Determination of the Sequence Distribution of Chlorines in Chlorinated Polyethylenes with the Aid of Monte Carlo Simulation

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ABSTRACT: Monte Carlo simulation was carried out to specify the most probable model sequence and to reveal the sequence distribution of chlorines in chlorinated poly-ethylene(CPE). The simulation was also applied to study those of hydrogenated poly-(vinyl chloride)(HPVC) and vinyl chloride—ethylene copolymer(VC—Et) for a comparison with those of CPE. The simulation was executed with the conditional probabilities of the second order defined in terms of the actual existence probabilities of triads which can be obtained by NMR spectroscopy. Monitor quantities relating to long methylene sequence and degree of chlorination were introduced into the simulation as a criterion of a convergence. When the convergence conditions were satisfied after a few trials, a linear model sequence composed of one thousand carbons was considered to be the most probable.

From the inspection of the model sequence thus determined, it can be pointed out that the distribution of chlorine atoms along the CPE chain is substantially random, being different from those of HPVC and VC—Et. The sequence distribution of various chemical units in the molecular chain was also determined readily and quantitatively without any contradiction by reckoning each sequential unit along the model sequence.

KEY WORDS   Chlorinated Polyethylene / Vinyl Chloride—Ethylene Copolymer / Hydrogenated Poly(vinyl chloride) / NMR Spectroscopy / Monte Carlo Method / Computer Simulation / Conditional Probability of the Second Order / Most Probable Model Sequence / Sequence Distribution of Chlorines /

It is well known that even if the monoad compositions are quite identical in copolymers, the physical properties are apt to depend strongly on the sequence distribution of different units along the molecular chain.   The difference of some viscoelastic properties of block, random and alternate copolymers[1-4] is just an example. Such being the case, it should be necessary to specify the sequence distributions of various units in the characterization of the microstructure of copolymers.

High-resolution nuclear magnetic resonance (NMR) spectroscopy is readily available for studying the microstructure of copolymers and was applied to the study of chlorinated poly-ethlyne(CPE).[5] However, direct information from NMR is usualy nothing more than triad informations or the like.   Thus, we must resort to some statistical calculations in order to obtain polyad information.

The sequence distributions of different units in copolymers are often evaluated from the reactivity ratios of monomers with the considera-tion of the effect arising from the penultimate unit.[6] On the other hand, with substituted polymers such as CPE and chlorosulfonated poly-ethylene(CSPE), a statistical calculation was skill-fully carried out by Frensdorff, *et al.*,[7] using the conditional probabilities estimated from the reac-tion selectivity of chlorinated *n*-paraffins. These calculations were especially applied to the sequence distribution of chlorines in CPE. A similar investigation was also developed for CSPE by Brame.[8]

In the statistical calculation stated above, how-ever, there are often rather inevitable deviations

from experimental results because of an inadequate estimation of conditional probabilities. For instance, though the formulation of Frensdorff, et al., is excellent and highly suitable for extending the triad information to the polyad information, their results for the monoad such as —(CCl$_2$)— and —(CHCl)— in CPE molecules are not entirely in agreement with those obtained by our NMR study.[5] From this fact, their estimation of the conditional probabilities may be inadequate for those of the chlorination of polyethylene. In this sense, if the triad information actually obtained from the NMR study were regarded as conditional probabilities of the second order instead of the estimation from model reactions of n-paraffins, the sequence distribution would be more exactly determined by the statistical calculation or by the Monte Carlo simulation by means of a computer. The latter simulation is used in the present investigation on the basis of quantitative triad informations from the NMR study described in our previous paper,[5] wherein the same sample-code as those in that paper are used in this article.

As was shown in the previous study,[5] it is very difficult by the NMR-spectroscopy to reveal the distribution of a longer methylene sequence than three in the CPE molecule. For this reason, a variable parameter (Y) which defines the mole fraction of asterisked methylene in the unit —CHCl—CH$_2$—($\overset{*}{\text{C}}$H$_2$)$_n$—CH$_2$—CHCl— is specifically introduced into the simulation. After a few trials of the simulation with the variation of Y, when the convergence conditions are satisfied, a simulated sequence of CPE will be considered as the most probable sequence as determined self-consistently, and useful information on the sequence distribution of various units will be readily obtained without any contradiction. This intention will succeed when the assignment and other treatments of calculation are throughly correct, and conversely the calculation will be verified when the above intentions turn out a success.

SIMULATIONAL

Description of Variables and Parameters

Variables such as a_1, a_2, a_3, b, ... f and g represent mole fraction of various chemical units as summarized in Table I. Mole fraction of

Table I. Mole fraction variables of chemical units[a]

Chemical units		Notation
—CHCl—($\overset{*}{\text{C}}$H$_2$)$_i$—CHCl—	$i \geq 5$	a_1
	$i = 4$	a_2
	$i = 3$	a_3
	$i = 2$	b
	$i = 1$	c
—CHCl—$\overset{*}{\text{C}}$H$_2$—CCl$_2$—		d
—CH$_2$—($\overset{*}{\text{C}}$HCl)$_j$—CH$_2$—	$j = 1$	e
	$j = 2$	f
	$j \geq 3$	g

[a] cf. Table I in the previous paper.[5]

polyads of longer than three methylene sequences are tentatively estimated from the following equations with parameters α and β as described in our previous paper,[5]

$$a_1 = K(1+\alpha)S_1 = A5 \qquad (1)$$
$$a_2 = K\{(1+\beta)S_2 - \alpha S_1\} = A4 \qquad (2)$$
$$a_3 = K(S_3 - \beta S_2) = A3 \qquad (3)$$
$$K = (a_1 + a_2 + a_3)/(S_1 + S_2 + S_3) \qquad (4)$$

where α and β are, so to speak, signal splitting parameters of overlapping signals appearing in the NMR spectrum arising from protons in long methylene sequences. K and S_i ($i = 1, 2, 3$) are a normalizing factor and relative peak area of the chemical shift, respectively. Parameters α and β are assumed to be 0.2 and 1.0, respectively, deduced from those of α, ω-dichloparaffins.[5]

