CHAPTER 5

MONOMER INVERSION IN EHYLENE-VINYL ALCOHOL COPOLYMER (EVOH)

In the ^{13}C-NMR spectra of ethylene-vinyl alcohol copolymer prepared by the hydrolysis of ethylene-vinyl acetate copolymer, six well-resolved methylene carbon lines have been observed, one of which has been assigned to anomalous 1,4-glycol structure arising from monomer inversion in the radical copolymerization. The six methylene carbon lines can be assigned to five-carbon sequences along a main chain, while the mole fractions of the dyad and triad monomer sequences can explicitly be determined from the intensities of the lines only when the monomer invention is negligible. A larger amount of the 1,4-glycol has been observed (2 to 6% of the total intensity of the methylene lines) for the samples polymerized at a higher temperature or with higher extents of conversions. From this observation and numerical calculations of "terpolymerization" on the basis of the first-order Markoffian statistics including monomer inversion, the reactivity ratio of the addition of a vinyl acetate monomer in the inverted (head-to-head) mode to the addition in the normal (head-to-tail) mode at an ethylene radical chain end has been determined to be 0.07 at 88°C and below 0.02 at 60°C. It has been confirmed that the probability of monomer inversion increases for the copolymerization in comparison with the homopolymerization of vinyl acetate, but, on the other hand, the normal head-to-tail linkage is still predominant even for the addition to an ethylene radical chain end.
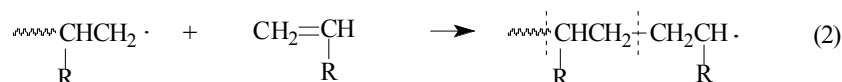
5.1 INTRODUCTION

Predominance of head-to-tail linkage in radical polymerization of vinyl monomers has generally been accepted, although three other different modes of linkage are formally possible, viz., head-to-head, tail-to-tail, and tail-to-head, where "inversion" of monomer in

polymerization is concerned. (The group = CHR is referred to as the head of a monomer.) This fact has been explained by some qualitative considerations of steric factors and resonance effects[1-3] and by theoretical treatments based on molecular orbital theory.[4] In practice, only a small amount of 1,2-glycol structure has been detected for poly(vinyl alcohol), obtained from the hydrolysis of poly(vinyl acetate): 1.5% at a polymerization temperature of 60°C and 2.0% at 100°C.[5,6]

More frequent occurrence of monomer inversion might be expected for ethylene-vinyl monomer copolymerization, because a steric hindrance between substituents is apparently absent even for the inverted addition of a vinyl monomer to an ethylene radical chain end as follows.

$$\sim\!\!CH_2CH\!\mid\!CH_2CH_2\cdot \;+\; CH\!\!=\!\!CH_2 \;\longrightarrow\; \sim\!\!CH_2CH\!\mid\!CH_2CH_2\!\mid\!CH\!\cdot\!CH_2\cdot \quad (1)$$
$$\quad\quad\;\; R \quad\quad\quad\quad\quad R \quad\quad\quad\quad\quad\quad R \quad\quad\quad R$$

A further propagation of the above sequence by the addition of a vinyl monomer in the normal mode forms the following tail-to-tail structure.

$$\sim\!\!CHCH_2\cdot \;+\; CH_2\!\!=\!\!CH \;\longrightarrow\; \sim\!\!CHCH_2\!\mid\!CH_2CH\cdot \quad (2)$$
$$\;\;\; R \quad\quad\quad\quad R \quad\quad\quad\quad\quad R \quad\quad R$$

Both reactions, (1) and (2), produce the same anomalous 1,4 structure in the copolymers.

Hence, the quantitative analysis of the 1,4 structure has fundamental significance for the characterization of ethylene-vinyl monomer copolymers as well as for the kinetic studies of the inversion of monomer in copolymerization. Such anomalous linkages have been investigated so far for ethylene-vinyl acetate (which will be abbreviated EVAC below),[7,8] ethylene-vinyl chloride,[7] and ethylene-propylene (by ionic polymerization)[9-20] copolymers, by using infrared, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. For EVAC copolymers, a considerable amount of 1,4 structure (about 45%) has been suggested by infrared spectroscopy,[7] while a rather smaller amount (4 to 13%) has been found by ^{1}H-NMR with the double resonance technique[8]

In the present work, ^{13}C-NMR spectroscopy has turned out to serve as a powerful tool for the quantitative analysis of the 1,4-glycol structure in ethylene-vinyl alcohol copolymers (which will be abbreviated to EVOH below) prepared by the hydrolysis of EVAC copolymers. No absorption line assigned to the 1,4 structure has been observed in the ^{13}C-NMR spectra of EVAC in the literature[21,22] probably due to the overlapping of lines.

There have been some complicated problems for the analysis of the methylene carbon lines in ethylene-vinyl monomer copolymers, generally. The complications arise essentially from an uncertainty about the assignment of methylene carbons to monomer units in the copolymers. First, in practice, all the methylene lines cannot simply be assigned to monomer sequences but to five-carbon sequences along a main chain in the first step, although direct assignments to monomer sequences are usually possible for the NMR spectra of homopolymers with stereoisomerism and for those of copolymers.[23] It is important, therefore, to distinguish between carbon sequences and monomer sequences in the present analysis. Second, we do not know how much of the line assigned to the 1,4 structure arises from ethylene between head-to-head vinyl monomers (*Equation* (1)) and how much arises from tail-to-tail monomer sequences (*Equation* (2))[15] Furthermore, the inversion of vinyl monomers does not necessarily show itself as a 1,4 structure but may also occur in the following propagation step:

$$\text{\textasciitilde}CH_2CH_2 \vdots CH_2CH_2 \vdots CHCH_2 \vdots CH_2CH_2 \cdot \qquad (3)$$
$$\underset{R}{|}$$
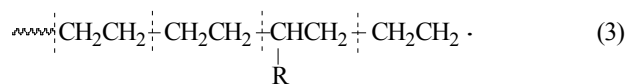
In this case, we cannot discriminate the inverted monomer from the normal one in the spectra.

Because of the apparent ambiguities about relationship between inversion and 1,4 structure, direct analysis does not seem feasible. In order to avoid these difficulties and in order to evaluate the probability of inversion, numerical calculations of "terpolymerization" including the inverted addition of vinyl monomer have been performed by using a reactivity ratio as a parameter. In this treatment, the intensities of the methylene carbon lines for EVOH have been theoretically deduced and have been compared with the observed data, and the reactivity ratio concerning the monomer inversion has been determined. A similar calculation of terpolymerization has also been discussed in the ^{13}C-NMR analysis of ethylene-propylene copolymers.[20]

5.2   EXPERIMENTAL

5.2.1   *Materials*

Nine samples of EVOH copolymers for NMR experiments were prepared by the hydrolysis of the EVAC copolymers polymerized under the different conditions shown in Table 4. Samples I to VII were polymerized in homogeneous systems with or without methanol as solvent and with α,α′-azobis(isobutyronitrile) as an initiator in a 1-L stainless steel autoclave with a stirrer. The temperature of the system and the pressure of ethylene gas was kept constant during copolymerization. Samples I to III were prepared at three different pressures of ethylene, in methanol, at about 60°C and with lower extents of conversions. The other four samples were polymerized under partly different conditions: at a higher temperature (sample IV), with a higher extent of conversion (V), with a higher content of methanol (VI), and without methanol (VII). The mole fraction of ethylene in the feed was determined from the solubility of ethylene in the copolymerization systems, while the solubility was obtained from the experimental conditions, pressure, temperature, and composition of solution, by reference to unpublished data obtained in our company.

