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High Resolution NMR Studies on Sequence Distribution of Vinylidene Chloride Copolymers

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SUMMARY:

Sequence distributions of several radical copolymers of vinylidene chloride were examined by NMR spectroscopy, including methyl methacrylate, benzyl methacrylate, methacryloyl chloride, methyl acrylate, α -methylstyrene, styrene, and vinyl acetate as comonomers. Except for the α -methylstyrene and styrene systems, some of the diad, triad, and tetrad sequences were observed in the CH_2 and αCH_3 resonances and are discussed in the light of the usual copolymerization theory.

ZUSAMMENFASSUNG:

Die Sequenzverteilung einiger radikalisch gebildeter Copolymerer des Vinylidenchlorids wurde durch NMR-Spektralanalyse untersucht, wobei als Comonomere Methylmethacrylat, Benzylmethacrylat, Methacrylsäurechlorid, Methacrylat, α -Methylstyrol, Styrol und Vinylacetat verwendet wurden. Ausgenommen bei den α -Methylstyrol und Styrol enthaltenden Systemen, wurden an Hand der CH_2 - und αCH_3 -Resonanzstellen einige Diaden, Triaden und Tetraden beobachtet und im Rahmen der üblichen Copolymerisationstheorie erörtert.

1. Introduction

Along with the developments of high resolution NMR spectroscopy in the field of polymer chemistry, the copolymerization mechanism has recently been discussed in terms of the monomer sequence distributions in some copolymer systems^{1–13}). With radical copolymers of styrene-methyl methacrylate and related systems, we have confirmed the usual copolymerization process using the MAYO and LEWIS equation^{5–7}). JOHNSEN has also successfully interpreted the normal and decoupled NMR spectra of vinylidene chloride/vinyl chloride copolymers^{1,9}), where the tetrad sequence distributions were observed from the peak separations of the CH_2 resonances. Recently, in the normal spectra of vinylidene chloride/isobutylene system, JOHNSEN *et al.*¹⁰) and FISCHER *et al.*^{11,12}) have observed clear peak separations in the CH_3 and CH_2 regions, which were ascribed to the triad and tetrad monomer sequences.

The observed peak separations in these chlorinated copolymers are apparently due to the presence of the electronegative Cl atoms in such a manner that the more down-field shift is caused by the increasing number of Cl atoms in a particular sequence of interest. Thus the CH_2 group of poly(vinylidene chloride) gives rise to a sharp single peak in sufficiently low fields as compared with those of other vinyl polymers, so that any peak separations in copolymer systems could rather readily be distinguished. These conditions are most favorable for the examination of sequence distribution, coupled with the absence of tacticity considerations in the vinylidene chloride sequences.

Under these considerations, we have attempted in this paper to examine the NMR spectra of several vinylidene chloride copolymers obtained by radical polymerization, including methyl methacrylate, benzyl methacrylate, methacryloyl chloride, methyl acrylate, α -methylstyrene, styrene, and vinyl acetate as comonomers. Some diad, triad, and tetrad sequences were observed and compared with those from the copolymerization theory in the same manner as reported by JOHNSEN *et al.*¹⁰.

2. Experimental

Monomers were purified by usual procedures and redistd. before polymerization. Bulk polymerization was carried out at 60°C using benzoyl peroxide to a conversion less than 10%. Polymers were collected in methanol and purified by reprecipitation from dioxane, tetrachloroethane, or dimethylformamide into methanol.

NMR spectra were measured at 60–110°C using a Japan Electron Optics Model JNM-C-60 Spectrometer working at 60 Mc. Tetrachloroethane, thionyl chloride, chloroform, or tetrachloroethylene were used as solvents, with tetramethylsilane as an internal standard.

The copolymer composition was determined either from the analysis of the NMR spectrum or from the Cl content of the copolymer. Monomer reactivity ratios were obtained by the FINEMAN-ROSS and line-intersection methods. The average monomer composition obtained from the values before and after polymerization was used for the calculations to correct the change in composition during the observed conversion.