Mole fractions of some triads listed in Table II are also estimated as

$$a_t = Ya_1 + a_2/2 + a_3/3 \qquad (5)$$
$$b_t = (1-Y)a_1 + b + a_2/2 + 2a_3/3 \qquad (6)$$
$$f_t = f + (1-Z)g \qquad (7)$$
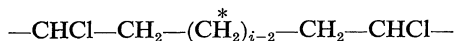$$g_t = Zg \qquad (8)$$

where Y and Z are mean mole fractions of

Table II. Mole fraction variables of triads

Triad	Notation
—CH$_2$—$\overset{*}{\text{C}}$H$_2$—CH$_2$—	a_t
—CHCl—$\overset{*}{\text{C}}$H$_2$—CH$_2$—	b_t
—CHCl—$\overset{*}{\text{C}}$HCl—CH$_2$—	f_t
—CHCl—$\overset{*}{\text{C}}$HCl—CHCl—	g_t

asterisked methylenes or methynes in following formulae, respectively.

$$-CHCl-CH_2-(\overset{*}{CH_2})_{i-2}-CH_2-CHCl-$$

$$-CH_2-CHCl-(\overset{*}{CHCl})_{j-2}-CHCl-CH_2-$$

If the mole fraction of i methylene sequences and j methyne sequences were ϕ_i and ψ_j, respectively, Y and Z are determined as follows:

$$Y = \sum_{i=3}^{\infty} \{(i-2)\phi_i\} / \sum_{i=3}^{\infty} i\phi_i \qquad (9)$$

$$Z = \sum_{j=3}^{\infty} \{(j-2)\psi_j\} / \sum_{j=3}^{\infty} j\psi_j \qquad (10)$$

As in a previous paper,[5] Z is assumed to be 0.8. On the other hand, Y is treated as a variable in the present simulation, because the variety of the methylene sequence length seemed to be more characteristic than the methyne sequence length in the CPE chain.

Definition of Conditional Probability

Carbon atoms in the skeletal chain of a CPE molecule are enumerated consecutively from the terminal one starting with the first, and the N-th carbon is designated as $IS(N)$. Chemical units such as CH_2, $CHCl$, and CCl_2 are represented by the integer 0, 1, and 2, respectively, according to the number of chlorine atoms substituted for a methylene. An existent probability of an arbitrary triad is written as $T(IJK)$ when the following conditions are satisfied

$$IS(N-2)=I, \quad IS(N-1)=J, \quad \text{and} \quad IS(N)=K \qquad (11)$$

where I, J, and K are one of the integers 0, 1, and 2. The triad probability $T(IJK)$ is readily

Table III. Existent probabilities of triads

$T(IJK)$	Variables
$T(000)$	a_t
$T(100)$	$0.5b_t$
$T(001)$	$0.5b_t$
$T(101)$	c
$T(102)$	$0.5d$
$T(201)$	$0.5d$
$T(010)$	e
$T(011)$	$(0.5f_t+0.1g_t)$
$T(110)$	$(0.5f_t+0.1g_t)$
$T(111)$	$0.8g_t$

determined from the mole fractions such as a_1, a_2, a_3, b, ... g. For computing $T(IJK)$, the symmetry,

$$T(IJK) = T(KJI) \qquad (12)$$

is taken into consideration. The $T(IJK)$'s are calculated with the variables listed in Tables I and II, as shown in Table III.

Next, a conditional probability $P\{K|IJ\}$ is defined in terms of the $T(IJK)$ as follows

$$P\{K|IJ\} = T(IJK) / \sum_{K=0}^{2} T(IJK) \qquad (13)$$

The conditional probability thus defined is considered to be the transition probability of the second order. Details of the conditional probabilities are summarized in Table IV, where the fact that the chemical unit CCl_2 exists in one and only sequence[5] such as

$$-(CHCl-CH_2-CCl_2-CH_2)_i-CHCl- \quad (i \geqq 1)$$
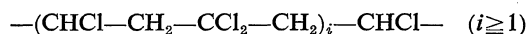
is under consideration, and the normalizing factors $\sum_{K=0}^{2} T(IJK)$ are shown in Table V. The

Table IV. Conditional probabilities

Conditions		Conditional probabilities		
$IS(N-2)$ I	$IS(N-1)$ J		$P\{K|IJ\}$	
		$K=0$	$K=1$	$K=2$
0	0	$T(000)/T00$	$T(001)/T00$	0.00
0	1	$T(010)/T01$	$T(011)/T01$	0.00
0	2	1.00	0.00	0.00
1	0	$T(100)/T10$	$T(101)/T10$	$T(102)/T10$
1	1	$T(110)/T11$	$T(111)/T11$	0.00
2	0	0.00	1.00	0.00
—	1	$\{T(010)+T(110)\}/T1$	$\{T(011)+T(111)\}/T1$	0.00

Table V. Normalizing factors

TIJ	$\sum T(IJK)$
T00	$T(000) + T(001)$
T01	$T(010) + T(011)$
T10	$T(100) + T(101) + T(102)$
T11	$T(110) + T(111)$
T1	$T01 + T11$

probability $P\{K|1\}$ listed in the last column of Table IV is used for the determination of $IS(2)$, and $IS(1)$ is assumed *a apriori* to be a methyne unit. However, the validity of the simulation is conserved in the case of such a large carbon number as one thousand as in the present simulation. The conditional probabilities concerned with the probabilities $T(000)$, $T(100)$ and $T(001)$ depend on the parameter Y, because $T(000)$, $T(100)$ and $T(001)$ are function of a_t and b_t, each depending on the parameter Y as shown in eq 5 and 6.