Table 4   Copolymerization conditions and some analytical data for the samples of ethylene-vinyl acetate copolymers

					sample no.				
	I	II	III	IV	V	VI	VII	VIII	IX
% of methanol	20	20	20	20	20	40	0		
Temp, °C	63	60	57	88	60	60	60	60	60
Pressure of ethylene, kg/cm^2	15.5	44.0	58.0	54.0	43.0	45.0	41.0	35.0	35.0
Reaction time, h	0.5	1.0	1.25	0.4	7.0	5.5	2.0	4.0	1.0
Extent of conversion of VAc, %	19.8	8.1	3.8	9.0	65.1	29.0	19.2	84.4	65.9
Mole fraction of ethylene in feed, %	13.28	45.16	60.20	45.73	43.98	50.53	39.71		
Mole fraction of ethylene in copolymer, %	7.90	29.95	43.54	29.85	33.38	38.61	25.90	31.20	19.80
$[\eta]$,[a] dL/g	1.33$_4$	0.93$_6$	1.09$_6$	0.76$_3$	0.67$_2$	0.62$_9$	1.25$_1$	1.17$_3$	1.15$_6$
Polymerization method			Solution polymerization					Suspension polymerization	

[a]Limiting viscosity number measured for the hydrolyzed samples in a phenol/water (85/15, w/w) mixture at 30°C.

Samples VIII and IX were prepared by suspension polymerization (vinyl acetate-water = 1:2, w/w) with higher extents of conversions in the 1-L autoclave. As a suspending agent, a partially hydrolyzed poly(vinyl alcohol) produced commercially for this purpose (PVAL L-8, Kuraray Co.) was used at a concentration of 0.15% in water.

The EVAC copolymers were hydrolyzed in methanol at 40°C using sodium hydroxide as catalyst. The degree of hydrolysis was found to be higher than 99.7 mol% for all the EVOH copolymers. The copolymer compositions shown in Table 4 were determined by analytical hydrolysis of EVAC and by titration. The limiting viscosity numbers of these EVOH samples in the phenol/water mixture (85/15, w/w) at 30°C were greater than 0.6 dL/g in all the cases.

5.2.2   Method

A phenol/deuterium oxide (80/20, w/w) mixture was used as solvent for EVOH in the ^{13}C-NMR experiments, because it is a good solvent and gives no resonance line in the chemical shift region of the methylene and methine carbons. The ^{13}C-NMR of EVAC was also observed in deuteriochloroform. The samples of approximately 20% (w/v) in 8 mm o.d. tubes were observed at 70°C and at 22.63 MHz with a Bruker SXP-4-100 pulse Fourier transform spectrometer interfaced with a Nicolet Model 1080-E computer. Deuterium in the solvents was used as internal heteronuclear lock signal, and proton noise decoupling was employed. The free induction decays of about 20 000 pulses were stored in 16K computer locations using a pulse width of 20 μs and a spectral width of 1500 Hz. Chemical shifts downfield from tetramethylsilane (Me$_4$Si) were determined from internal dioxane and deuteriochloroform as secondary standards.

5.3   ^{13}C-NMR SPECTRA OF EVOH AND EVAC

Figure 25 shows ^{13}C-NMR spectra of EVOH and EVAC of sample VIII containing 31.2 mol% ethylene units. In the left region of the spectra, five to six methine carbon resonance lines are observed with microstructure overlapping one another. As reported in the previous ^{13}C-NMR studies of EVAC,[21,22] the methine carbon lines for EVOH can also be assigned to the six A-centered triad sequences as shown, EAE, *m*E, *mm*, *r*E, *mr,* and *rr.* E and A denote ethylene and vinyl alcohol (or vinyl acetate) monomer units, respectively, while *m* and *r* denote the meso and racemic configurations, respectively, of AA dyad sequences. The presence of inverted monomer is neglected in this assignment. This

assignment is based on the comparison with ^{13}C-NMR spectra of poly(vinyl alcohol) (or poly(vinyl acetate))[24-26] and on the intensities of lines. A difference in the relative positions of the corresponding lines has been found between EVOH and EVAC. The mole fractions of triad monomer sequences can be determined from the intensities of the methine lines in principle, although overlapping of lines is rather large.
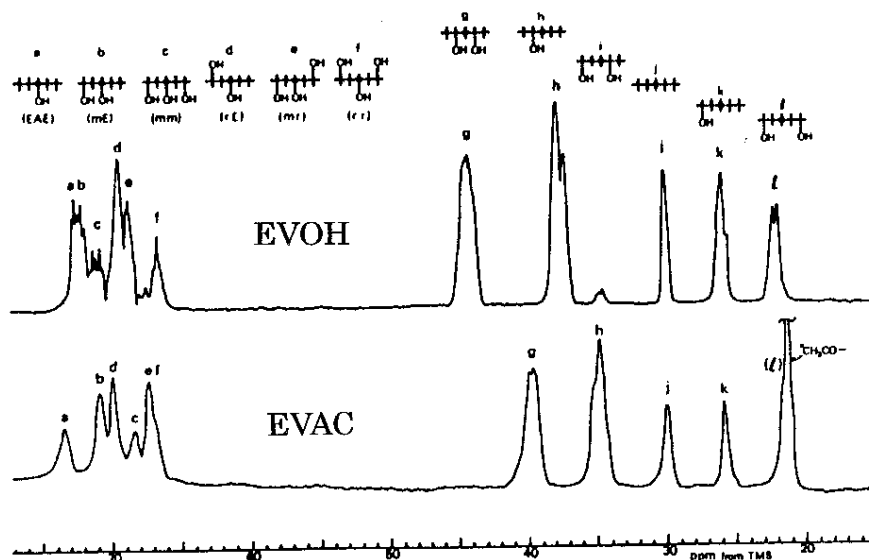

Figure 25   The 22.63-MHz ^{13}C-NMR spectra of an ethylene-vinyl acetate copolymer (EVAC) containing 31.20 mol% ethylene units and of the hydrolyzed sample of the EVAC, an ethylene-vinyl alcohol copolymer (EVOH). The resonance lines are assigned to the five-carbon sequences shown.

On the other hand, six well-resolved absorption lines, named g, h, i, j, k, and l, are observed for the methylene carbons in EVOH. The h and l lines appear as doublets. The six lines can be assigned to the five-carbon sequences along the main chain as shown. The basis for the assignment and an analytical method of monomer sequence distribution are discussed in the following sections. It should be noted that a small absorption line named i can be observed at 34.2 ppm in the spectrum of EVOH, because it can be assigned to the