Thus, the average vinylidene chloride composition in monomer mixture (\bar{F}_D) was obtained by

$$\bar{F}_D = \frac{F_D - f_D \cdot m/2}{1 - m/2}$$

where F_D and f_D are the mole fractions of vinylidene chloride in feed and copolymer, respectively, and m is the fractional conversion on molar basis, which in turn was obtained from the observed fractional conversion in weight (w) by

$$m = w \frac{M_D F_D + M_M F_M}{M_D f_D + M_M f_M}$$

with M_D and M_M denoting the mol. wts. of the vinylidene chloride and comonomer, and F_M and f_M the mole fractions of the comonomer in feed and copolymer, respectively. Similarly, the average composition of the comonomer in the monomer mixture (\bar{F}_M) was given by

$$\bar{F}_M = \frac{F_M - f_M \cdot m/2}{1 - m/2}$$

In these relations, $f_D \cdot m/2$ and $f_M \cdot m/2$ correspond to the average fractions of vinylidene chloride and comonomer which were polymerized during the observed average conversion ($m/2$).

3. Results

In the following, vinylidene chloride is denoted by D and the comonomer by M.

3.1. Vinylidene chloride/methyl methacrylate system

Poly(vinylidene chloride) gives a single CH_2 peak at 6.2τ , while poly-(methyl methacrylate) from radical polymerization gives an OCH_3 peak at 6.4τ , a CH_2 peak at about 8.1τ , and αCH_3 peaks at $8.8\text{--}9.1 \tau$, depending upon the microtacticity¹⁴⁻¹⁷. However, several additional peaks are

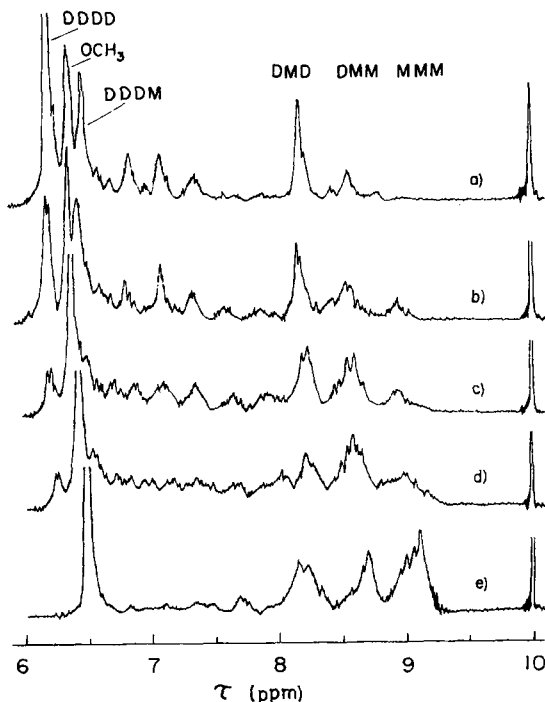


Fig. 1. NMR spectra of vinylidene chloride (D)/methyl methacrylate (M) copolymers in $\text{Cl}_2\text{CHCHCl}_2$ at 110°C (60 Mc). VDC mole fraction in copolymer: a) 0.852, b) 0.738, c) 0.591, d) 0.477, e) 0.207

observed in the NMR spectra of the copolymer, as given in Fig. 1, apparently caused by the presence of various monomer sequences in the chain. The peak assignments indicated in the spectra were performed as follows, based on those reported by JOHNSEN *et al.*^{9,10}.

The αCH_3 resonance consists of the three main peaks at 8.9–9.1, 8.5 to 8.7, and 8.0–8.2 τ , with the latter peak area increasing with the D content of the copolymer. Considering the effects of Cl atoms, these three peaks were assigned to the αCH_3 groups of the central M units in the triad sequences MMM, DMM (or MMD), and DMD, respectively with decreasing magnetic field. The peak of the DMD triad about 8.0–8.2 τ overlaps in part with the CH_2 resonances, particularly in the copolymer of high M content. The fine structure observed in the respective αCH_3 peaks might be ascribed to the effects of more remote monomer units such as in the pentad sequences and to the tacticity differences in the M-consecutive sequences. It will be noted here that the configurational sequences need be considered neither in the alternating –DM– or –MD– units nor in the –DD– units because the D units is symmetrical in nature in the chain.