Determination of $IS(N)$

The degree of chlorination of the N-th carbon, $IS(N)$ is determined from comparison of the N-th pseudorandom number, $RDN(N)$ generated by the subroutine equipped in a computer (IBM 360-4H)[9] with the conditional probability as follows,

$$a\ priori \dots\dots\dots\dots\dots\dots IS(1)=1 \quad (14)$$

$$RDN(2)_n \leqq (P\{0|1\}+n-1)/k \dots IS(2)=0 \quad (15)$$

$$RDN(2)_n > (P\{0|1\}+n-1)/k \dots IS(2)=1 \quad (16)$$

where the terminal unit of CPE chain is assumed to be methyne and $IS(2)$ is not equal to 2, because the —CHCl—CCl₂— is absent in the CPE chain as reported in a previous paper.[5]

As for the succeeding $N(N \geqq 3)$, the following operations are repeated.

$$RDN(N)_n \leqq (P\{0|IJ\}+n-1)/k \dots. IS(N)=0 \quad (17)$$

$$(P\{0|IJ\}+n-1)/k < RDN(N)_n$$
$$\leqq (P\{0|IJ\}+P\{1|IJ\}+n-1)/k$$
$$\dots. IS(N)=1 \quad (18)$$

$$RDN(N)_n > (P\{0|IJ\}+P\{1|IJ\}+n-1)/k$$
$$\dots. IS(N)=2 \quad (19)$$

In these equations, n and k are integers for improvement on inferior independence between successive numbers in the series of pseudorandom

numbers generated by a computer. Details on an application of the pseudorandom number are described in the appendix of this paper.

Flow Chart of Computer Simulation

The computer simulation is carried out according to the flow chart as briefly shown in Figure 1. For a given arbitrary value of the parameter Y and the triad probability determined by NMR spectroscopy, the first trial (a count number M is equal to unity) is executed and further trials are repeated after Y_{M+1}, $A5_{M+1}$, $A4_{M+1}$, and $A3_{M+1}$
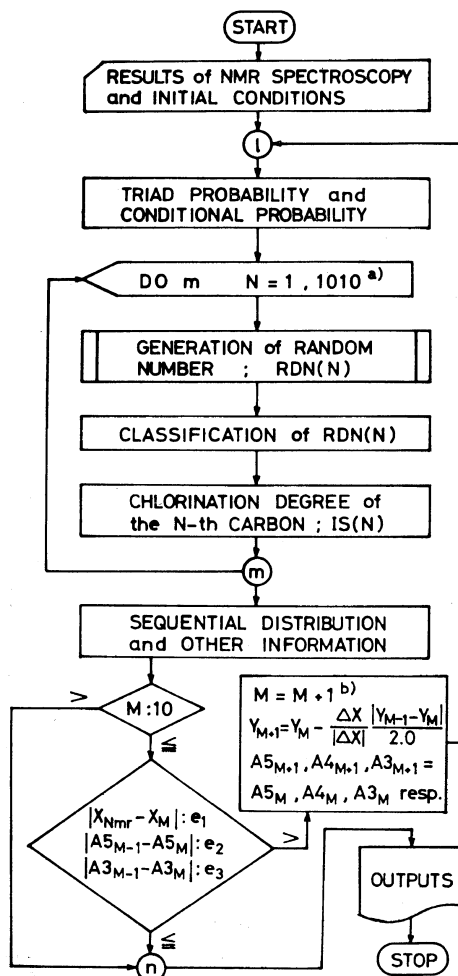

Figure 1. The outline of the flow in the computer simulation. [a] The statement in FORTRAN language which means recurrent calculation till N reaches to one thousand and ten starting with unity. [b] The statement in FORTRAN language which means substituting $(M+1)$ for M.

SAMPLE	IS(N)	X_S (wt %)
A1FE	000101000010000000001000000101000000000001000000000001000000000000000000000000000000000000000000001	16.3
A4W	000101000010100000001010100101000000000001000000000001000000000000000000000000000000000010000000001	21.9
A5FC	00000000101010100000000101000000000010100001000100001000000000000000001000001000100010010000000100	31.0
S4W	01001000001000101010000101000100010100010010101000101000000001001010001001000010001010000010101010 0	40.6
A10W	101020100010001010100001010101000101000100101010001010000000010010100010010100101010201000010101010 0	43.2
A11FE	00000001020100100101010101010101010100010110001000100000100100101010001010101001101001020100000001001	49.5
A13FE	1010100102011011010101020101010101001011010010101010010101010010101010010101010010110111011020110101010201	57.8
A15FE	1010110201102011020102010201020101011110101110201010201120101010201111111020102010201101010111102	66.6
HPVC	101001010100100100000101010101010100010100000001010101000000010001010010100010001001010100100101	44.9
VC–Et	1010100010101010101010100c000c00000c0101010101010100000100001010100000010101010101010000101000000001000	47.8

Figure 2. Partial sequence in the most probable model sequence of CPE's, HPVC and VC—Et by the Monte Carlo simulation; where X_s is the mean chlorine content of a molecular chain determined by the simulation.

Table VI. Comparison of simulated results with input data

Parameter	AIFE $X_c=0.166$[b]		A4W $X_c=0.244$		A5FC $X_c=0.311$		S4W $X_c=0.416$		A10W $X_c=0.432$	
	Ante S	Post S	Ante S	Post S	Ante S	Post S	Ante S	Post S	Ante S	Post S
X[a]	0.176	0.163	0.246	0.219	0.310	0.310	0.399	0.406	0.379	0.432
E_1	0.916	0.924	0.872	0.890	0.825	0.825	0.744	0.736	0.772	0.721
V_1	0.084	0.076	0.128	0.110	0.175	0.175	0.257	0.264	0.218	0.265
D_1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.014
$T000$	0.759	0.790	0.617	0.718	0.458	0.517	0.302	0.306	0.299	0.295
$T100$	0.131	0.118	0.198	0.126	0.313	0.265	0.338	0.332	0.333	0.295
$T101$	0.026	0.017	0.057	0.047	0.054	0.043	0.103	0.098	0.122	0.104
$T102$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.028
$T010$	0.084	0.075	0.128	0.109	0.175	0.175	0.257	0.264	0.218	0.265
$T110$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$T111$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$T020$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.014
Y_M	0.891		0.878		0.879		0.879		0.797	