anomalous 1,4-glycol structure arising from the inverted addition of vinyl acetate in the propagation reaction of copolymerization. The methylene carbons in EVAC show a similar spectrum (which has previously been reported in the literature[21,22]), but the lines corresponding to the i and l lines in the spectrum of EVOH have apparently not been resolved. They must overlap with other absorption lines, probably the j line and the line of the acetoxy methyl carbon.
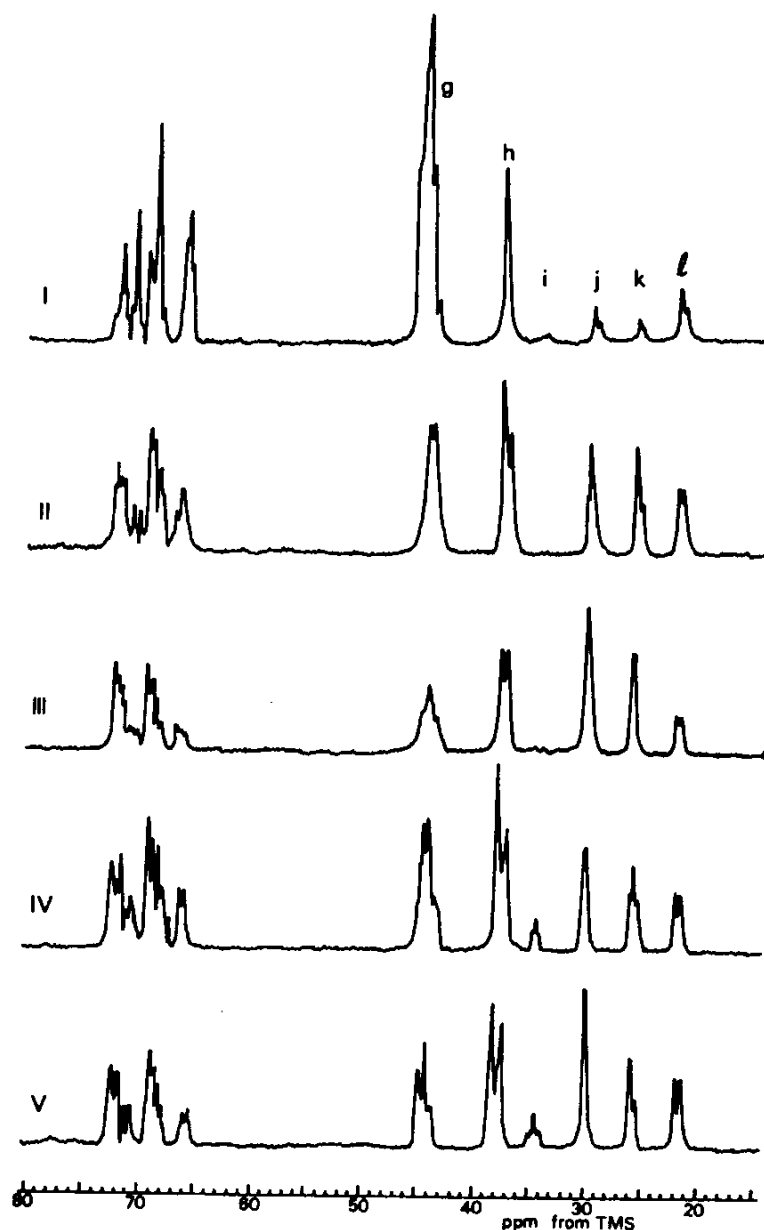

Figure 26   The 22.63-MHz ^{13}C-NMR spectra of the five samples of ethylene-vinyl alcohol copolymers.

Figure 26 shows the ^{13}C-NMR spectra of the EVOH copolymers of samples I-V. The area intensities of the methylene lines, expressed as percents of the total area, are listed in Table 5. The lower limit of detection is estimated as about 1% in intensity. The i line can be observed with measurable intensities for samples I, IV, VII, VIII, and IX, and not clearly for II, III, and VI. By reference to the polymerization conditions in Table 4, the results can be summarized as follows.

1) For the samples polymerized in methanol with lower extents of conversions at about 60°C (I, II, III, and VI), the i line was observed only below 1%, i.e., the amounts of 1,4-glycol are small.

2) At a higher temperature of polymerization (88°C), the amount of 1,4-glycol increases (IV).

2) The amount of 1,4-glycol is also larger for the sample polymerized in methanol with a higher extent of conversion (65.1% for sample V) or for the sample prepared by bulk polymerization(VII) .

3) For the samples by suspension polymerization with extents of conversion above 65%, larger amounts of 1,4-glycol have been observed (VIII and IX).

It can be understood that the amount of 1,4-glycol structure increases with the polymerization temperature because the probability of inversion of vinyl acetate must increase at higher temperatures. It is not clear, however, why it depends on the other polymerization conditions such as extent of conversion, solvent, or polymerization method. One possible explanation is that for some viscous copolymerization systems, temperature may increase locally due to the imperfect elimination of head of reaction.

Table 5 (A) Observed area intensities of the methylene carbon lines in the ^{13}C-NMR spectra of ethylene-vinyl alcohol copolymers. (B)-(G) The monomer sequence distributions and the monomer reactivity ratios deduced from the present data on the assumption that the conversion of vinyl acetate monomer is negligible

	sample no.								
	I	II	III	IV	V	VI	VII	VIII	IX
(A) Intensities of Methylene Carbon Lines, %									
g	78.2	33.3	18.7	31.8	29.7	25.4	38.3	30.7	54.6
h	13.2	31.0	33.9	32.1	29.9	32.9	28.2	32.9	22.9
I	0.8	0	0	3.0	6.2	0	2.4	3.8	3.8
j	1.3	12.7	23.4	11.9	12.5	18.0	10.2	11.9	4.7
k	0.8	12.3	15.5	11.3	12.3	14.8	10.1	8.8	5.3
l	5.9	10.7	8.6	9.9	9.4	9.0	10.8	12.0	8.8
$2l + k$	12.6	33.7	32.7	31.1	31.1	32.8	31.7	32.8	22.9
(B) Mole Fractions of Dyads, %									
(AA)	84.8	45.2	27.4	43.7	43.1	35.8	51.7	42.8	67.3
(AE)	14.3	42.0	49.7	44.2	43.4	46.3	38.0	45.8	28.2
(EE)	0.9	12.8	22.9	12.1	13.5	17.9	10.3	11.4	4.5
(C) Ethylene Content,^{a} mol%									
[E]	8.1	33.8	47.8	34.2	35.2	41.1	29.3	34.3	18.6
(D) Mole Fractions of Triads, %									
(EEE)	6.3	12.5	24.5	12.8	12.8	18.2	11.0	15.3	6.8
(AEE)	11.2	46.8	48.6	46.5	49.4	50.9	43.0	35.8	35.0
(AEA)	82.5	40.7	26.9	40.7	37.8	30.9	46.0	48.9	58.2
(E) Block Character									
η	0.96	0.94	1.00	0.98	0.95	0.96	0.92	1.02	0.93
(F) Product of Reactivity Ratios									
$r_A r_E$	1.49	1.31	1.02	1.08			1.48		
(G) Reactivity Ratios									
r_A	(1.82)	1.77	1.67	1.67			1.79		
r_E	(0.82)	0.74	0.61	0.66			0.82		

^{a} The values are derived from the dyad data, for comparison.

Table 6 Calculation of the ^{13}C chemical shifts for the methylene carbons in the seven-carbon sequences in
an ethylene-vinyl alcohol copolymer (observed chemical shifts and assignment are also shown)

Five-Carbon Sequences	Seven-Carbon Sequences	Calculated Chemical Shifts (ppm) R = CH₃	Subst. Effects	R = OH	Observed Chemical Shifts (ppm)	Assignment
		43.86		45.9		
		44.11	$2C_2$	46.1	44.2	g
		44.36		46.4		
		41.17	$2C_2+C_3$	42.2	—	(p)
		41.42		42.4		
		36.91		37.9		
		37.16	C_2	38.2	37.6 {37.4, 37.8}	h
		37.16		38.2		
		37.41		38.4		
		34.22		34.2		
		34.47	C_2+C_3	34.5	34.2	i
		34.47		34.5		
		34.72		34.7		
		34.22	C_2+C_3	34.2	—	(m)
		34.47		34.5		
		31.53	C_2+2C_3	30.5	—	(n)
		31.78		30.8		
		29.96		30.0		
		30.21	—	30.2	30.0	j
		30.46		30.5		
		27.27		26.3		
		27.52	C_3	26.5	25.8	k
		27.52		26.5		
		27.77		26.8		
		24.58	$2C_3$	22.6	22.0	ℓ
		24.83		22.8		

5.4   ASSIGNMENT

The assignment of the methylene lines in EVOH has been determined mainly on the basis of the empirical additivity rules concerning ^{13}C chemical shifts[27] for substituted alkanes. Calculations have been performed using the equation and parameters for alkanes presented by Lindeman and Adams[28] and using the parameters for substituent effects summarized by Levy and Nelson.[29] The results are shown in Table 6. The chemical shifts of central carbons in all the possible seven-carbon sequences are calculated for an ethylene-propylene copolymer (R = CH3) and for an EVOH (R = OH) by the addition of the parameters for small substituent effects (C_2 = 1, C_3 = -1) upon replacement of methyl groups by hydroxyl groups. Consideration of seven carbons along the main chain is sufficient for the present calculation, including the shielding effects of carbon atoms located at α through ε positions. The two ε carbons on the main chain are not apparently contained because it is not necessary to distinguish between methine and methylene carbons for them. End groups or branches[30] have been regarded as negligible in the present analysis.