The CH_2 group in the main chain gives rise to several peaks in the region of 6.2 to 8.0 τ . With increasing M content of the copolymer, the resonances shift to higher fields, accompanied by poorer peak separations. The peak at the lowest field (6.2 τ) was assigned to the central CH_2 group of the tetrad DDDD, because this peak lies in the same position as that of poly(vinylidene chloride). The next peak at about 6.45 τ was then assigned to the tetrad DDDM (or MDDD). The other eight possible tetrads probably lie in the region 6.6–8.0 τ , but clear assignments were not possible because of the ill-defined peak separations. This appears to be due to a complication caused by the tacticity differences of the sequences including M consecutive units (–MM–), which might become serious with increasing M content as observed.

The OCH_3 resonance appears as a single peak at 6.4 τ , independent of the composition, indicating that the ester group is almost insensitive to the sequence distribution in the systems on hand.

The concentrations (in mole fractions) of the assigned triads and tetrads can be estimated from the measurements of the corresponding peak areas using the following relations. Note here that 3 protons are present in the αCH_3 group, 2 protons in the CH_2 and the D unit, and 8 protons in the M unit.

$$A_{\text{MMM}} = \frac{3P_3\{\text{MMM}\}}{2P_1\{\text{D}\} + 8P_1\{\text{M}\}} \quad (1)$$

$$A_{\text{DMM}} = \frac{3 \cdot 2 P_3\{\text{DMM}\}}{2 P_1\{\text{D}\} + 8 P_1\{\text{M}\}} = \frac{3 \cdot 2 P_3\{\text{MMD}\}}{2 P_1\{\text{D}\} + 8 P_1\{\text{M}\}} \quad (2)$$

where

$$P_3\{\text{MMM}\} + 2 P_3\{\text{DMM}\} + P_3\{\text{DMD}\} = P_1\{\text{M}\} \quad (3)$$

with

$$P_3\{\text{DMM}\} = P_3\{\text{MMD}\}$$

$$A_{\text{DDDD}} = \frac{2 P_4\{\text{DDDD}\}}{2 P_1\{\text{D}\} + 8 P_1\{\text{M}\}} \quad (4)$$

$$A_{\text{DDDM}} = \frac{2 \cdot 2 P_4\{\text{DDDM}\}}{2 P_1\{\text{D}\} + 8 P_1\{\text{M}\}} = \frac{2 \cdot 2 P_4\{\text{MDDD}\}}{2 P_1\{\text{D}\} + 8 P_1\{\text{M}\}} \quad (5)$$

with $P_4\{\text{DDDM}\} = P_4\{\text{MDDD}\}$. The A 's represent the respective specific peak areas, while $P_1\{\cdot\}$, $P_3\{\dots\}$, and $P_4\{\dots\}$ are the corresponding monomer, triad, and tetrad concentrations in the copolymer, respectively. Copolymer compositions $P_1\{\text{M}\}$ and $P_1\{\text{D}\}$, where $P_1\{\text{M}\} + P_1\{\text{D}\} = 1$, were determined from the Cl analyses, and the monomer reactivity ratios were obtained as

$$r_{\text{M}} = 2.5 \pm 0.3 \quad \text{and} \quad r_{\text{D}} = 0.34 \pm 0.05$$

in fair accord with the reported values¹⁸⁾.

On the other hand, the above concentrations can be calculated according to the usual copolymerization theory (terminal model) as follows^{10,12,19)}.

$$P_1\{\text{M}\} = 1 - P_1\{\text{D}\} = \frac{P_{\text{DM}}}{P_{\text{MD}} + P_{\text{DM}}} \quad (6)$$

$$P_3\{\text{MMM}\} = P_1\{\text{M}\} P_{\text{MM}}^2 \quad (7)$$

$$P_3\{\text{DMM}\} = P_3\{\text{MMD}\} = P_1\{\text{M}\} P_{\text{MM}} P_{\text{MD}} \quad (8)$$

$$P_3\{\text{DMD}\} = P_1\{\text{D}\} P_{\text{DM}} P_{\text{MD}} = P_1\{\text{M}\} P_{\text{MD}}^2 \quad (9)$$

$$P_4\{\text{DDDD}\} = P_1\{\text{D}\} P_{\text{DD}}^3 \quad (10)$$

$$P_4\{\text{DDDM}\} = P_4\{\text{MDDD}\} = P_1\{\text{D}\} P_{\text{DD}}^2 P_{\text{DM}} \quad (11)$$

where P_{DM} , for example, is the probability of a D unit being followed by an M unit. Using the monomer reactivity ratios, these probabilities are written as

$$P_{\text{DM}} = 1 - P_{\text{DD}} = \frac{1}{1 + r_{\text{D}} x} \quad (12)$$

$$P_{\text{MD}} = 1 - P_{\text{MM}} = \frac{1}{1 + r_{\text{M}}/x} \quad (13)$$

with x representing the monomer mole ratio in the polymerizing system, $x = [D]/[M]$.

