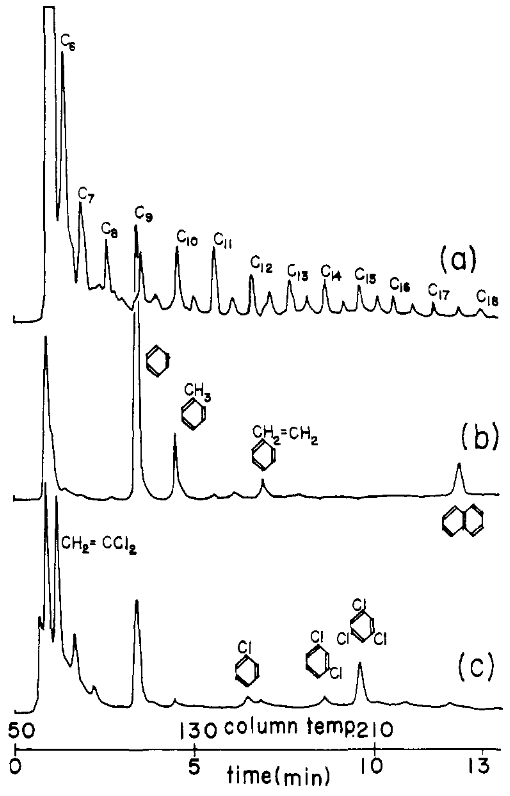

Figure 3. Same as figure 2 with the following reference materials: a, PE; b, PVC; c, PVdC; C_i, normal olefines with i carbons.

for 1 min under a flow of carrier gas (N_2) at 660°. The relatively high pyrolysis temperature of 660°, which reflects the fairly good thermal stability of CPE, was determined experimentally with a view to obtaining quantitative and characteristic pyrograms.

Gas chromatographic conditions are the same as described in the previous work.[3] Separation columns (3 mm i.d. × 2 m) containing 10 wt % Carbowax 6000 coated on Diasolid L (80–100 mesh) were used with a programmed increase in temperature from 50 to 210° at a rate of 16°/min.

Identification of the peaks appearing on the pyrograms was carried out by use of the retention data of various pure substances which were identified by mass spectra of the degradation products of the polymers.

Results and Discussion

Figure 2 shows typical pyrograms of CPE at the pyrolysis temperature of 660°, and Figure 3 shows those of PE, PVC and PVdC as references.

It is apparent from these pyrograms that with increasing chlorine/carbon ratio (R), increasing amounts of aromatic hydrocarbons such as benzene, toluene, styrene and naphthalene, and chlorine-containing aromatics such as chlorobenzene and dichlorobenzenes are observed. These characteristic compounds, which are not observed at all in the pyrogram of PE, are formed from CPE by dehydrochlorination reaction

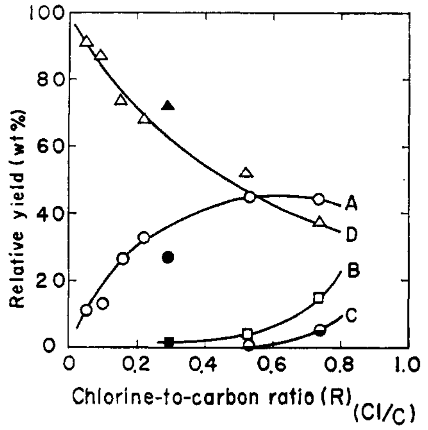

Figure 4. Relationships between *R* and observed relative yield of the degradation products: A, aromatic hydrocarbons (benzene + toluene + styrene + naphthalene); B, chlorobenzene; C, *o*-, *m*-, and *p*-dichlorobenzenes; D, others, mainly C_1–C_8hydrocarbons; ○, amorphous samples; ●, crystalline sample.

followed by subsequent cyclization under the atmosphere of nitrogen at the high temperature.

As pointed out by Oswald and Kubu,[2] the possible structures in CPE can be divided as follows: ethylene ($-CH_2CH_2-$, E), vinyl chloride ($-CH_2CHCl-$, V), 1,2-dichloroethylene ($-CHClCHCl-$, D) and vinylidene chloride ($-CH_2CCl_2-$, Vd), provided that chlorines are located at random along the backbone chain of PE. However, vinylidene chloride and 1,3,5-trichlorobenzene, which are characteristic to the pyrogram of PVdC, are not seen in that of CPE with the highest chlorine content (R = 0.74), and therefore the presence of Vd structure is not considered in the following discussion.

As the main degradation products of PVC are such aromatic hydrocarbons as benzene, toluene, styrene and naphthalene, the appearance of these on the pyrograms of CPE may indicate successive vinyl chloride (V) structures although there may be some contribution from sequences such as –DEV–, –DEVVV–, $-(DE)_2V-$, etc. The formation of chlorobenzene, observed in pyrograms of CPE (Figure 2) and not in PVC (Figure 3b), may result mainly from such sequences as –VVD– and –VDV–, although a slight contribution of –EDD– or –DED– has to be taken into account. On the other hand, *o*-, *m*- and *p*-dichlorobenzenes will be formed from such sequences as –DDV– and –DVD–. We may summarize by stating that the aromatic hydrocarbons and chlorobenzenes have close relationships to the V structure and to the D structure, respectively.

It is thus possible to get information about the distribution of chlorine in CPE by measuring the yield of these characteristic degradation compounds. Relative yields of the degradation products of CPE are tabulated in Table I. These values are calculated from the relative peak areas appearing on the pyrograms with appropriate weight sensitivity corrections for the flame ionization detector.

In the following discussion, the chlorine–carbon ratio (R) is used to designate chlorine content in CPE.

Distribution of Chlorine in CPE. Figure 4 shows the relationships between R and the observed yield of total aromatic hydrocarbons, chlorobenzene and dichlorobenzenes.

In the region of low R, a rapid increase in the yield of the aromatic hydrocarbons is observed as the rise of R, but chlorobenzenes are not seen. This observation suggests that the chlorination reaction produces mainly V structure at the beginning.

However, the appearance of chlorobenzene from CPE with R = 0.29, which is far lower than that of PVC (R = 0.5), indicates that D structure has already been in competition with V structure at this stage of chlorination.

From CPE with R = 0.74, dichlorobenzenes are observed in addition to considerable amounts of chlorobenzene, but vinylidene chloride and 1,3,5-trichlorobenzene are not seen. On the other hand, the yield of the aromatic hydrocarbons, which has an increasing tendency with the rise of R, begins to decrease slightly at the stage. These observations suggest that further chlorination takes place by chlorinating the V structure to the D structure and that detectable amounts of Vd structure are not formed.

These results are on the whole in fairly good agreement with those reported by Oswald and Kubu[2] from ir measurements. Among CPE samples used, the half-crystalline sample (5-C in Table I) yielded smaller amounts of aromatic hydrocarbons than those expected from the other amorphous samples and is designated by solid dots in Figure 4. This finding implies that the distribution of chlorine in CPE samples even with the same R may differ from one another according to the crystallinity of the original PE and the method of chlorination.