# Radical copolymers of 2-vinyl pyridine with methyl acrylate and methacrylate. A study of microstructures by $^1H$ n.m.r.

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Radical copolymerization of 2-vinyl pyridine with methyl acrylate and methacrylate, respectively, has been carried out in benzene solution with low conversion. The reactivity ratios for the two systems, have been determined using the Fineman–Ross and Kelen–Tüdös methods. The values obtained satisfy the terminal model of copolymerization. The signals sensitive to sequence distribution and configuration in the $^1H$ n.m.r. spectra are $\alpha CH_3$ and $OCH_3$ from methyl methacrylate, $OCH_3$ from methyl acrylate and the aromatic proton signal from 2-vinyl pyridine. The configurational model for the two types of copolymers is discussed using the information from the signals together with influence of the neighbouring and next-neighbour units on signal splitting.

## INTRODUCTION

Copolymer sequence distributions and configurations can be determined using $^1H$ n.m.r. spectroscopy[1]. For copolymers containing an acrylic unit and an aromatic substituted unit, the methoxy signal splitting is discussed in terms of sequence fractions and configuration[2]. Triad or pentad assignments are proposed[3,4]. The microstructure of 2-vinyl pyridine radical copolymers with methyl acrylate and methacrylate, respectively, can be studied analysing the aromatic, $OCH_3$ and $\alpha CH_3$ proton signals.

## EXPERIMENTAL

### *Methyl acrylate – 2-vinyl pyridine copolymers*

*Determination of reactivity ratios.* Initial feed ratios and the copolymer composition are given in *Table 1*, for a series of methyl acrylate (MA, $M_1$) – 2-vinyl pyridine (2VPy, $M_2$) copolymers. In order to calculate the sequence distribution it is necessary to know the values of the reactivity ratio. The Fineman–Ross and Kelen–Tüdös[5] methods are used together with a computer program based on a Gaussian linearization of the points. The correlation factor for the Kelen–Tüdös method is:

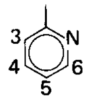
$$\alpha = \frac{x_{\min} x_{\max}}{(n_{\min} n_{\max})^{1/2}} = 6.212$$

The results are:

Fineman–Ross $r_1 = 0.21$ $r_2 = 2.14$
Kelen–Tüdös $r_1 = 0.20$ $r_2 = 2.09$

The two methods give very similar values. The triad sequence fractions are calculated using the Harwood's algorithm[6].

*Aromatic signals in $^1H$ n.m.r. spectra. Figure 1* represents the aromatic zone in the $^1H$ n.m.r. spectra of the eight samples. All the signals show a high field shift with increasing 2VPy content in the copolymer. The spectrum of sample 8 is very similar to that of poly(2-vinyl pyridine)[7], which has individual signals for the four protons of the aromatic pyridine nucleus:



$\delta_{H3} = 6.95$ ppm; $\delta_{H5} = 6.42$ ppm
$\delta_{H4} = 7.23$ ppm; $\delta_{H6} = 8.38$ ppm

The spectrum of sample 1 may be divided into three parts: $\delta_{H6} = 8.50$ ppm and two equally intense signals centred at 7.08 and 7.57 ppm. If the resonance region of the 3, 4 and 5 aromatic protons is divided into three parts: (I) centred at 7.57 ppm (sample 1) to 7.23 ppm (8); (II) centred at 7.08 ppm (1) to 6.95 ppm (8); (III) centred at 6.77 ppm (1) to 6.42 ppm (8). The 222 triad sequences have one proton in each part and the 121 sequences (which predominate in sample 1) have 1.5 protons in the first two parts. (The number 2 indicates the 2VPy structural unit in the sequence, while number 1 indicates the acrylic structural unit.) Considering the low field shift effect produced by a methyl acrylate unit enchainment as additive, the proton resonances of the 122 sequences are distributed as in *Table 2*. Thus, taking *F* the aromatic part fraction and *f* the triad sequence fraction, we can write:

*Table 1* MA–2VPy copolymer samples

| Sample | $x = [M_1]/[M_2]$ | $n = d[M_1]/d[M_2]$ |
|---|---|---|
| 1 | 19.000 | 4.372 |
| 2 | 10.765 | 2.916 |
| 3 | 7.000 | 1.875 |
| 4 | 3.000 | 0.820 |
| 5 | 1.670 | 0.583 |
| 6 | 1.000 | 0.382 |
| 7 | 0.492 | 0.223 |
| 8 | 0.205 | 0.090 |

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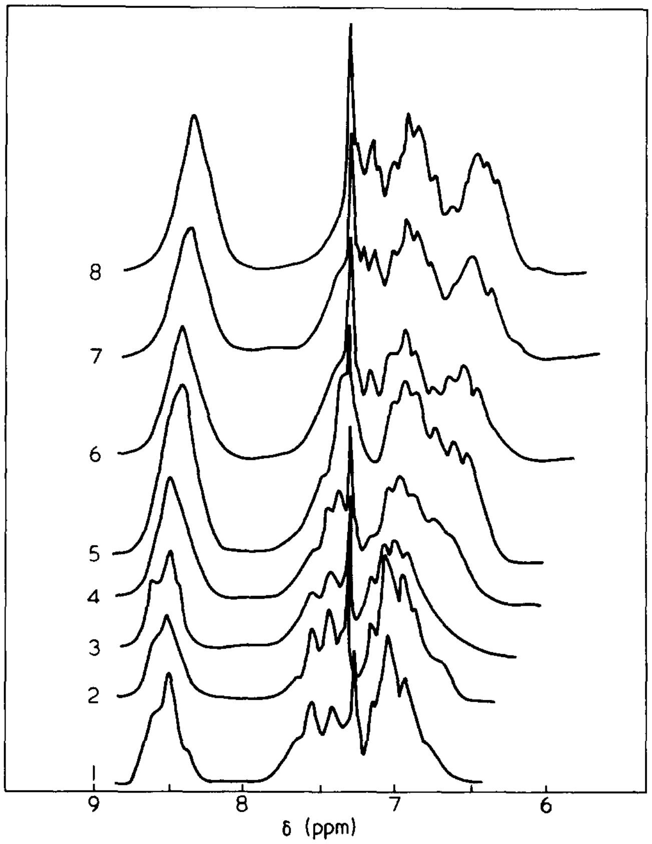