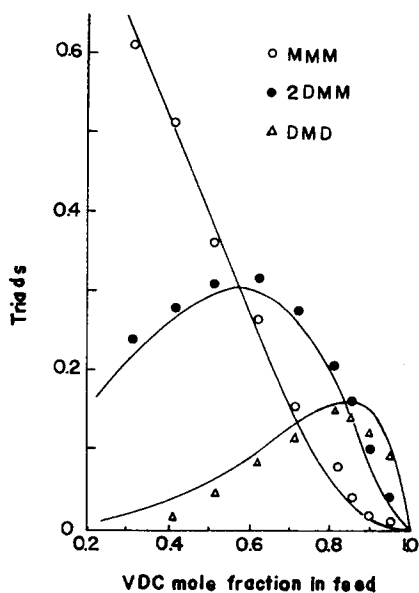


Fig. 2

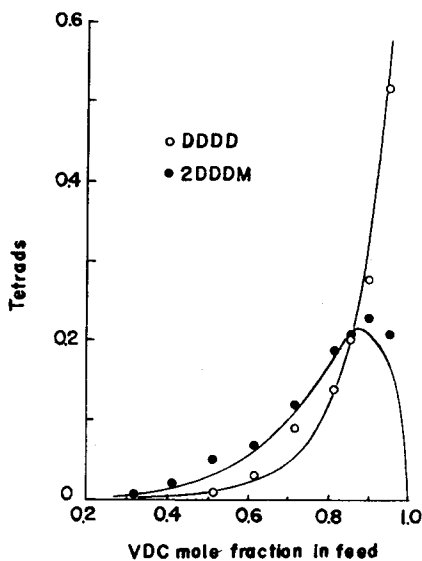


Fig. 3

Fig. 2. Mole fraction of triads vs. mole fraction of VDC in monomer feed for the system of VDC/methyl methacrylate. Solid lines: calcd. from $r_D = 0.34$, $r_M = 2.5$

Fig. 3. Mole fraction of tetrads vs. mole fraction of VDC in monomer feed for the system of VDC/methyl methacrylate. Solid lines: calcd. from $r_D = 0.34$, $r_M = 2.5$

In Figs. 2 and 3, the observed triad and tetrad concentrations are plotted against the mole fraction of vinylidene chloride (VDC) in the monomer mixture, along with the theoretical curve calculated from Eqs. (6)–(13) using the monomer reactivity ratios.

3.2. Vinylidene chloride/benzyl methacrylate system

In the present and following systems, the analyses were performed similarly as in the above system. The determined peak assignments are indicated in the spectra and the triad or tetrad concentrations were estimated by relations similar to Eqs. (1)–(5), and the theoretical concentrations were calculated by Eqs. (6)–(13).

As shown in Fig. 4, the phenyl and benzyl methylene protons appear as separate peaks at 2.9 and 5.1 τ , respectively, and were used to determine the copolymer compositions. The αCH_3 and CH_2 resonances show

similar patterns as in the methyl methacrylate system, though the fine structure in each of the DDDD and DDDM tetrad peaks apparently indicates a further line splitting due to the longer sequences such as hexads,