Parameter	A11FE $X_c=0.507$		A13FE $X_c=0.595$		A15FE $X_c=0.702$		HPVC-1 $X_c=0.428$		Vc—Et $X_c=0.504$	
	Ante S	Post S	Ante S	Post S	Ante S	Post S	Ante S	Post S	Ante S	Post S
X	0.484	0.495	0.578	0.578	0.674	0.666	0.420	0.449	0.503	0.478
E_1	0.661	0.648	0.523	0.527	0.313	0.347	0.720	0.686	0.612	0.648
V_1	0.317	0.329	0.435	0.427	0.602	0.562	0.280	0.313	0.389	0.352
D_1	0.022	0.024	0.043	0.047	0.084	0.091	0.000	0.000	0.000	0.000
$T000$	0.191	0.160	0.048	0.031	0.007	0.002	0.248	0.251	0.188	0.227
$T100$	0.274	0.296	0.157	0.169	0.019	0.016	0.254	0.243	0.142	0.137
$T101$	0.152	0.146	0.231	0.235	0.120	0.147	0.219	0.192	0.282	0.284
$T102$	0.044	0.048	0.086	0.093	0.168	0.183	0.000	0.000	0.000	0.000
$T010$	0.302	0.306	0.332	0.333	0.149	0.134	0.280	0.313	0.389	0.352
$T110$	0.015	0.022	0.078	0.063	0.226	0.224	0.000	0.000	0.000	0.000
$T111$	0.000	0.000	0.025	0.029	0.227	0.203	0.000	0.000	0.000	0.000
$T020$	0.022	0.024	0.043	0.047	0.084	0.091	0.000	0.000	0.000	0.000
Y_M	0.798		0.798		0.798		0.798		0.798	

[a] X under the row of *ante S* and *post S* are mean chlorine content determined by the NMR-spectroscopy (X_N) and by the simulation (X_S), respectively.

[b] X_c is that by the chemical analysis.

are substituted by Y_M, $A5_M$, $A4_M$ and $A3_M$, respectively, till the conditions of convergence are satisfied.

As in a previous report,[10] when the signal splitting parameters α and β were treated as variables, the convergency was very poor. Accordingly in this paper, parameters α and β are assumed to be constant (*i.e.*, $\alpha=0.2$, $\beta=1.0$) which were reasonably estimated from those of α, ω-dichloroparaffins. On the other hand, Y is con-

sidered to be a variable parameter. As a result, good convergency is attained by a few trials in the calculating loop of the Monte Carlo simulation.

RESULTS AND DISCUSSION

Model Sequence of CPE Chain

The most probable model sequences of some CPE's having various mean degree of chlorination, and those of HPVC and VC—Et are partly

Table VII. Existent probability, $Pr(N)$, of $-(CH_2)_N-$ unit to total carbon number (%)

Sample	Sequence number (N)															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	$N\geqq15$	$N\geqq5$
A1FE	1.69	1.19	0.89	0.79	0.99	2.38	0.00	0.79	4.46	3.97	2.18	1.19	6.45	2.78	62.65	87.84
A4W	4.66	1.39	0.60	1.19	2.48	2.98	0.69	2.38	1.79	4.96	2.18	2.38	6.45	2.78	52.09	81.84
A5FC	4.27	6.55	6.55	5.16	5.46	8.33	5.56	5.56	0.89	5.95	3.27	2.38	5.16	5.56	11.85	59.97
S4W	9.82	12.30	11.31	6.75	8.43	6.55	4.86	7.94	1.79	0.99	1.09	0.00	0.00	0.00	1.77	33.42
A10E	14.02	10.12	10.12	6.75	6.94	6.55	4.86	6.35	1.79	1.98	0.00	0.00	1.29	0.00	1.33	31.09
A11FE	19.34	13.49	11.61	7.14	6.45	3.57	1.39	0.79	0.89	0.00	0.00	0.00	0.00	0.00	0.00	13.09
A13FE	32.84	12.50	3.87	2.78	0.00	0.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.60
A15FE	32.93	1.39	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HPVC-1	19.24	7.74	7.74	7.14	6.45	5.36	3.47	6.35	0.89	0.00	2.18	0.00	0.00	0.00	2.04	26.74
VC—Et	28.37	3.57	3.87	3.18	3.47	4.17	2.08	0.79	0.00	2.98	3.27	1.19	3.87	0.00	3.99	25.81
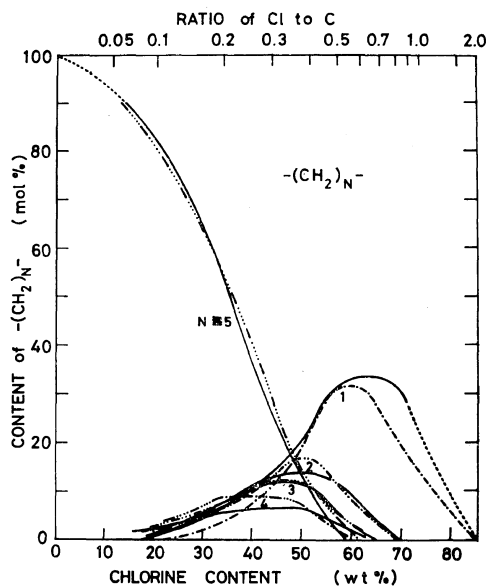
Figure 3. Content of methylene sequences, $-(CH_2)_N-$, as a function of chlorine content (X_s); where the solid line and the dot-dash-line are those determined by the simulation and by eq 21, respectively.

shown in Figure 2, where the integer 0, 1, and 2 represent the chemical units of CH_2, $CHCl$, and CCl_2, respectively.

