BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3597—3601 (1970)

High Resolution NMR Study of Vinyl Chloride-Ethylene Copolymers

Akira MISONO and Yasuzo UCHIDA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

and Kunikazu YAMADA

Research Laboratory, Sekisui Chemical Co., Shimamoto-cho, Mishima-gun, Osaka

(Received May 14, 1970)

The high resolution NMR spectra of vinyl chloride-ethylene copolymers obtained by trialkylboron catalyst have been analyzed. The copolymer composition could be determined from the resonance peak area, and the monomer reactivity ratios thus obtained were in good consistency with those determined from the results of elementary analysis. The fine structure of the copolymers have been elucidated in terms of the run number concept, and the distribution of dyads as well as the average sequence lengths of the monomer unit have been determined. It was found that the observed values fitted theoretical values, indicating that a terminal model holds in this copolymerization.

High resolution NMR spectroscopy has been proved to be a superior method in investigation of fine structures of copolymers, and many copolymer systems have been analyzed thus for the purpose of obtaining precise information concerning the nature of copolymerization.[1-12] Vinyl chloride copolymers have been prepared and consumed on an industrial scale since long ago. However, they have not been studied by high resolution NMR spectroscopy probably because of complexities of the spectra. Vinyl chloride - ethylene copolymer, in which the ethylene unit has no substituent group, gives a more simple NMR spectrum than the vinyl copolymers with substituted ethylenic comonomers. We have presented a qualitative interpretation of the spectra.[13-15] Schaefer[16] as well as Wilkes and coworkers[17] have also reported on the NMR studies of vinyl chloride - ethylene copolymers. In this paper, we wish to report results of our high resolution NMR study of the copolymer concerning the determination of the monomer reactivity ratios as well as the elucidation of the fine structure of the copolymer obtained by the tri-*n*-butylboron/*t*-butyl hydroperoxide catalyst system.

Experimental

The samples were prepared by using a catalyst system consisting of tri-*n*-butylboron and *t*-butyl hydroperoxide in a water-methanol mixture (1 : 1 by volume) at 0°C.[13] Most of the copolymer samples were obtained in conversions lower than 10%. However, a few samples were obtained in conversions between 10 and 13%. The composition of the copolymer was determined from the results of elementary analysis of C and Cl. The NMR spectrum of the copolymer was measured with a Japan Electron Optics high resolution NMR spectrometer, model, JNM-C-60, in a 10wt/vol% monochlorobenzene solution of the sample at 60 MHz and 110°C using tetramethylsilane as an internal standard. The NMR spectrum was copied and each peak was separated by cutting, and then weighed for the determination of relative peak area.

1) F. A. Bovey, *J. Polym. Sci.*, **62**, 197 (1962).
2) A. Nishioka, Y. Kato and N. Ashikari, *ibid.*, **62**, S10 (1962).
3) R. Chujo, S. Sato and E. Nagai, *ibid.*, **A2**, 895 (1964).
4) Y. Kato, N. Ashikari and A. Nishioka, This Bulletin, **37**, 1630 (1964).
5) J. L. McClanahan and S. A. Previtera, *J. Polym. Sci.*, **A3**, 3919 (1965).
6) K. Ito and Y. Yamashita, *ibid.*, **B3**, 625, 637 (1965).
7) T. Harada and N. Ueda, *Kobunshi Kagaku*, **22**, 685 (1965).
8) U. Johnsen, *Ber. Bunsenges.*, **70**, 320 (1966).
9) T. Fischer, J. B. Kinsinger and C. W. Wilson, *J. Polym. Sci.*, **B4**, 379 (1966).
10) K. Ito and Y. Yamashita, *ibid.*, **A4**, 631 (1966).
11) J. B. Kinsinger, T. Fischer and C. W. Wilson, *ibid.*, **B5**, 285 (1967).
12) R. Yamadera and M. Murano, *ibid.*, **A5** 2259 (1967).
13) A. Misono, Y. Uchida and K. Yamada, This Bulletin, **39**, 2458 (1966).
14) A. Misono, Y. Uchida and K. Yamada, *ibid.*, **40**, 2366 (1967).
15) A. Misono, Y. Uchida, K. Yamada and T. Saeki, *ibid.*, **41**, 2995 (1968).
16) J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966).
17) C. E. Wilkes, J. C. Westfahl and R. H. Backderf, *Amer. Chem. Soc. Polymer Preprints*, **8(1)**, 386 (1967).