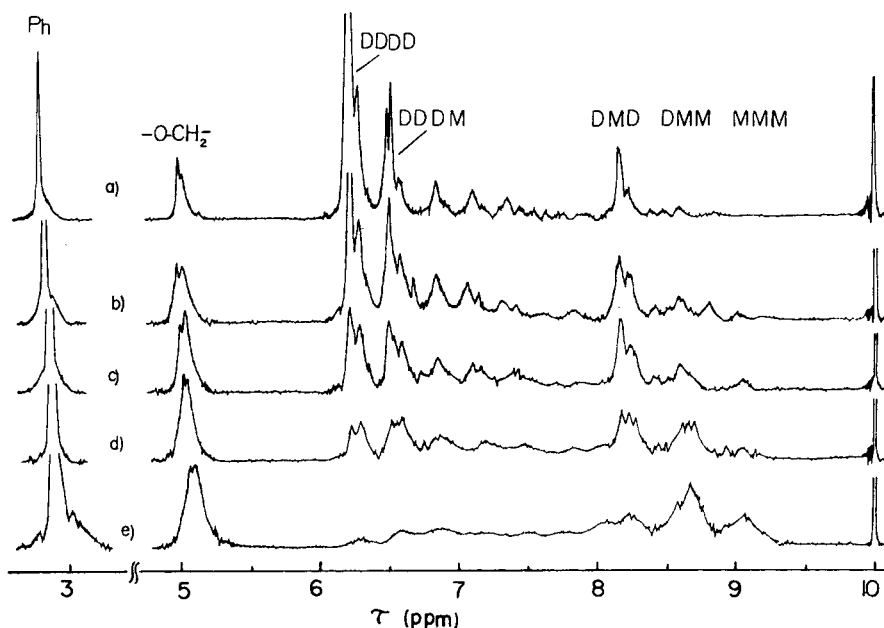


Fig. 4. NMR spectra of vinylidene chloride/benzyl methacrylate copolymers in SOCl_2 at 85°C (60 Mc). VDC mole fraction in copolymer: a) 0.901, b) 0.839, c) 0.799, d) 0.713, e) 0.537

as pointed out by JOHNSEN^{9,10}. Figs. 5 and 6 compare the experimental triad and tetrad concentrations with the theoretical curves using the reactivity ratios

$$r_M = 3.3 \pm 0.5 \text{ and } r_D = 0.34 \pm 0.05$$

3.3. Vinylidene chloride/methacryloyl chloride system

Similar spectrum patterns are also evident in this system, as shown in Fig. 7, except that the αCH_3 resonances appear in relatively lower fields, probably due to the deshielding effect by the acyl chloride group. In Figs. 8 and 9, the observed triad and tetrad concentrations are compared with the theoretical lines from the parameters

$$r_M = 2.0 \pm 0.6 \text{ and } r_D = 0.30 \pm 0.06$$

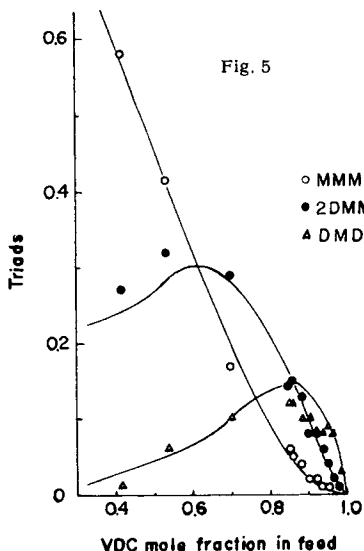


Fig. 5. Mole fraction of triads vs. mole fraction of VDC in monomer feed for the system of VDC/benzyl methacrylate. Solid lines: calcd. from $r_D = 0.34$, $r_M = 3.3$

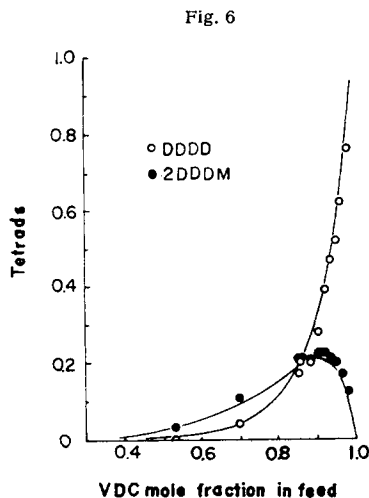


Fig. 6. Mole fraction of tetrads vs. mole fraction of VDC in monomer feed for the system of VDC/benzyl methacrylate. Solid lines: calcd. from $r_D = 0.34$, $r_M = 3.3$