The observed chemical shifts are also listed in Table 6 for comparison. It should be noted that the six well-resolved methylene carbon lines can be definitely assigned to the five-carbon sequences instead of the seven-carbon sequences, the ε effects are insensitive to differences of structure. Among the possible nine five-carbon sequences, the three sequences, m, n, and p, have not been assigned to any lines observed. Their contributions may be negligibly small because they all contain 1,2-glycol (head-to-head) structure. The
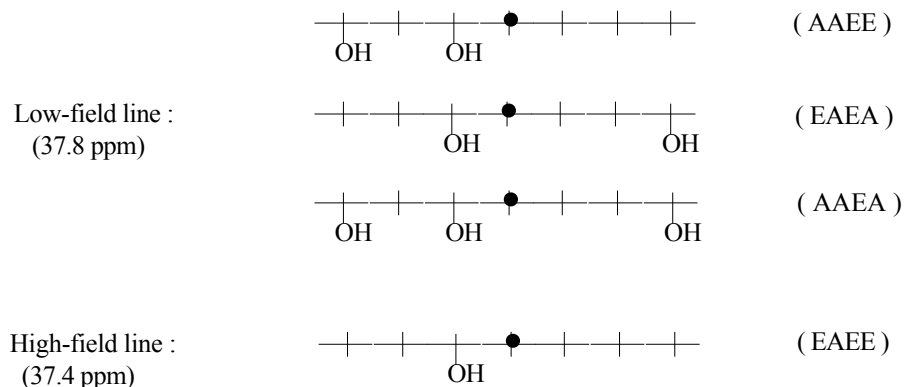
calculations described later predict that the intensities of their lines must be below 0.5%.

The assignment of the i line to 1,4-glycol has also been ascertained by its model compound, hexane 2,5-diol, where the line assigned to the carbon 3 and 4 was observed at 34.5 ppm. Another calculation of chemical shift for an EVAC predicts that the methylene carbons of 1,4 structure in it should be observed at about 31.3 ppm ($C_2 = -2$ and $C_3 = -1$ for an acetoxyl group). Absence of the i line in the case of EVAC must be due to the overlapping with the j line observed at 30.0 ppm.

The two lines appearing as fine structures in the h line located at 37.4 and 37.8 ppm in the spectra of EVOH may be assigned to the following seven-carbon sequences on the basis of the trends of chemical shifts calculated in Table 6.

In the parentheses, the assignment in terms of tetrad monomer sequences is also shown, where the inverted mode of monomer ($\bar{A}$) is neglected. This assignment is consistent with the observation that the intensity of the high-field line increases with increasing ethylene units in EVOH. Fine structure is also observed in the l line, where the relative intensities of the two lines are approximately equal and insensitive to the amount of ethylene units. They might arise from the two stereoisomers as follows.

(meso)　　　(racemic)
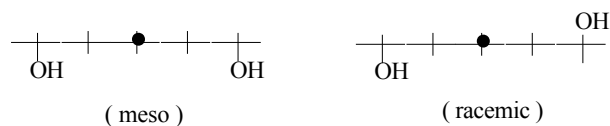
5.5　MONOMER SEQUENCE ANALYSIS

5.5.1　Monomer Sequence and Carbon Sequence.

Table 7 lists all the possible (27) triad monomer sequences in an ethylene-vinyl monomer copolymer, including inverted vinyl monomer units denoted by $\bar{A}$. The schematic diagrams of sequences are also illustrated, where methylene carbons of central monomers are assigned in terms of the signs of the five-carbon sequences, g-p, defined in Table 6. In the present treatment of a three-component copolymer system, the pairs of triads where the

monomer sequences	assignment	monomer sequences	assignment
AAA , ĀĀĀ	g	EAE , EĀE	h
ĀAA , ĀĀA	i	EEE	j j
AAĀ , AĀĀ	p	AEE , EEĀ	h k
AĀA , ĀAĀ	n	EEA , ĀEE	j k
AAE , EĀĀ	g	AEA , ĀEĀ	h l
EAA , ĀĀE	h	ĀEA	k k
ĀAE , EĀA	i	AEĀ	i i
EAĀ , AĀE	m		

order of monomers in sequences are mutually reversed, AAE and EAA, for example, should
be kept distinct from each other. On the other hand, the pairs of triads each placed in the
same rows, such as AAA and ĀĀĀ, are mirror image sequences of each other which cannot
apparently be distinguished in copolymers.

From the assignment indicated, the following relations can be derived between the molar
concentrations of the five-carbon sequences and the mole fractions of the triad monomer
sequences.

$$g = [AAA]+[ĀĀĀ]+[AAE]+[EĀĀ] \tag{4}$$

$$h = [EAA]+[ĀĀ E]+[EAE]+[EĀE]+[AEE]+[EEĀ]+ [AEA]+[ĀEĀ] \tag{5}$$

$$i = [ĀAA]+[ĀĀA]+[ĀAE]+[EĀA]+2[ĀEA] \tag{6}$$

$$j = 2[EEE]+[EEA]+[ĀEE] \tag{7}$$

$$k = [AEE]+[EEA]+[EEA]+[ĀEE]+2[ĀEA] \tag{8}$$

$$l = [AEA]+[ĀEĀ] \tag{9}$$

$$m = [EAA]+[AĀE] \tag{10}$$

$$n = [AĀA]+[ĀAĀ] \tag{11}$$

$$p = [AĀĀ]+[AAĀ] \tag{12}$$

The signs, g to p, are used now as the molar concentrations, and the brackets denote the
mole fractions.

5.5.2   Statistical Stationary.

The following relations must hold among the mole fractions of monomer sequences from
the statistical stationary approximation.[31,32]

$$[A] = [AA]+[AĀ]+[AE] = [AA]+[ĀA]+[EA] \tag{13}$$

$$[\bar{A}] = [\bar{A}A]+[\bar{A}\bar{A}]+[\bar{A}E] = [A\bar{A}]+[\bar{A}\bar{A}]+[E\bar{A}] \tag{14}$$

$$[E] = [EA]+[E\bar{A}]+[EE] = [AE]+[E\bar{A}]+[EE] \tag{15}$$

$$[AA] = [AAA]+[AA\bar{A}]+[AAE] = [AAA]+[\bar{A}AA]+[EAA] \tag{16}$$

$$[A\bar{A}] = [A\bar{A}A]+[A\bar{A}\bar{A}]+[A\bar{A}E] = [AA\bar{A}]+[\bar{A}A\bar{A}]+[EA\bar{A}] \tag{17}$$

$$[AE] = [AEA]+[AE\bar{A}]+[AEE] = [AAE]+[\bar{A}AE]+[EAE] \tag{18}$$

$$[\bar{A}A] = [\bar{A}AA]+[\bar{A}A\bar{A}]+[\bar{A}AE] = [A\bar{A}A]+[\bar{A}\bar{A}A]+[E\bar{A}A] \tag{19}$$

$$[\bar{A}\bar{A}] = [\bar{A}\bar{A}A]+[\bar{A}\bar{A}\bar{A}]+[\bar{A}\bar{A}E] = [A\bar{A}\bar{A}]+[\bar{A}\bar{A}\bar{A}]+[E\bar{A}\bar{A}] \tag{20}$$

$$[\bar{A}E] = [\bar{A}EA]+[\bar{A}E\bar{A}]+[\bar{A}EE] = [A\bar{A}E]+[\bar{A}\bar{A}E]+[E\bar{A}E] \tag{21}$$

$$[EA] = [EAA]+[EA\bar{A}]+[EAE] = [AEA]+[\bar{A}EA]+[EEA] \tag{22}$$

$$[E\bar{A}] = [E\bar{A}A]+[E\bar{A}\bar{A}]+[E\bar{A}E] = [AE\bar{A}]+[\bar{A}E\bar{A}]+[EE\bar{A}] \tag{23}$$

$$[EE] = [EEA]+[EE\bar{A}]+[EEE] = [AEE]+[\bar{A}EE]+[EEE] \tag{24}$$

Even with the help of these relations, unfortunately the mole fractions of the 27 triads cannot generally be solved in terms of the mole fractions of the five-carbon sequences.