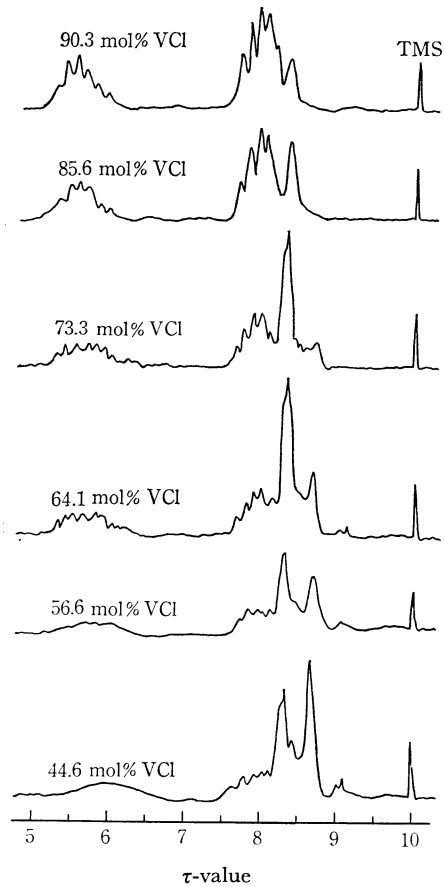

Fig. 1. NMR spectra of copolymers.

Results and Discussion

Peak Assignment. In Fig. 1 are shown the NMR spectra of several copolymers. A multiplet observed between 5.5 and 6.0 τ can be assigned to the methylene proton of vinyl chloride sequence based on the results of other workers.[18-21] The multiplet shifts to higher magnetic fields and becomes weaker in intensity as the vinyl chloride content of copolymer decreases. Since no methine proton absorption is observed at lower fields than those observed for pure polyvinyl chloride, and the infrared spectrum of the copolymer shows no absorption due to the $-(CH_2)_2-$ and the $-(CH_2)_4-$ sequences,[22] occurrence of the head-to-head or tail-to-tail linkage of vinyl chloride units can be ruled out.

In the region of methylene proton resonance, three groups of peaks can be observed in the spectrum of the copolymer; a multiplet centered at 7.85 τ, a singlet at 8.35 τ and a singlet at 8.65 τ. An additional peak is observed at 8.55 τ in the spectrum of the copolymer with a higher ethylene content. Hereafter, the methylene peaks are denoted by A, B and C, respectively, for the sake of convenience. The position of these methylene peaks does not seem to shift with change in copolymer composition.

The NMR spectra of polyvinyl chloride and polyethylene are shown in Fig. 2 and those of 2,6-di-

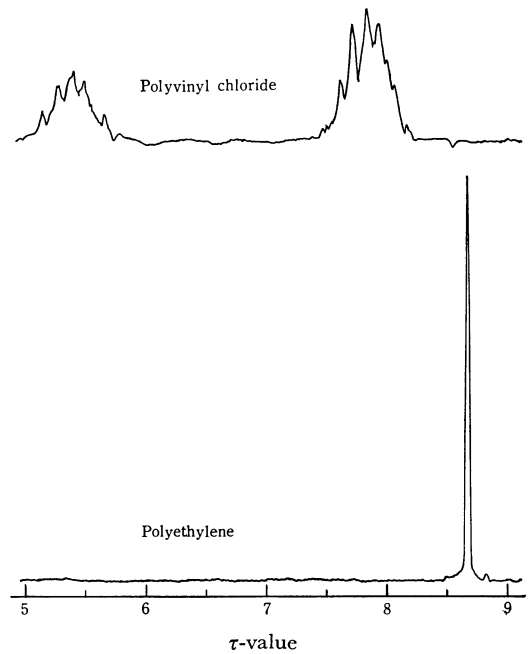

Fig. 2. NMR spectra of polyvinyl chloride and polyethylene.