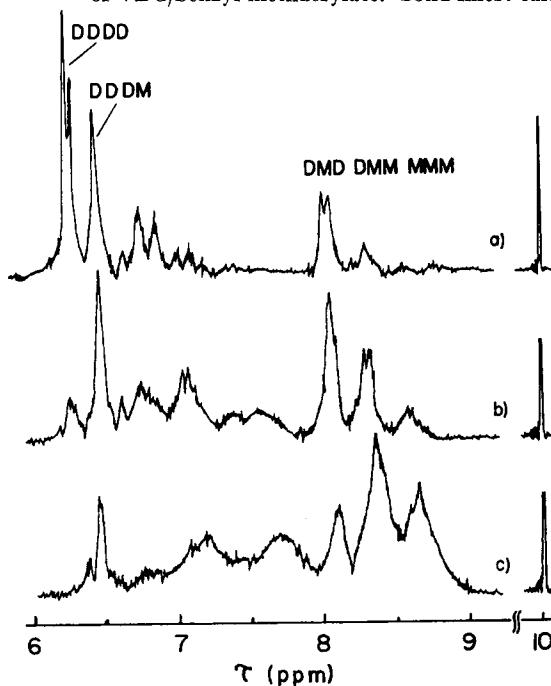


Fig. 7. NMR spectra of vinylidene chloride/methacryloyl chloride copolymers in $\text{Cl}_2\text{CHCHCl}_2$ at 110°C (60 Mc). VDC mole fraction in copolymer: a) 0.85, b) 0.45, c) 0.32

Fig. 8

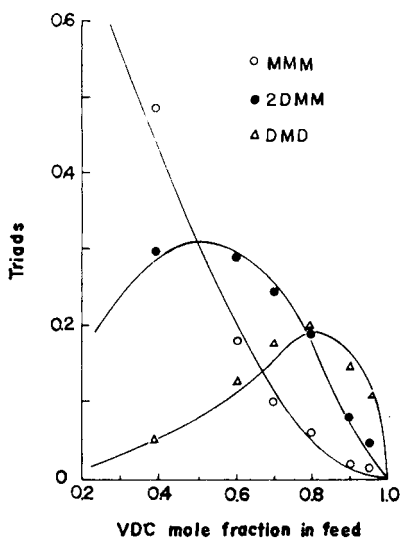


Fig. 9

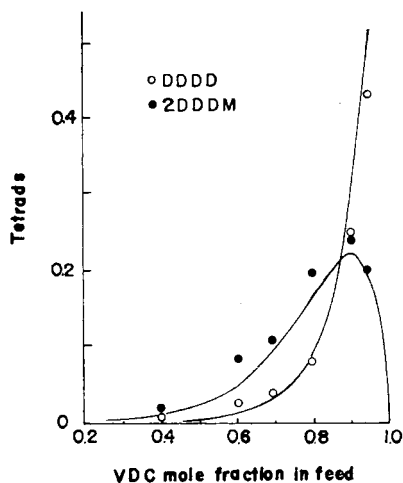


Fig. 8. Mole fraction of triads vs. mole fraction of VDC in monomer feed for the system of VDC/methacryloyl chloride. Solid lines: calcd. from $r_D = 0.3$, $r_M = 2.0$

Fig. 9. Mole fraction of tetrads vs. mole fraction of VDC in monomer feed for the system of VDC/methacryloyl chloride. Solid lines: calcd. from $r_D = 0.3$, $r_M = 2.0$

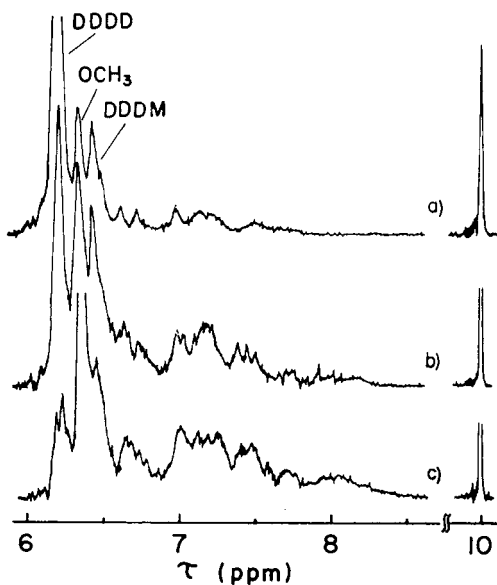


Fig. 10. NMR spectra of vinylidene chloride/methyl acrylate copolymers in CHCl_3 at 60°C (60 Mc). Molar ratio in feed ($[\text{D}]/[\text{M}]$): a) 89.7/10.3, b) 81.1/18.9, c) 65.7/34.3

3.4. Vinylidene chloride/methyl acrylate system

The NMR spectra in Fig. 10 show the CH_2 resonances of the tetrads DDDD at 6.2τ and DDDM (MDDD) at 6.5τ and the OCH_3 resonance at 6.4τ . The other region is rather complicated by the presence of CH group in the chain and could not be assigned.