5.5.3   The Case where $\bar{A}$ is Negligible.

For the EVOH samples polymerized under some usual conditions, in methanol at about 60°C with lower extents of conversions, the 1,4-glycol structure has been essentially not observed in their ^{13}C spectra. In this case where the inversion of vinyl acetate, $\bar{A}$, in copolymerization may be negligible, the above relations, can be simplified to a great extent.

First, from the relations concerning statistical stationary, the following usual relations are derived.

$$[AE] = [EA], \quad [AAE] = [EAA],$$
$$[AEE] = [EEA] \tag{25}$$

In this case, the mole fractions of sequences may more simply be denoted by parentheses instead of brackets as follows.

$$(AE) = [AE] + [EA],$$
$$(AAE) = [AAE] + [EAA], \tag{26}$$
$$(AEE) = [AEE] + [EEA]$$

The mole fractions of dyads are given by

$$(AA) = (AAA) + (AAE)/2 \tag{27}$$
$$(AE) = (AEA) + (EAE) + (AEE)/2 + (AAE)/2(AE) = 2(AEA) + (AEE) \tag{28}$$
$$(EE) = (EEE) + (AEE)/2 \tag{29}$$

Next, the relations in *Equations* (4) to (12) can be simplified as follows.

$$g = (AAA) + (AAE)/2 \tag{30}$$

$$h = (EAE) + (AEA) + (AAE)/2 + (AEE)/2 \tag{31}$$

$$j = 2(EEE) + (AEE)/2 \tag{32}$$

$$k = (AEE) \tag{33}$$

$$l = (AEA) \tag{34}$$

From *Equations* (27) to (34), one obtains

$$(EEE) = (j - k/2)/2 \tag{35}$$

$$(AEE) = k \tag{36}$$

$$(AEA) = l \tag{37}$$

$$(AA) = g \tag{38}$$

$$(AE) = h \tag{39}$$

$$(EE) = (j + k/2)/2 \tag{40}$$

$$h = 2l + k \tag{41}$$

The last is a redundant relation which should hold among the molar concentrations of the five-carbon sequences when $\bar{A}$ is negligible.

The mole fractions of the three E-centered triads and those of the three dyads in a copolymer can be determined from the observed line intensities by the use of the above relations, on the assumption of essentially equal enhancement due to the nuclear Overhauser effect among all the methylene carbon lines.[33] The results for the present samples are tabulated in Table 5. For the samples in which the 1,4-glycol structure has been observed, the same calculations have formally been performed. The redundant relation obtained theoretically, *Equation* (41), holds approximately for the observed intensities of h and $2l + k$ for each case within the difference below 10%.

Table 5 shows also the block characters, η, the products of reactivity ratios, $r_A r_E$, and the reactivity ratios calculated from the following formulas[32]

$$\eta = (AE)/\{2 \cdot (A) \cdot (E)\} \tag{42}$$

$$r_A \cdot r_E = 4 \cdot (AA) \cdot (EE)/(AE)^2 \tag{43}$$

$$r_A = 2 \cdot (AA)/\{(AE) \cdot x\} \quad r_E = 2 \cdot (EE) \cdot x/(AE) \tag{44}$$

where $x = f_A/f_E$, the ratio of the molar concentrations of monomers in feed. The η values are found close to unity for all the samples so that the sequence distributions can be regarded as approximately random. The same conclusion has been presented for EVAC so far.[21,22,34,35] *Equations*, (43) and (44), must be applicable only for the samples with lower extents of conversion and with negligible amounts of $\bar{A}$. The results, $r_A = 1.67 - 1.79$ and r_E

= 0.61 - 0.82 for samples II, III, IV, and VII, are close to the values $r_A = 1.515$ and $r_E = 0.743$ reported by German and Heikens[36] on the basis of the Fineman-Ross method from the least-squares fits of data for nine ethylene-vinyl acetate copolymerizations. Our results support their conclusion, although several different values of reactivity ratios have been presented so far for the copolymerization.[7,37-39]

5.6   CALCULATION OF "TERPOLYMERIZATION"

When the inversion of monomer is concerned, the mole fractions of the 27 triads (or nine dyads) can not be deduced directly from the observed intensities of the six methylene lines although the relations, *Equations* (4) to (24), have been established. Instead of such direct analysis of sequence distribution in copolymers, kinetic calculations of "terpolymerization" have been performed below in order to correlate the observed 1,4-glycol with the monomer inversion. In the treatment based on first-order Markoffian statistics,[40-43] the mole fractions of monomer sequences and then the intensities of ^{13}C-NMR lines of EVOH have been deduced by using a reactivity ratio, r', as a parameter. The r' is defined, as shown in Table 8, as a ratio of the addition of a vinyl acetate monomer in the inverted (head-to-head) mode to the addition in the normal (head-to-tail) mode at an ethylene radical chain end. The calculation results have been compared with the experimental result for sample IV, polymerized at 88°C with a lower extent of conversion, in order to evaluate r'.

5.6.1   *Monomer Reactivity Ratios.*

Six monomer reactivity ratios defined in Table 8, $r_{A\bar{A}}$, r_{AE}, $r_{\bar{A}A}$, $r_{\bar{A}E}$, r_{EA}, and $r_{E\bar{A}}$, are necessarily used in the present treatment of propagation reaction including inversion of vinyl monomer. The stereochemical effects are not taken into account. Another reactivity ratio, r', is also used below as parameter for convenience. The former six reactivity ratios can approximately be evaluated or expressed in terms of r' on some simplifying assumptions as follows.

First, the following r_{AE} and r_{EA} can approximately be chosen.

$$r_{AE} = 1.67, \quad r_{EA} = 0.66 \tag{45}$$

They have been determined for sample IV in the preceding section on the assumption of the neglect of monomer inversion. Next, from the definition of r',

Table 8   Definitions of the monomer reactivity ratios in the copolymerization of ethylene and a vinyl monomer including inverted addition

---

$r_{A\bar{A}} = k_{AA}/k_{A\bar{A}}$

      vv $CH_2CRH \cdot + CH_2 = CRH \xrightarrow{\quad k_{AA} \quad}$ vv $CH_2CRHCH_2CRH \cdot$

      vv $CH_2CRH \cdot + CRH = CH_2 \xrightarrow{\quad k_{A\bar{A}} \quad}$ vv $CH_2CRHCRHCH_2 \cdot$

$r_{AE} = k_{AA}/k_{AE}$

      vv $CH_2CRH \cdot + CH_2 = CRH \xrightarrow{\quad k_{AA} \quad}$ vv $CH_2CRHCH_2CRH \cdot$

      vv $CH_2CRH \cdot + CH_2 = CH_2 \xrightarrow{\quad k_{AE} \quad}$ vv $CH_2CRHCH_2CH_2 \cdot$

$r_{\bar{A}A} = k_{\bar{A}\bar{A}}/k_{\bar{A}A}$

      vv $CRHCH_2 \cdot + CRH = CH_2 \xrightarrow{\quad k_{\bar{A}\bar{A}} \quad}$ vv $CRHCH_2CRHCH_2 \cdot$

      vv $CRHCH_2 \cdot + CH_2 = CRH \xrightarrow{\quad k_{\bar{A}A} \quad}$ vv $CRHCH_2CH_2CRH \cdot$