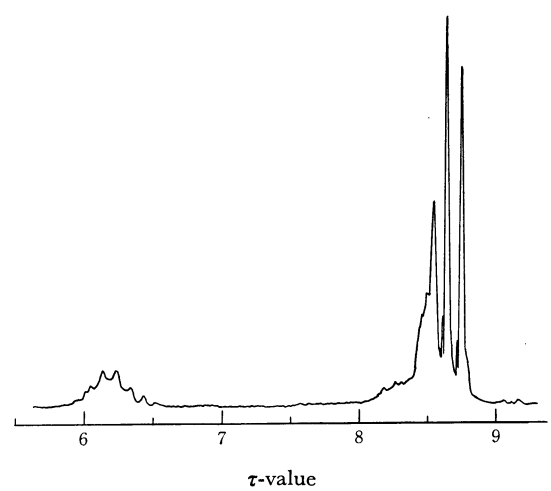

Fig. 3. NMR spectrum of 2,6-dichloroheptane.

18) U. Johnsen, *J. Polym. Sci.*, **54**, S6 (1961).
19) W. C. Tincher, *ibid.*, **62**, S148 (1962).
20) R. Chujo, S. Sato, T. Ozeki and F. Nagai, *ibid.*, **61** S12 (1962).
21) F. A. Bovey and G. V. D. Tiers, *Chem. & Ind.*, **1962**, 1826.
22) A. Misono, Y. Uchida and K. Yamada, This Bulletin, **40**, 2696 (1967).

chloroheptane in Fig. 3. Peaks A and C are also observed in the spectrum of polyvinyl chloride and polyethylene, respectively, and thus can be assigned to the methylene proton absorption of $(CH_2–CHCl)_m$ and $(CH_2–CH_2)_n$ sequence, respectively, where m and n are greater than two. The observations of the NMR spectrum of the copolymer enable us to deduce that peak B can be assigned to the methylene group of a boundary structure located at a junction point of vinyl chloride unit and ethylene unit. In the spectrum of 2,6-dichloroheptane, a resonance peak is observed at 8.55 τ which can be assigned to a methylene group having two methylene groups in both nearest neighbors. Accordingly, the methylene peak mentioned previously appearing in the copolymer richer in ethylene may arise from the structure CHCl–CH_2–CH_2*–CH_2–CHCl. Thus, it seems reasonable to assign peak B to the methylene group having a methine and a methylene group in the nearest neighbors, namely CHCl–CH_2*–CH_2.

Table 1. Assignment of dyads

Dyad	Chemical shift (τ)	Structure
V–V	7.85	CH_2–CHCl–CH_2*–CHCl
V–E	8.35	CH_2–CHCl–CH_2*–CH_2
E–V	8.35	CH_2–CH_2–CH_2*–CHCl
E–E	8.65	CH_2–CH_2*–CH_2*–CH_2

If one describes the fine structure of the copolymer in terms of dyads, the above mentioned relationship can be summarized as shown in Table 1. Since each vinyl chloride unit contains one methylene group and each ethylene unit contains two, the mole fraction of each dyad can be easily calculated by using the following relationships taking into account the double counting of methylene group belonging to the E–E dyad, a part of which consists of the V–E or the E–V dyad.

$$f(\mathrm{V–V}) = 2a/\{2a+2b+(c-b/2)\} \quad (1)$$

$$2f(\mathrm{V–E}) = 2b/\{2a+2b+(c-b/2)\} \quad (2)$$

$$f(\mathrm{E–E}) = (c-b/2)/\{2a+2b+(c-b/2)\} \quad (3)$$

$$f(\mathrm{V–V}) + 2f(\mathrm{V–E}) + f(\mathrm{E–E}) = 1 \quad (4)$$

where a, b and c denote the relative peak areas of peaks A, B and C, respectively.

Determination of Monomer Reactivity Ratios. In Table 2 are shown the copolymer composition and the percentage of the methylene peak areas a, b and c. The vinyl chloride or ethylene mole fraction of the copolymer can be readily calculated by using the following equations derived from the above relationships of dyad distribution, where $F(\mathrm{V})$ and $F(\mathrm{E})$ denote the mole fraction of vinyl chloride and ethylene in the copolymer, respectively.