3.5. Vinylidene chloride/ α -methylstyrene and /styrene systems

The spectra of these systems shown in Fig. 11 are very complex except for the phenyl proton resonances at 3.0τ . The shielding effects by the phenyl ring and the deshielding effects by the Cl groups appear to cause the complication of the spectra.

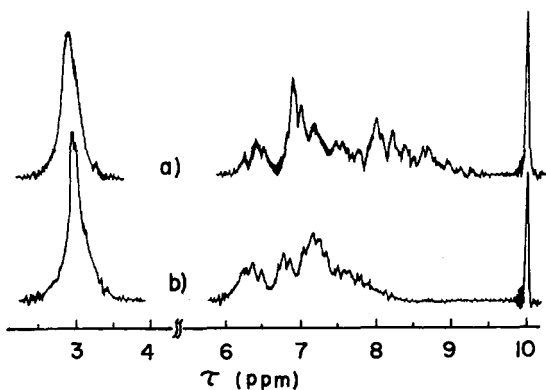


Fig. 11. NMR spectra of vinylidene chloride/ α -methylstyrene (a) and vinylidene chloride/styrene (b) copolymers in tetrachloroethylene at 110°C (60 Mc)

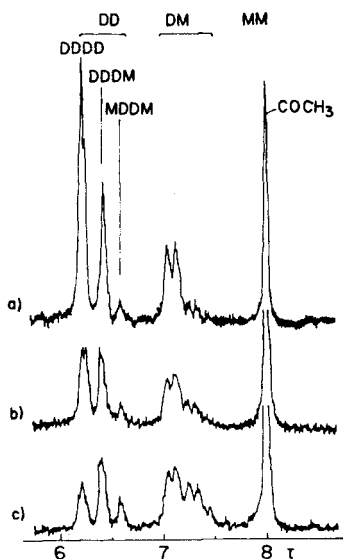


Fig. 12. NMR spectra of vinylidene chloride/vinyl acetate copolymers in SOCl_2 at 70°C (60 Mc). VDC mole fraction in copolymer: a) 0.828, b) 0.752, c) 0.664

3.6. Vinylidene chloride/vinyl acetate system

Fig. 12 shows the spectra of the CH_2 and COCH_3 resonances. The CH resonance, which appears as an ill-defined, very broad peak at about 5.2τ , was omitted in the figure.

The CH_2 spectra in this system resemble very much those in the reported vinylidene chloride/isobutylene system¹⁰⁻¹²), and can explicitly be divided into three groups. The first group appearing at $6.2-6.6 \tau$ can be assigned to the DD diad. This group in turn is composed of the three distinct peaks at $6.2, 6.4,$ and 6.6τ , corresponding to the tetrads DDDD, DDDM (MDDD), and MDDM, respectively. The second group at $7.0-7.5 \tau$ corresponds to the DM or MD diad which consists of the four kinds of tetrads, DDMD (DMDD), MDMD (DMDM), DDMM (MMDD), and MDMM (MMDM). However, the tetrad assignments and concentrations in this group were not determined because each of these resonances should be a doublet peak due to the spin coupling with an αCH group. The third group at about 8.0τ corresponds to the MM diad but is not clear because of the overlap with the strong COCH_3 peak.