$r_{\bar{A}E} = k_{\bar{A}\bar{A}}/k_{\bar{A}E}$

      vv $CRHCH_2 \cdot + CRH = CH_2 \xrightarrow{\quad k_{\bar{A}\bar{A}} \quad}$ vv $CRHCH_2CRHCH_2 \cdot$

      vv $CRHCH_2 \cdot + CH_2 = CH_2 \xrightarrow{\quad k_{\bar{A}E} \quad}$ vv $CRHCH_2CH_2CH_2 \cdot$

$r_{E\bar{A}} = k_{EE}/k_{E\bar{A}}$

      vv $CH_2CH_2 \cdot + CH_2 = CH_2 \xrightarrow{\quad k_{EE} \quad}$ vv $CH_2CH_2CH_2CH_2 \cdot$

      vv $CH_2CH_2 \cdot + CH_2 = CRH \xrightarrow{\quad k_{E\bar{A}} \quad}$ vv $CH_2CH_2CH_2CRH \cdot$

$r_{EA} = k_{EE}/k_{EA}$

      vv $CH_2CH_2 \cdot + CH_2 = CH_2 \xrightarrow{\quad k_{EE} \quad}$ vv $CH_2CH_2CH_2CH_2 \cdot$

      vv $CH_2CH_2 \cdot + CRH = CH_2 \xrightarrow{\quad k_{EA} \quad}$ vv $CH_2CH_2CRHCH_2 \cdot$

$r' = k_{E\bar{A}}/k_{EA}$

      vv $CH_2CH_2 \cdot + CRH = CH_2 \xrightarrow{\quad k_{E\bar{A}} \quad}$ vv $CH_2CH_2CRHCH_2 \cdot$

      vv $CH_2CH_2 \cdot + CH_2 = CRH \xrightarrow{\quad k_{EA} \quad}$ vv $CH_2CH_2CH_2CRH \cdot$

$$r_{E\bar{A}} = r_{EA}/r' \tag{46}$$

is deduced. The reactivity ratios for an inverted vinyl monomer radical, $r_{\bar{A}A}$ and $r_{\bar{A}E}$, might be regarded as approximately equivalent to those for an ethylene radical, because of the similar steric circumstances.[44] According to this assumption, $r_{\bar{A}A}$ and $r_{\bar{A}E}$ can be expressed as follows.

$$r_{\bar{A}A} = r' \tag{47}$$

$$r_{\bar{A}E} = 1/r_{E\bar{A}} = r'/r_{EA} \tag{48}$$

Last, $r_{A\bar{A}}$ has been estimated from the reported mole fraction of 1,2-glycol, namely [A$\bar{A}$], in poly(vinyl alcohol), about 2 mol% at 90°C.[6]

$$[A\bar{A}] = 1/(r_{\bar{A}A} + r_{\bar{A}A} + 2) = 0.02 \tag{49}$$

This can be rewritten as

$$r_{A\bar{A}} = 48 - r_{\bar{A}A} = 48 - r' \tag{50}$$

Then, the following calculations of terpolymerization can be performed using one unknown parameter, r'.

5.6.2 Probabilities.

By using the six reactivity ratios defined in Table 8 and by using the mole fractions of monomer in feed, f_A and f_E, the nine conditional probabilities in the propagation reaction can be computed as a special case of the usual treatment of terpolymerization.

$$P_{AA} = f_A/Z_A \tag{51}$$

$$P_{A\bar{A}} = f_A/r_{A\bar{A}}/Z_A \tag{52}$$

$$P_{AE} = f_E/r_{AE}/Z_A \tag{53}$$

$$P_{\bar{A}A} = f_A/\boldsymbol{r}_{\bar{A}A}/Z_{\bar{A}} \tag{54}$$

$$P_{\bar{A}\bar{A}} = f_A/Z_{\bar{A}} \tag{55}$$

$$P_{\bar{A}E} = f_E/r_{\bar{A}E}/Z_{\bar{A}} \tag{56}$$

$$P_{EA} = f_A/r_{EA}/Z_E \tag{57}$$

$$P_{E\bar{A}} = f_A/r_{E\bar{A}}/Z_E \tag{58}$$

$$P_{EE} = f_E/Z_E \tag{59}$$

where

$$Z_A = f_A(1 + 1/r_{A\bar{A}}) + f_E/r_{AE} \tag{60}$$

$$Z_{\bar{A}} = f_A(1 + 1/r_{\bar{A}A}) + f_E/r_{\bar{A}E} \tag{61}$$

$$Z_E = f_A(1/r_{EA} + 1/r_{E\bar{A}}) + f_E \tag{62}$$

The mole fractions of monomer units in the present "terpolymer" can be calculated by

$$[A] = u/(u + v + w) \qquad (63)$$

$$[\bar{A}] = v/(u + v + w) \qquad (64)$$

$$[E] = w/(u + v + w) \qquad (65)$$

where

$$u = P_{\bar{A}E}P_{EA} + P_{EA}P_{\bar{A}A} + P_{\bar{A}A}P_{E\bar{A}} \qquad (66)$$

$$v = P_{EA}P_{A\bar{A}} + P_{A\bar{A}}P_{E\bar{A}} + P_{E\bar{A}}P_{AE} \qquad (67) \qquad w = P_{\bar{A}A}P_{AE} + P_{AE}P_{\bar{A}E} + P_{\bar{A}E}P_{\bar{A}A} \qquad (68)$$

The mole fraction of inverted vinyl monomer units among all the vinyl monomer units in a copolymer is now denoted by $[\bar{A}]_A$, namely,

$$[\bar{A}]_A = [\bar{A}]/([A] + [\bar{A}]) \qquad (69)$$

The mole fractions of the dyad and triad sequences can be calculated as follows

$$[XY] = [X]P_{XY} \qquad (70)$$

$$[XYZ] = [X]P_{XY}P_{YZ} \qquad (71)$$

where X, Y, and Z denote A, $\bar{A}$, or E. Finally, the intensities of the methylene carbon lines, g-p, can be computed from the triad intensities by the use of *Equations* (4)-(12).
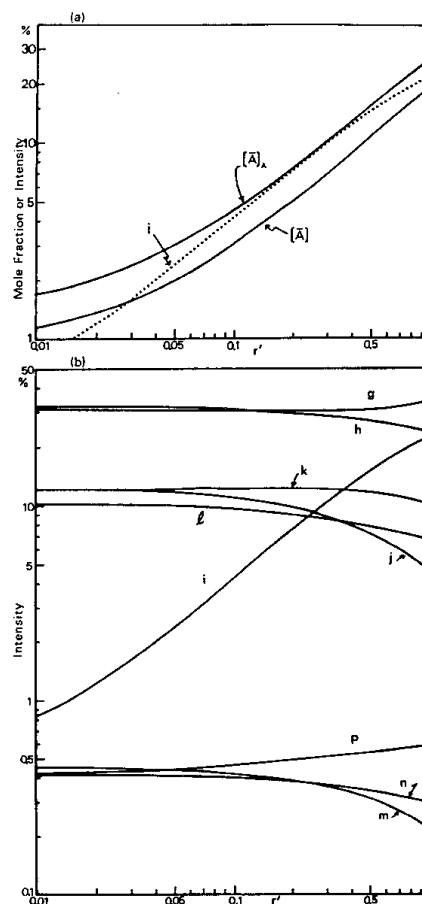

5.6.3 Numerical Calculations

In Table 9, some results of the numerical calculations of "terpolymerization" are listed for a mole fraction of ethylene in feed, $f_E = 0.46$ (this corresponds to the condition in samples IV and II), with values of r' varying from 0.01 to 1 as a parameter. The calculated mole fractions of inverted vinyl acetate monomer, $[\bar{A}]$ and $[\bar{A}]_A$, and the theoretical intensities of the methylene lines are also plotted in Figure 27 against r'. The intensity of the i line considerably increases from 0.8 to 22.1% with the increase of r' from 0.01 to 1, while only small changes in intensity are observed for the other eight lines. Therefore, the value of r' may be determined with reasonable accuracy from the observed intensity of the i line. For sample IV, polymerized at 88°C, the intensity of the i line was observed to be 3.0%, from which r' is obtained as 0.07. From $r' = 0.07$, one can conclude that the probability of addition of a vinyl acetate monomer in the inverted mode to an ethylene radical chain end is 6.5% $(0.07/(1 + 0.07) = 0.065)$ at 88°C. The mole fraction of inverted vinyl acetate monomer units has been computed as $[\bar{A}] = 2.4\%$ and $[\bar{A}]_A = 3.7\%$ for sample IV. For sample II, polymerized at 60°C, on the other hand, the i line has not been observed because its intensity must be below the lower limit of detection (about 1%). From Figure 27, r' has

been evaluated as below 0.02 in this case.