The model sequences provide us with various informations such as mean chlorine content (X_s), mole fraction of the units $CH_2(E_1)$, $CHCl(V_1)$, $CCl_2(D_1)$ and mole fraction of various triads and polyads. These results are summarized in the row designated as *post S* in Table VI and the input data obtained by NMR spectroscopy are also listed in the row of *ante S* in the same table. The parameter Y_M was also listed in Table VI. It can be pointed out that quantities such as $T(IJK)$, X_s, E_1, V_1, and D_1 between *ante* and *post* simulations are substantially in close agreement with each other. This fact verifies an availability of the simulation and also the adequancy of the assignments on triads described in a previous paper.[5]

Content of Long Methylene Sequences

The frequency to locate $-(CH_2)_N-$ in a CPE chain, $Fr(N)$, can be readily obtained by the simulation. Hence the existence probability of

Table VIII. Existent frequency, $Fr(N)$, of $-(CHCl-CH_2)_N-$ unit to total carbon number (%)

Sample	Sequence number (N)												
	1	2	3	4	5	6	7	8	9	10	11	12	13
A1FE	4.5	1.2	0.1	0.1									
A4W	3.7	1.2	1.0	0.1	0.3								
A5FC	9.9	2.6	0.4	0.3									
S4W	10.6	3.6	1.3	0.5	0.2	0.3							
A10W	8.1	3.5	1.6	0.2	0.5	0.1	0.1						
A11FE	6.8	4.1	2.1	0.8	0.4	0.1	—	0.1					
A13FE	5.3	3.6	2.3	1.1	0.7	0.3	—	0.1	0.1	—	0.2		
A15FE	5.5	2.7	0.7	0.1									
HPVC-1	4.7	2.9	1.9	0.8	1.0	0.4	0.1	0.1	0.2	—	—	0.1	
VC—Et[a]	1.8	1.2	0.9	0.4	0.4	0.4	0.3	0.4	0.1	0.2	—	0.3	0.2

[a] More long sequences ($N \geqq 13$) exist i.e., 0.1 ($N=16$), 0.1 ($N=20$), 0.2 ($N=21$).

Table IX. Existent frequency, $Fr(N)$ of $-(CHCl-CH_2-CCl_2-CH_2)_N-CHCl-$ unit to total carbon number (%)

Sample[a]	Sequence number (N)			
	2	4	6	8
A10W	1·0	0.2		
A11FE	2.2	0.1		
A13FE	4.4	0.2		
A15FE	6.4	0.8	0.1	0.2

[a] Other samples do not contain the unit $-(CHCl-CH_2-CCl_2-CH_2)_N-CHCl-$.

that, $Pr(N)$, is determined by following equation:

$$Pr(N) = NFr(N) \qquad (20)$$

The results thus calculated by eq 20 are summerized in Table VII. While $Fr(N)$ can be also determined by the theoretical treatment of Frensdorff, et al.,'s work[7] as follows,

$$Fr(N) = E_1(1.0 - A - B)^2(A+B)^{N-1} \qquad (21)$$

where A, B, and E_1 are the mole fraction of chemical units such as $-(CH_2)_N-$ ($N \geqq 3$), $-(CH_2)_2-$ and $-(CH_2)-$, respectively, which are directly obtained NMR spectroscopy. $Pr(N)$, ($N=1, 2, 3, 4,$ and $N \geqq 5$), determined by the simulation and by the latter theoretical calculation with eq 21 are substantially in close agreement each other as shown in Figure 3. The question about the extraordinarily high value of $Pr(4)$ as shown in Figure 7 of the previous paper[5] seemed to be resolved by the simulation. This fact is one of availabilities of the computer simulation.

Sequence Distribution of Various Units in a Molecular Chain

Sequence distributions of various units such as $-(CHCl-CH_2)_N-$, $-(CHCl-CH_2-CCl_2-CH_2)_N-CHCl-$ and $-(CHCl)_N-$ are expressed in terms of $Fr(N)$ to locate them in a molecular

Table X. Existent frequency, $Fr(N)$, of $-(CHCl)_N-$ unit to total carbon number (%)

Sample	Sequence number (N)											
	1	2	3	4	5	6	7	8	9	10	11	12
A1FE	7.5											
A4W	10.9											
A5FC	17.5											
S4W	26.4											
A10W	26.5											
A11FE	30.6	1.1										
A13FE	33.3	1.7	1.0	0.1	0.3	0.2						
A15FE	13.4	4.1	3.0	1.3	0.8	0.8	0.2	0.7	0.2	0.1	0.1	0.1
HPVC-1	31.3											
VC—Et	35.2											
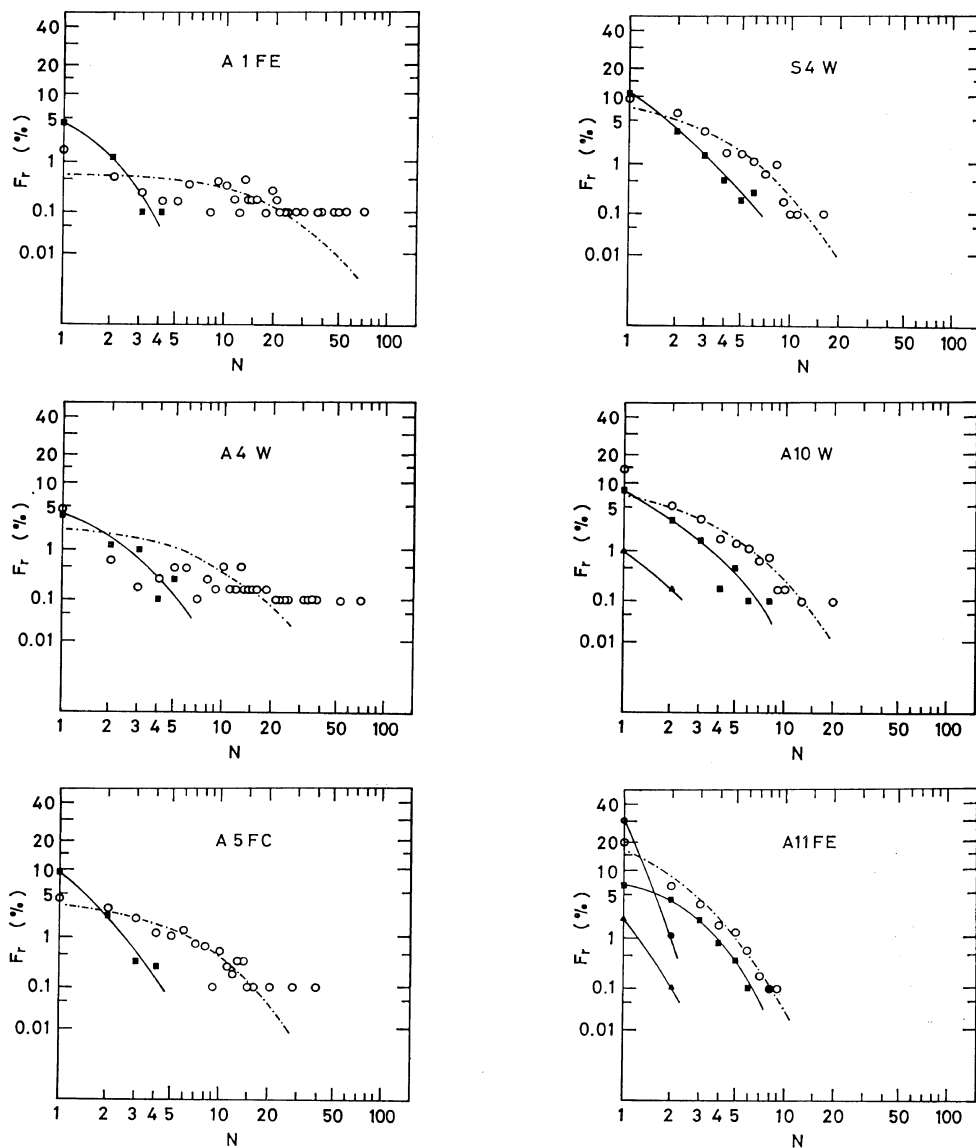
Figure 4. Sequence distribution of various units in the molecular chain of CPE's, HPVC, and VC—Et. ○, ■, ▲, and ● indicate the frequency to find a unit such as —(CH₂)N—, —(CHCl—CH₂)N—, —(CHCl—CH₂—CCl₂—CH₂)N—CHCl— and —(CHCl)N—, respectively. The dot-dash-line is that of —(CH₂)N— by eq 21. The sample code in the figure is the same code as used in Table VI and Figure 2.