Table 2. Relative peak of methylene resonance

Copolymer composition (VCl mol%)	f_A	f_B	f_C
44.6	12.5	33.5	53.9
56.6	20.5	39.2	40.4
64.1	28.7	36.6	34.8
73.3	39.0	40.7	20.3
78.8	52.6	32.3	15.1
81.0	53.3	32.4	14.3
85.6	69.3	21.7	9.0
90.3	79.5	15.0	5.5
99.0	94.5	5.5	0

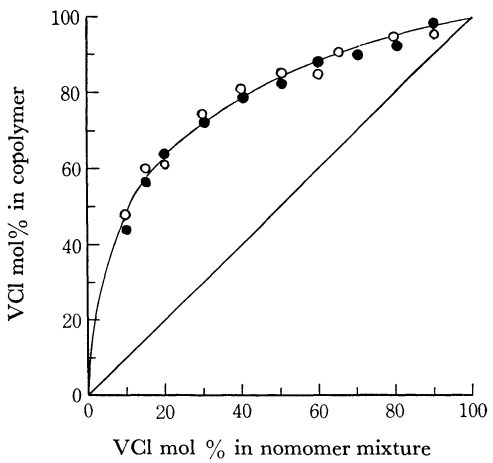

Fig. 4. Determination of copolymer composition.
open circle: from NMR peak area
closed circle: from C analysis

$$F(\mathrm{V}) = f(\mathrm{V–V}) + 2f(\mathrm{V–E})/2 = (a+b)/(2a+3b/2+c) \quad (5)$$

$$F(\mathrm{E}) = f(\mathrm{E–E}) + 2f(\mathrm{V–E})/2 = (b/2+c)/(2a+3b/2+c) \quad (6)$$

In Fig. 4 are compared the copolymer composition calculated from the results of elementary analysis and those obtained from NMR peak areas. Coincidence between the results from the two methods is obvious. Figure 5 shows the result of the determination of the monomer reactivity ratios using the fraction of the V–E dyad with the relationship given by Kinsinger and Colton.[23]

$$F_0\{1-2f(\mathrm{V–E})\}/f(\mathrm{V–E}) = r_2 + r_1F_0^2 \quad (7)$$

where F_0 denotes the monomer feed ratio, namely vinyl chloride/ethylene molar ratio in initial monomer mixture. The monomer reactivity ratios determined by means of the two methods are good agreement with each other:

23) J. B. Kinsinger and D. Colton, *J. Polym. Sci.*, **B3**, 797 (1965).

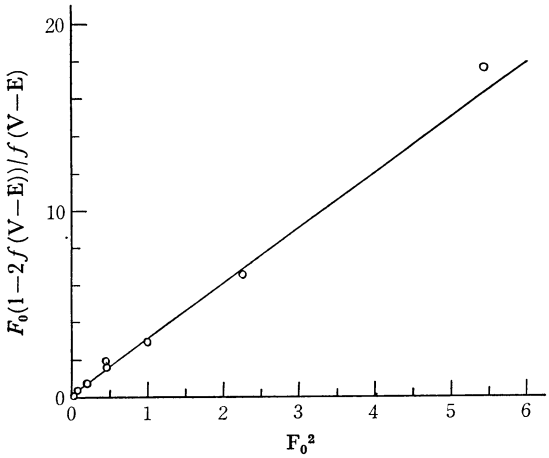

Fig. 5. Determination of monomer reactivity ratios by Kinsinger-Colton relationship

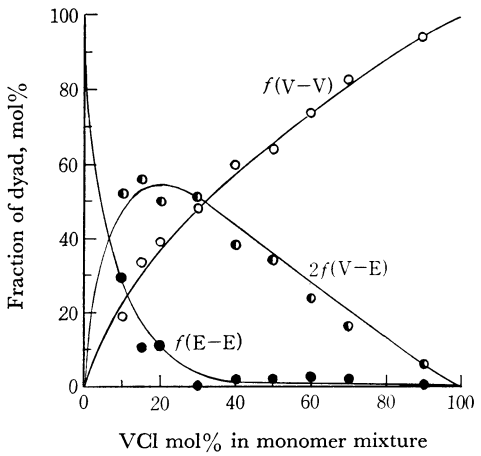

Fig. 6. Change in fraction of dyad as a function of monomer composition.

From elementary analysis,

$$r_1\,(\mathrm{V}) = 3.39 \text{ and } r_2\,(\mathrm{E}) = 0.20$$

From NMR peak area,

$$r_1\,(\mathrm{V}) = 2.96 \text{ and } r_2\,(\mathrm{E}) = 0.20$$

Elucidation of Fine Structure. Fine structures of copolymers have been nicely characterized by means of the run number (R) concept proposed by Harwood.[24] R has been defined as the average number of monomer sequences (runs) occurring in the copolymer per 100 monomer units. According to the definition, R can be easily calculated by means of Eq. (2) because R equals the mole fraction of the V–E and E–V dyads. Hence

$$R_{\mathrm{obs}} = 2f\,(\mathrm{V-E}) = 2b/(2a+3b/2+c) \qquad (8)$$

In an ideally random copolymerization in the sense of Mayo-Lewis statistics of copolymerization, R should be expressed by the relationship[24]

$$R_{\mathrm{calc}} = 200/(r_1x+r_2/x+2) \qquad (9)$$

where x represents the monomer feed ratio. If R_{obs} is greater than R_{calc} the monomer units tend to alternate in the copolymer, and if R_{obs} is smaller than R_{calc} the monomer units tend to cluster in blocks of like units.