The value $r' = 0.07$ at 88°C is certainly larger than the reciprocal of a reactivity ratio, $1/r_{A\bar{A}} = k_{A\bar{A}}/k_{AA}$, which has been determined as 0.02 for the homopolymerization of vinyl acetate at 90°C. Accordingly, it has been confirmed that inversion of vinyl acetate in propagation occurs more frequently for the copolymerization with ethylene than for the homopolymerization. However, on the other hand, the result has also shown that normal (head-to-tail) addition is still predominant even at an ethylene radical chain end, although it is expected that steric hindrance between substituents may be absent in such linkages.

Figure 27 Calculated curves for the mole fractions of inverted vinyl alcohol units, [Ā] and [Ā]$_A$, and for the intensities of the methylene carbon lines in an ethylene-vinyl alcohol copolymer polymerized with a mole fraction of ethylene in feed, f_E = 0.46. The parameter r' is a reactivity ratio concerning the monomer inversion. The intensity of the i line assigned to 1,4-glycol is shown in both parts, a and b.

Another theoretical calculation has been performed by varying the molar concentration of ethylene in the feed, f_E, using 0.07 as r'. The results are shown in Figure 28, where the mole fractions of inverted vinyl acetate, [Ā] and [Ā]$_A$, and the line intensities are plotted against f_E. The mole fractions of inverted monomer among all vinyl acetate units, [Ā]$_A$,

increases monotonously from 2.1 to 6.8% with the increase of f_E, while the mole fraction among all monomer units, $[\bar{A}]$, at first increases slowly to a maximum at about 40% of f_E and then falls rapidly to zero with the increase of f_E. An inspection of Figures 27 and 28 shows that the two curves of the intensity of i line and of $[\bar{A}]$ are approximately similar in their dependence of f_E and on r', and in their numerical values. Therefore, the intensity of the i line might be adopted as a measure of $[\bar{A}]$ with a rough approximation.
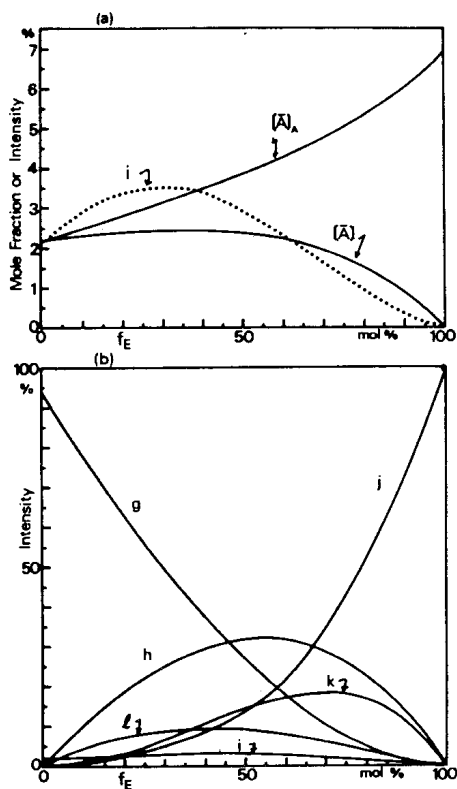

Figure 28 Calculated curves for the mole fractions of inverted vinyl alcohol units, $[\bar{A}]$ and $[\bar{A}]_A$, and for the intensities of the methylene carbon lines in an ethylene-vinyl alcohol copolymer against a mole fraction of ethylene in feed, f_E, for the values of the reactivity ratios, $r' = 0.07$, $r_{A\bar{A}} = 48$, $r_{\bar{A}E} = 1.67$, $r_{AA} = 0.07$, $r_{AE} = 0.106$, $r_{EA} = 0.66$, and $r_{E\bar{A}} = 9.43$. The intensity of the i line assigned to 1,4-glycol is shown in both parts, a and b.

Table 9 Results of numerical calculations of the copolymerization of ethylene and vinyl acetate including inverted addition for a mole fraction of ethylene in feed, $f_E = 0.46$[a]

					r'				
		0.01	0.03	0.05	0.07	0.1	0.3	0.5	1
(a)	$r_{A\bar{A}}$	48	48	48	48	48	48	48	47
	r_{AE}	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
	$r_{\bar{A}\bar{A}}$	0.01	0.03	0.05	0.07	0.1	0.3	0.5	1
	$r_{\bar{A}E}$	0.0152	0.0455	0.0758	0.106	0.152	0.4545	0.758	1.515
	r_{EA}	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66
	$r_{E\bar{A}}$	66	22	13.2	9.43	6.6	2.2	1.32	0.66
(b)	[A]	64.71	64.43	64.14	63.86	63.44	60.77	58.31	52.95
	[Ā]	1.11	1.54	1.98	2.42	3.06	7.14	10.90	19.09
	[E]	34.18	34.03	33.88	33.73	33.50	32.10	30.79	27.96
(c)	$[\bar{A}]_A$	1.69	2.33	2.99	3.65	4.60	10.51	15.75	26.50
(d)	[AAA]	27.61	27.49	27.37	27.25	27.07	25.93	24.88	22.59
	[AAĀ]	0.57	0.57	0.57	0.57	0.56	0.54	0.52	0.47
	[AAE]	14.08	14.02	13.96	13.90	13.81	13.23	12.69	11.52
	[AĀA]	0.56	0.55	0.54	0.53	0.52	0.44	0.38	0.28
	[AĀĀ]	0.01	0.02	0.03	0.04	0.05	0.13	0.19	0.28
	[AĀE]	0.31	0.31	0.30	0.30	0.29	0.25	0.22	0.16
	[AEA]	13.71	13.48	13.26	13.04	12.72	10.87	9.42	6.89
	[AEĀ]	0.14	0.40	0.66	0.91	1.27	3.26	4.71	6.89
	[AEE]	7.71	7.58	7.45	7.33	7.15	6.11	5.30	3.87
	[ĀAA]	0.46	0.63	0.80	0.97	1.20	2.51	3.45	4.87
	[ĀAĀ]	0.01	0.01	0.02	0.02	0.03	0.05	0.07	0.10
	[ĀAE]	0.24	0.32	0.41	0.49	0.61	1.28	1.76	2.48
	[ĀĀA]	0.01	0.02	0.04	0.06	0.11	0.62	1.28	2.91
	[ĀĀĀ]	0.00	0.00	0.00	0.00	0.01	0.19	0.64	2.91
	[ĀĀE]	0.00	0.01	0.02	0.04	0.06	0.35	0.72	1.63
	[ĀEA]	0.25	0.34	0.43	0.51	0.62	1.16	1.44	1.63
	[ĀEĀ]	0.00	0.01	0.02	0.04	0.06	0.35	0.72	1.63
	[ĀEE]	0.14	0.19	0.24	0.29	0.35	0.65	0.81	0.92
	[EAA]	14.20	13.96	13.72	13.50	13.16	11.26	9.75	7.13
	[EAĀ]	0.30	0.29	0.29	0.28	0.27	0.23	0.20	0.15
	[EAE]	7.24	7.12	7.00	6.89	6.72	5.74	4.97	3.64
	[EĀA]	0.14	0.40	0.65	0.89	1.21	2.78	3.62	4.26
	[EĀĀ]	0.00	0.01	0.03	0.06	0.12	0.83	1.81	4.26
	[EĀE]	0.08	0.23	0.37	0.50	0.68	1.56	2.03	2.39
	[EEA]	7.77	7.55	7.33	7.12	6.82	5.20	4.07	2.39
	[EEĀ]	0.08	0.23	0.37	0.50	0.68	1.56	2.04	2.39
	[EEE]	4.37	4.24	4.12	4.00	3.83	2.93	2.29	1.35
(e)	g	31.08	30.99	30.89	30.81	30.72	30.42	30.60	32.26
	h	32.07	31.81	31.53	31.28	30.89	28.61	26.72	23.11
	i	0.83	1.62	2.41	3.16	4.25	10.38	14.93	22.12
	j	12.41	12.10	11.81	11.52	11.11	8.86	7.23	4.70
	k	12.08	12.11	12.14	12.16	12.17	11.99	11.55	10.03
	l	10.22	10.07	9.92	9.78	9.57	8.50	7.75	6.66
	m	0.45	0.45	0.44	0.43	0.42	0.36	0.32	0.24
	n	0.42	0.42	0.42	0.41	0.41	0.37	0.34	0.30
	p	0.42	0.44	0.45	0.46	0.46	0.51	0.54	0.59