chain. The $Fr(N)$'s are summarized in Tables VIII—X, and depicted in Figure 4 as well as that of —(CH₂)N—. Discussions on sequence distribution of various units are as follows.

Low Chlorine-Content Region $(X_s \leqq 0.25)$. As shown in Figure 4 (A1FE, A4W), the frequency

of —CHCl—(CH₂)N—CHCl— is almost equal to 0.1—0.2 in the region of sequence number, $10 \leqq N \leqq 100$, and these results deviate remarkably from an estimation by eq 21.

Also it is notable that the unit of —(CHCl—CH₂—CHCl)— is present more than is estimated,
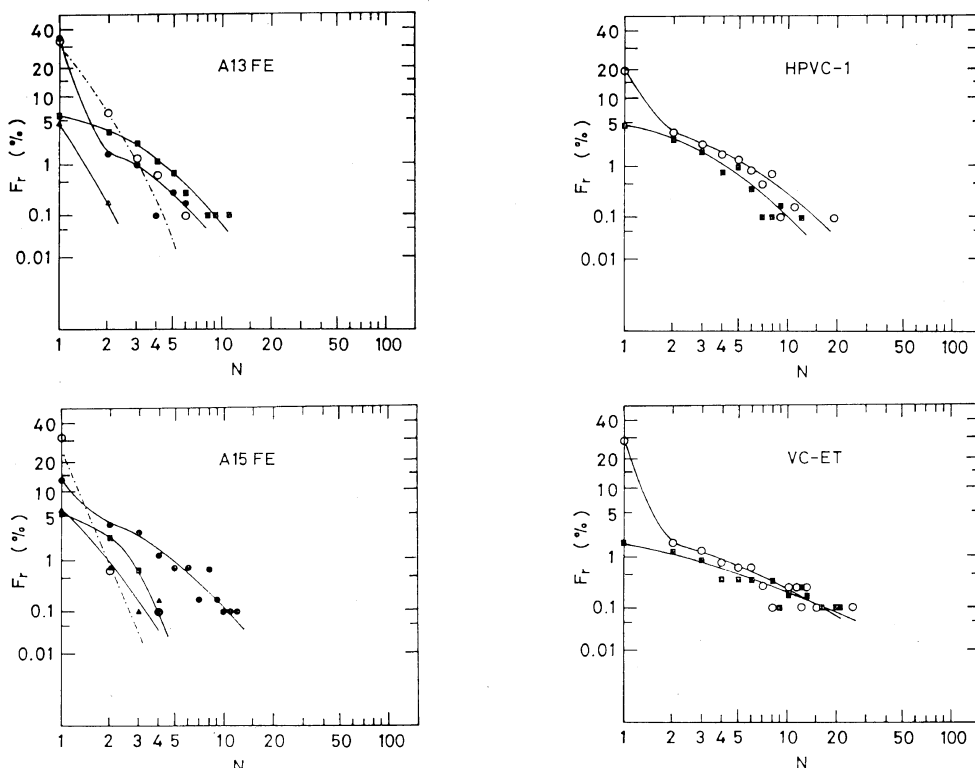
Figure 4. (Continued)

although the sequence length of —(CHCl—CH$_2$)$_N$— is at most five or so, and a ratio of the methyne unit taken part in the formation of a sequence —(CHCl—CH$_2$—CHCl)— is equal to 73%(A1FE)—78%(A4W) per total methyne units.