Fig. 13

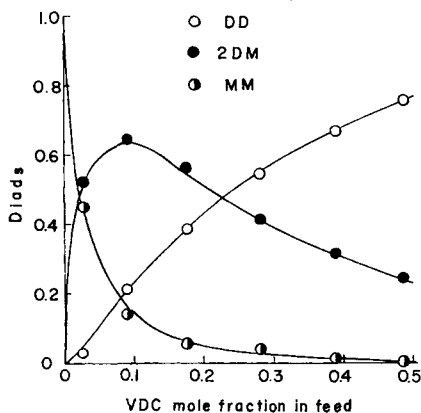


Fig. 14

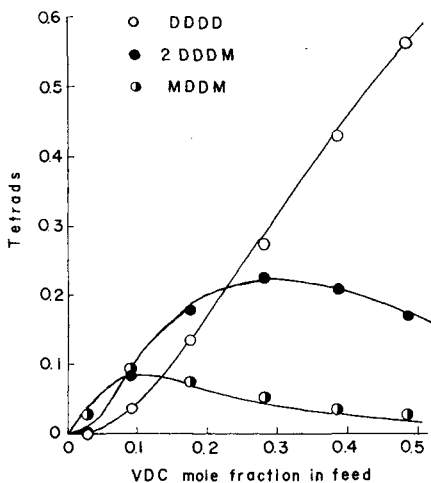


Fig. 13. Mole fraction of diads vs. mole fraction of VDC in monomer feed for the system of VDC/vinyl acetate. Solid lines: calcd. from $r_D = 6.7$, $r_M = 0.05$

Fig. 14. Mole fraction of tetrads vs. mole fraction of VDC in monomer feed for the system of VDC/vinyl acetate. Solid lines: calcd. from $r_D = 6.7$, $r_M = 0.05$

The peak separations in this system are thus well-defined as compared with those in the acrylic systems mentioned above. This becomes under-

standable when considering that the CH_2 resonances are less sensitive to the tacticity in the former than in the latter systems, as expected from the spectra of the corresponding homopolymers^{14-17,20-22}).

The COCH_3 group, which was observed as a sharp single peak like the ester groups in the acrylic systems, is probably too remote from the main chain to be sensitive to the sequence distribution.

The diad concentrations $P_2\{\dots\}$ were also estimated from the corresponding peak areas according to relations similar to Eqs. (1)–(5), where $P_2\{\text{DD}\} + 2P_2\{\text{DM}\} + P_2\{\text{MM}\} = 1$. In Figs. 13 and 14, the observed diad and tetrad concentrations are compared with the theoretical curves calculated from the reactivity ratios,

$$r_M = 0.05 \pm 0.03, \text{ and } r_D = 6.7 \pm 0.5$$

which are in reasonable accord with the reported values^{23,24}).

4. Discussion

The triad and tetrad concentrations in the methyl methacrylate, benzyl methacrylate, and methacryloyl chloride systems (Figs. 2, 3, 5, 6, 8, 9) show reasonable agreement with the theoretical sequence distributions, when considering the experimental errors involved in the peak area measurements and in the reactivity ratio determinations. The DDDD and DDDM tetrads in the methyl acrylate system (Fig. 10) also agreed with the calculated concentrations using the reported reactivity ratios²⁵).

With these results we conclude that the usual copolymerization scheme of the MAYO and LEWIS type (terminal model) is satisfactory for giving the observed sequence distributions. Thus any preceding monomer units other than the terminal ones can be neglected in determining the reactivity of the growing polymer radical. According to JOHNSEN^{1,9,10}), the presence of head-to-head or tail-to-tail linkages, which was previously suggested by some authors in the interpretation of the spectra of the vinyl chloride system^{26,27}), can also be neglected. This is clearly supported by the diad and tetrad concentrations in the vinyl acetate system (Figs. 13, 14), whose peak separations (Fig. 12) are well-defined to permit the more accurate determinations of peak areas, resulting in better agreement between experiment and theory.

In the vinylidene chloride/vinyl chloride systems, JOHNSEN^{1,9}) also was led to the same conclusion from the determination of diad and tetrad concentrations. However, in the isobutylene systems, JOHNSEN¹⁰) and

FISCHER^{11,12)} and their coworkers have reported some deviations from the usual copolymerization theory. The reason for this discrepancy is not clear at present, though the copolymerization of isobutylene might be expected to be influenced by such abnormal effects as depropagation and penultimate monomer units of the growing chain as suggested¹²⁾.

We are indebted to Mr. SADA O IKUMA, Yokkaichi Research and Development Dept., Mitsubishi Monsanto Chemical Co. Ltd., for the experiment of the vinylidene chloride/vinyl acetate system

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