[a]Monomer reactivity ratios (a), compositions of copolymers, %(b), mole fractions of inverted units among vinyl acetate units, %(c), mole fraction of triad sequences, %(d), and intensities of methylene carbon resonances, %(e), are listed against a reactivity ratio, r', as a parameter.

REFERENCES

1   Bagdasarjan, Ch. S., *Theory of Radical Polymerization*, Izdachelistvo Academy Nauk SSSR, Moscow, 1959.

2   Jenkins, A. D. (ed.), *Polymer Science*, North-Holland Publishing Co., Amsterdam, 1972.

3   Bamford C. H. and Tipper, C. F. H. (ed.), *Comprehensive Chemical Kinetics*, Vol. 14A,

Elsevier Scientific Publishing Co., Amsterdam, 1976.

4   Yonezawa, T., Hayashi, K., Nagata, C., Okamura, S. and Fukui, K., *J. Polym. Sci.*, 1954, **14,** 312; Hayashi, K., Yonezawa, T., Nagata, C., Okamura, S. and Fukui, K., *J. Polym. Sci.*, 1956, 20, 537.

5   Flory, P. J. and Leutner, F. S., *J. Polym. Sci.*, 1948, **3**, 880 , 1950, **5**, 267.

6   Unpublished data obtained in Kuraray Co.

7   Lyubetzky, S., Erussalimsky, B. and Goldenberg, A., *International Symposium on Macromolecular Chemistry*, 1966, No. 1.1.10, Tokyo; Erussalimsky, B., Tumarkin, N., Duntoff, F., Lyubetzky S. and Goldenberg, A., *Makromol. Chem.*, 1967, **104**, 288.

8   German, A. L. and Heikens, D., *Eur. Polym. J.*, 1975, **11**, 555.

9   Bucci, G. and Simonazzi, T., *J. Polym. Sci. Part C*, 1964, **7**, 203.

10   Tosi, C. and Ciampelli, F., *Adv. Polym. Sci.*, 1973, **12**, 87.

11   Crain, W. O., Zambelli, A. and Roberts, J. D., *Macromolecules*, 1971, **4**, 330.

12   Zambelli, A., Gatti, G., Sacchi, C., Crain, W. O. and Roberts, J. D., *Macromolecules*, 1971, **4**, 475.

13   Carman, C. J. and Wilkes, C. E., *Rubber Chem. Technol.*, 1971, **44**, 781.

14   Zambelli, A., Tosi, C. and Sacchi, C., *Macromolecules*, 1972, **5**, 649.

15   Wilkes, C., Carman, C. J. and Harrington, R. A., *J. Polym. Sci. Polym. Symp.*, 1973, **43**, 237.

16   Tanaka, Y. and Hatada, K., *J. Polym. Sci. Polym. Chem. Ed.*, 1973, **11**, 2057.

17   Bovey, F.A., Sacchi, M. C. and Zambelli, A., *Macromolecules*, 1974, **7**, 752.

18   Locatelli, P., Provasoli, A. and Zambelli, A., *Makromol. Chem.*, 1975, **176**, 2711.

19   Ray, G. J., Johnson, P. E. and Knox, J. R., *Macromolecules*, 1977, **10**, 773.

20   Carman, C. J., Harrington, R. A. and Wilkes, C. E., *Macromolecules*, 1977, **10**, 536.

21 Delfini, M., Segre, A. L. and Conti, F., *Macromolecules*, 1973, **6**, 456.

22 Wu, T. K., Ovenall, D. W. and Reddy, G. S. J*., Polym. Sci. Polym. Phys. Ed.*, 1974, **12**, 901.

23 Bovey, F. A. *High Resolution NMR of Macromolecules*, Academic Press, New York, 1972.

24 Inoue, Y., Chujo, R., Nishioka, A., Nozakura, S. and Iimuro, H., *Polym. J.*, 1973, **4**, 244.

25 Wu, T. K. and Ovenall, D. W., *Macromolecules*, 1973, **6**, 582.

26 Chapter 4 in this thesis; Moritani, T. and Fujiwara, Y., *Macromolecules*, 1977, **10**, 532.

27 Grant, D. M. and Paul, E. G., *J. Am. Chem. Soc.*, 1964, **86**, 2984.

28 Lindeman, L. P. and Adams, J. Q., *Anal. Chem.*, 1971,**43**, 1245.

29 Levy, G. C. and Nelson, G. L., *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley-Interscience, New York, 1972, Table 3.7 in p 47.

30 Dorman, D. E., Otocka, E. P. and Bovey, F. A., *Macromolecules*, 1972, **5**, 574.

31 Coleman, B. D. and Fox, T. G., *J. Polym. Sci. Part A*, 1963, **1**, 3183.

32 Ito, K. and Yamashita, Y., *J. Polym. Sci. Part A*, 1965, **3**, 2165.

33 Schaefer, J. and Natusch, D. F. S., *Macromolecules*, 1972, **5**, 416.

34 Wu, T. K., *J. Polym. Sci. Part A-2*, 1970, **8**, 167; Wu, T. K., *J. Polym. Sci. Polym. Phys. Ed.*, 1976, **14**, 343.

35 Schaefer, J., *J. Phys. Chem.*, 1966, **70**, 1975.

36 German, A. L. and Heikens, D., *J. Polym. Sci. Part A-1*, 1971, **9**, 2225.

37 Burkhart, R. D. and Zutty, N.L., *J. Polym. Sci. Part A*, 1963, **1**, 1137.

38 Terteryan, R. A., Dintses, A. I. and Rysakow, M. V., *Neftekhimiya*, 1963, **3**, 719.

39 Brown, F. E. and Ham, G. E., *J. Polym. Sci. Part A*, 1964, **2**, 3623.

40 Alfrey, T. and Goldfinger, G., *J. Chem. Phys.*, 1944, **12**, 322.

41 Price, F. P., *J. Chem. Phys.*, 1962, **36**, 209.

42 Pyun, C. W., *J. Polym. Sci. Part A-2*, 1970, **8**, 1111; 1971, **9**, 577.

43 The Society of Polymer Science, Japan, *Copolymerization*, Vol. 1, Baifukan, Tokyo, 1975.

44 Chapter 6 in this thesis; Moritani, T. and Fujiwara, Y., *J. Chem. Phys.*, 1973, **59**, 1175.