On the contrary, the selective formation of 1,3-dichloride sequence such as that in the CPE chain cannot be observed in *n*-paraffin dichlorides

Table XI. Yields of dichlorides at 20°C (mole fraction) after Colebourne, *et al.*[11]

Mono-chlorides	Dichlorides					
1-Cl·C$_6$H$_{13}$	$\overset{\displaystyle Cl}{\overset{\displaystyle \vert}{C}}$ — C — C — C — C — C					
	0.0214	0.111	0.116	0.293	0.280	0.127
2-Cl·C$_6$H$_{13}$	C — $\overset{\displaystyle Cl}{\overset{\displaystyle \vert}{C}}$ — C — C — C — C					
	0.0176	0.032	0.202	0.262	0.330	0.154
3-Cl·C$_6$H$_{13}$	C — C — $\overset{\displaystyle Cl}{\overset{\displaystyle \vert}{C}}$ — C — C — C					
	0.091	0.218	0.07	0.17	0.294	0.158

studied by Colebourne, *et al.*,[11] as shown in Table XI. Therefore, it seems to be a characteristic that 1,3-dichloride units are selectively formed in the CPE molecules even at low chlorine-content.

Middle Chlorine-Content Region $(0.25 < X_s \leqq 0.50)$. Though the frequencies of methylene sequence become considerably close in agreement with those estimated by eq 21, $Fr(1)$ and $Fr(N \geqq 20)$ of methylene sequences are higher than those estimated as shown in Figure 4 (A5FC, S4W, A10W).

The sequence length of vinyl chloride is still short, *viz.*, $Fr(N > 5)$ of —(CHCl—CH$_2$)$_N$— are less than 0.3% as listed in Table VIII, then the unit —(CHCl—CH$_2$)$_N$— $(N > 5)$ can hardly exist in this region of mean chlorine-content. After the mean chlorine-content approaches 40wt%, the CCl$_2$ units become observable in a sequence such as

—(CHCl—CH$_2$—CCl$_2$—CH$_2$)$_N$—CHCl—

as listed in Table IX.

High Chlorine-Content Region $(X_s > 0.50)$. In this region, long methylen sequence decreases

rapidly, and the sequence lengths such as —(CHCl—CH$_2$)$_N$—, —(CHCl)$_N$—, and —(CHCl —CH$_2$—CCl$_2$—CH$_2$)$_N$—CHCl— increase more and more with the increasing mean chlorine content as shown in Figure 4 (A11FE, A13FE, A15FE).

At the mean chlorination degree above 60wt%, the sequence of —(CHCl)$_N$— as listed in Table X are dominantly formed as compared with other sequences, whereas long sequences of —(CHCl— CH$_2$)$_N$— ($N\geq10$) and —(CHCl—CH$_2$—CCl$_2$— CH$_2$)$_N$—CHCl— ($N\geq6$) have only a low frequency even above 60wt% of chlorine as listed in Tables VIII and IX, respectively. This is also a characteristic of the CPE sequence.

Comparison of Sequence Distribution of CPE with Those of HPVC, VC—Et Copolymer and PVC. The most remarkable difference among the sequences of HPVC, VC—Et, PVC, and CPE is in the sequence length distribution of vinyl chloride unit at nearly equal chlorine content. In the sequence of HPVC and VC—Et, there is pretty long sequence of vinyl chloride unit like that of block copolymers as shown in Figure 4 (HPVC, VC—Et). On the other hand, there is few longer vinyl chloride sequences than five in the CPE molecules as shown in Figure 4 (S4W, A10W). This trend is typically observed in the sequence of CPE of which mean chlorine content is almost equal to that of PVC as shown in Figure 4 (A13FE).

These facts suggest that the hydrogenation of PVC with a cocatalyzer of lithium aluminum hydride[12] heterogeneously occurs on the surface of the catalyzer and the copolymerization of VC—Et with a catalyzer of trialkyl boron[13] is rather similar to block copolymerization. On the other hand, the chlorination of PE is seemed to be substantially random substitution reaction. Therefore, the dehydrochlorination-behavior of these polymers will reflect their characteristic distribution of chlorines along the molecular chain.
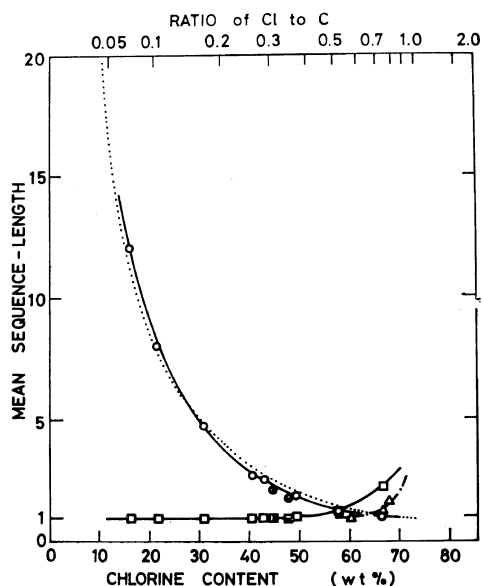
Mean Sequence-Length of Methylenes and Methynes

The mean sequence length in sequence number of chemical units ($\bar{l}$) is readily calculated by the following equation,

$$\bar{l}= \sum_{N=0}^{\infty} Pr(N)/ \sum_{N=0}^{\infty} Fr(N) \qquad (22)$$

where $Pr(N)$ and $Fr(N)$ are the existence prob-

Table XII. Mean sequence length of methylenes ($\bar{l}_{CH_2}$) and methynes ($\bar{l}_{CHCl}$)

| Sample | Chlorine content (wt fraction), X_s | Mean sequence number | |
		$\bar{l}_{CH_2}$	$\bar{l}_{CHCl}$
A1FE	0.163	12.03	1.00
A4W	0.219	8.09	1.00
A5FC	0.310	4.72	1.00
S4W	0.406	2.78	1.00
A10W	0.432	2.58	1.00
A11FE	0.495	1.90	1.04
A13FE	0.578	1.28	1.17
A15FE	0.666	1.03	2.28
HPVC-1	0.449	2.18	1.00
VC—Et	0.478	1.84	1.00

Figure 5. Mean sequence length of methylene and methyne units as a function of mean chlorine content (X_s). ○, ◑, and ◓ indicate mean length of methylene sequence of CPE's, HPVC and VC— Et, respectively, by the simulation, and the dotted line is a theoretical curve of that by eq 44 in our previous paper.[5] □, ◩, and ▣ indicate mean length of methyne sequence of CPE's, HPVC, and VC—Et, respectively, by the simulation, and △ indicates that of ClPVC provided by Svegliado, *et al.*[14]

ability and the frequency to locate methylene or methyne sequences in the most probable model sequences, respectively. The results are listed in Table XII and depicted in Figure 5. The

mean sequence lengths obtained by the computer simulation are in close agreement with those of the statistical calculation by means of Frensdorff, et al.,'s work.[7]

It is also revealed by the simulation that the mean sequence length of methyne unit are unity below 50wt% of chlorine, however those increase rapidly above 60wt% and that those of CPE are longer than those of chlorinated PVC(CIPVC) deduced from Figure 4 of the paper provided by Svegliado, et al.[14] Therefore, it can be said that the vicinal dichloride sequence is apt to form in a CPE chain at high chlorination-degree more than in a chain of CIPVC.