The mole fractions of the V–V and E–E dyads can be calculated by using the theoretical run number with the following equations.

$$f\,(\mathrm{V-V})_{\mathrm{calc}} = F(\mathrm{V}) - R_{\mathrm{calc}}/2 \qquad (10)$$

$$f\,(\mathrm{E-E})_{\mathrm{calc}} = F(\mathrm{E}) - R_{\mathrm{calc}}/2 \qquad (11)$$

In Fig. 6 are compared the observed and calculated mole fractions of the three dyads as a function of the monomer feed ratio. We see that the observed points fit well the calculated lines over the whole range of the monomer feed ratio. This indicates that the copolymerization initiated by the trialkylboron catalyst should be described as a random or zeroth-order Markoffian process.[25] This means that the rates of four propagation processes involved in the copolymerization depend only on the kind of terminal monomer unit (terminal model), and is in agreement with what has been found in most cases of radical copolymerization, though an exceptional case has been reported.[9]

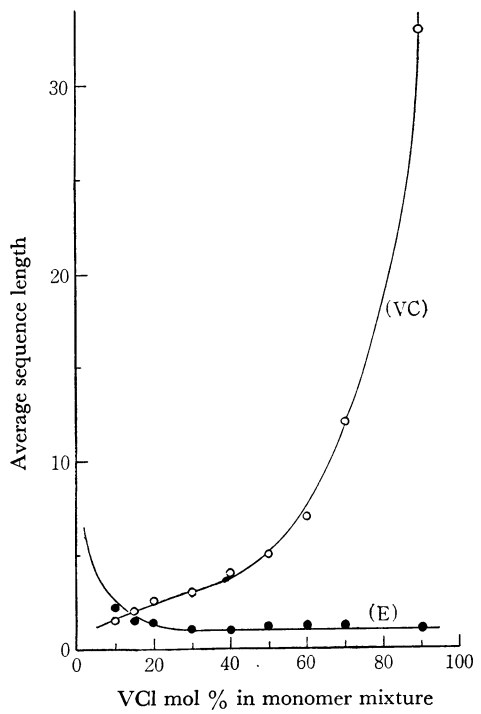

Fig. 7. Change in average sequence length as a function of monomer composition.

24) H. J. Harwood and W. M. Ritchey, *J. Polym. Sci.*, **B2**, 610 (1964).

25) F. P. Price, *J. Chem. Phys.*, **36**, 209 (1962).

Recently, the occurrence of the complexed radical propagation mechanism has been proposed by Arimoto[26] in order to elucidate the ineffectiveness of radical inhibitors on vinyl polymerization initiated by trialkylboron. Hydroquinone did not inhibit the reaction at all in our case of copolymerization either. In spite of this appreciable existence of complexed radical propagation, it might have only a little, if any, significance on the monomer reactivity ratios and the fine structure of the copolymer.

Figure 7 shows the observed and calculated average monomer sequence lengths as a function of the monomer feed ratio. The following relationships were used for the calculation.

$$\text{av. sequence length of } V = F(\mathrm{V})/R/2 \tag{12}$$

$$\text{av. sequence length of } E = F(\mathrm{E})/R/2 \tag{13}$$

where R is the observed or calculated run number.

The average sequence length of vinyl chloride unit decreases rapidly as the vinyl chloride fraction in the monomer feed decreases, whereas that of ethylene unit increases only slowly from unity according to the increase in ethylene fraction in the monomer feed. It seems interesting to note that the average sequence lengths of both monomer units reach *ca.* 2 when the copolymer composition approaches 50 : 50 molar ratio. As in the dyad distribution the observed average sequence lengths fit the calculated values.

26) F. S. Arimoto, *J. Polym. Sci.*, **A4**, 275 (1966).