CONCLUDING REMARKS

The most probable model sequence of CPE chain could be determined self-consistently with the aid of a computer simulation on the basis of the triad informations obtained by the NMR spectroscopy. The sequence distribution of various units was also determined by the simulation.

The self-consistency of the simulation leads to extensive remarks that the present method for obtaining the polyad information effects an inspection of evidence of the triad assignments, and it can be generally applied for determining a sequence distribution of other copolymers or substituted polymers on the basis of suitable spectroscopic knowledge when polyad informations are required.

It will be expected that the structure-sensitive properties of CPE such as glass transition temperature, cohesive energy density, refractive index and dehydrochlorination behavior can be discussed in the light of the sequence distribution of chlorines in the CPE chain.

APPENDIX

Testing and Application of Pseudorandom Numbers

Pseudorandom numbers, $RDN(I)$ used in the present article are generated by a computer with the multiplicative congruential method as following subroutine;[8]
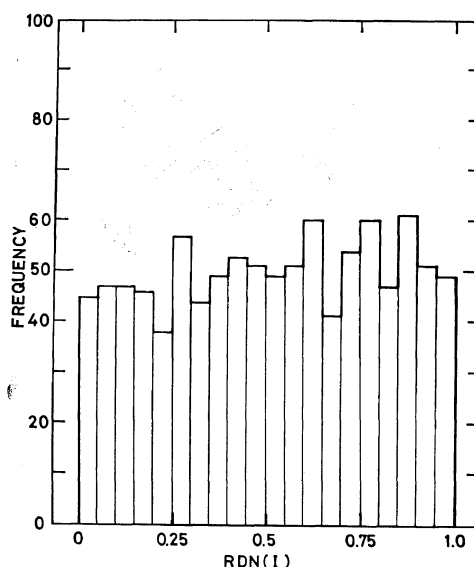

Figure 6. Histogram of one thousand pseudo random numbers, $RDN(I)$, in the range of [0, 1]; here X_0 in eq 23 is equal to 63751093.

X_0=an arbitrary positive odd integer
  less than 10^9 (23)

$X_i = 65539 X_{i-1}$ (i, natural number) (24)

$RDN(I) = 0.4656613 X_i \times 10^{-9}$ (25)

in this paper, the value of X_0 is defined to be an integer 63751093.

A histogram of one thousand $RDN(I)$'s thus generated is shown in Figure 6, from which the distribution of $RDN(I)$ appears to be pretty uniform. However, an independency of $RDN(I+1)$ on $RDN(I)$[15] is unsatisfactory except some partial ranges of [0, 1] as shown in Figure 7. Therefore, it is not fully available to apply $RDN(I)$ as generated to the Markovian process. Then, the following operations were used in the present paper:
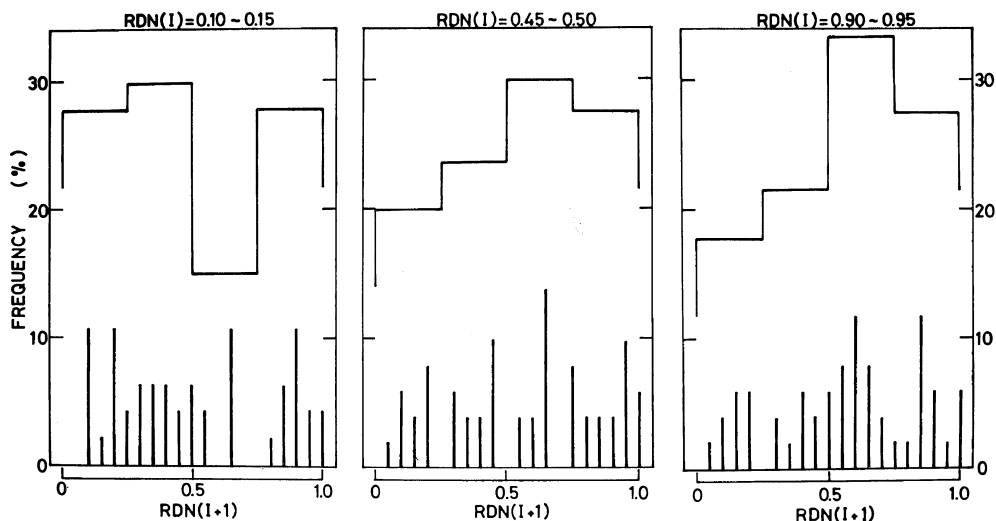
(i) to divide the range [0, 1] into k subranges, i.e., $[(n-1)/k, n/k]$, where n and k are integers ($1 \leq n \leq k$)

(ii) to classify $RDN(I)$ into the n-th subrange and to rewrite $RDN(I)$ as $RDN(I)_n$

(iii) to reduce the conditional probability $P\{K|IJ\}$ to $P\{K|IJ\}/k$

(iv) to compare $RDN(I)_n$ with reduced conditional probability as shown in eq 15—19

Figure 7. Histogram of $RDN(I+1)$ in the range of $[0, 1]$ when the range of $RDN(I)$ is defined. X_0 is the same as that in Figure 6.

where k is tentatively defined, in this paper, to be five. The convergency of the present calculation was improved by the above operations.

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