*Figure 1* Aromatic zone of the $^1$H n.m.r. spectra for MA–2VPy copolymers

*Table 2* Number of protons in the three parts of the aromatic zone

| | Part | | |
|---|---|---|---|
| Sequence | I | II | III |
| 222 | 1 | 1 | 1 |
| 221 | 1.25 | 1.25 | 0.5 |
| 121 | 1.5 | 1.5 | 0 |

$$F_{\mathrm{I}} = 0.333f_{222} + 0.417f_{221} + 0.500f_{121}$$

$$F_{\mathrm{II}} = 0.333f_{222} + 0.417f_{221} + 0.500f_{121}$$

$$F_{\mathrm{III}} = 0.333f_{222} + 0.167f_{221}$$

$$(F_{\mathrm{I}} + F_{\mathrm{II}} + F_{\mathrm{III}} = 1)$$

The relation between the calculated aromatic signal fractions and the experimental ones is given in *Figure 2*. The aromatic proton signal seems to be sensitive only to the triad sequence distribution and not to the configuration.

*Determination of copolymer configuration.* The three part splitting of the $OCH_3$ signal is generally assigned to the spatial screening effect of the aromatic nucleus. The screening effect is thought to be additive, the chemical shift due to the different substitution is not considered[2]. The $OCH_3$ signal of the MA–2VPy copolymers is also split into three main parts: A, 3.61 ppm, B, 3.47 ppm and C, 3.36 ppm in *Figure 3*.

It is clear, however, that part C can be also divided into several parts (samples 4–8).

The methoxy signal analysis can be carried out using the Harwood–Ritchey equations[3]:

$$(F_A - f_{111})/f_{212} = (1 - \sigma)f_{211}/f_{212} + (1 - \sigma)^2$$

$$F_B/f_{212} = \sigma f_{211}/f_{212} + 2\sigma(1 - \sigma)$$

$$F_C/f_{212} = \sigma^2$$

where $\sigma$ = the probability of coisotactic alternating addition, or according to the Ito–Yamashita treatment[2]:

$$1/(1 - F_A^{1/2}) = (1/\sigma) + (r_1/\sigma)x$$

$$1 + 2F_A/F_B = (1/\sigma) + (r_1/\sigma)x$$

$F_A$, $F_B$ and $F_C$ fractions are determined for each sample. The coincidence of the values obtained with the triad fractions (*Figure 4*) gives $\sigma = 1$, directly, without it being necessary to verify the above equations.

*Methyl methacrylate – 2-vinyl pyridine copolymers*

*Determination of reactivity ratios. Table 3* gives the monomer feed ratios and the copolymer composition for the methyl methacrylate (MMA, $M_1$) – 2-vinyl pyridine ($M_2$) system. The reactivity ratio determination by the Fineman–Ross and Kelen–Tüdös methods ($\alpha = 4.202$) gives:

| | | |
|---|---|---|
| Fineman–Ross | $r_1 = 0.30$ | $r_2 = 1.13$ |
| Kelen–Tüdös | $r_1 = 0.27$ | $r_2 = 1.10$ |

*Aromatic signal in the $^1$H n.m.r. spectra.* The signal evolution according to the copolymer composition is very similar to that of the MA-2VPy samples. The difference is due to the area ratio of 2:1 between parts I and II in sample 9 (having mostly 121 sequences). The assignment Table for the three parts of the signal is *Table 4*, and the equations can be written:

$$F_{\mathrm{I}} = 0.333f_{222} + 0.333f_{221} + 0.333f_{121}$$

$$F_{\mathrm{II}} = 0.333f_{222} + 0.500f_{221} + 0.667f_{121}$$

$$F_{\mathrm{III}} = 0.333f_{222} + 0.167f_{221}$$

$$(F_{\mathrm{I}} + F_{\mathrm{II}} + F_{\mathrm{III}} = 1)$$

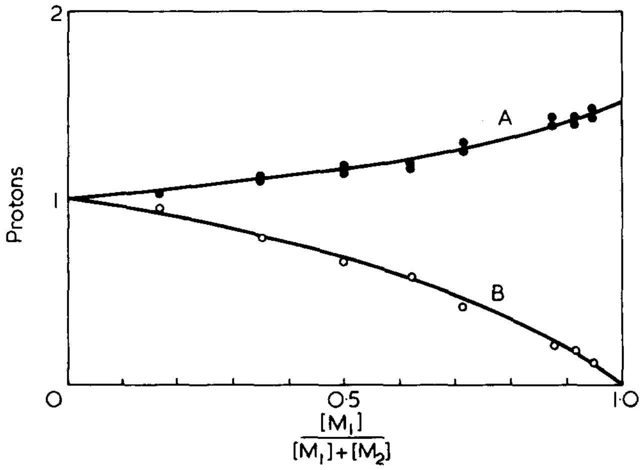

*Figure 2* Aromatic signal fractions. Full line = calculated, points = measured. A, I, II; B, III

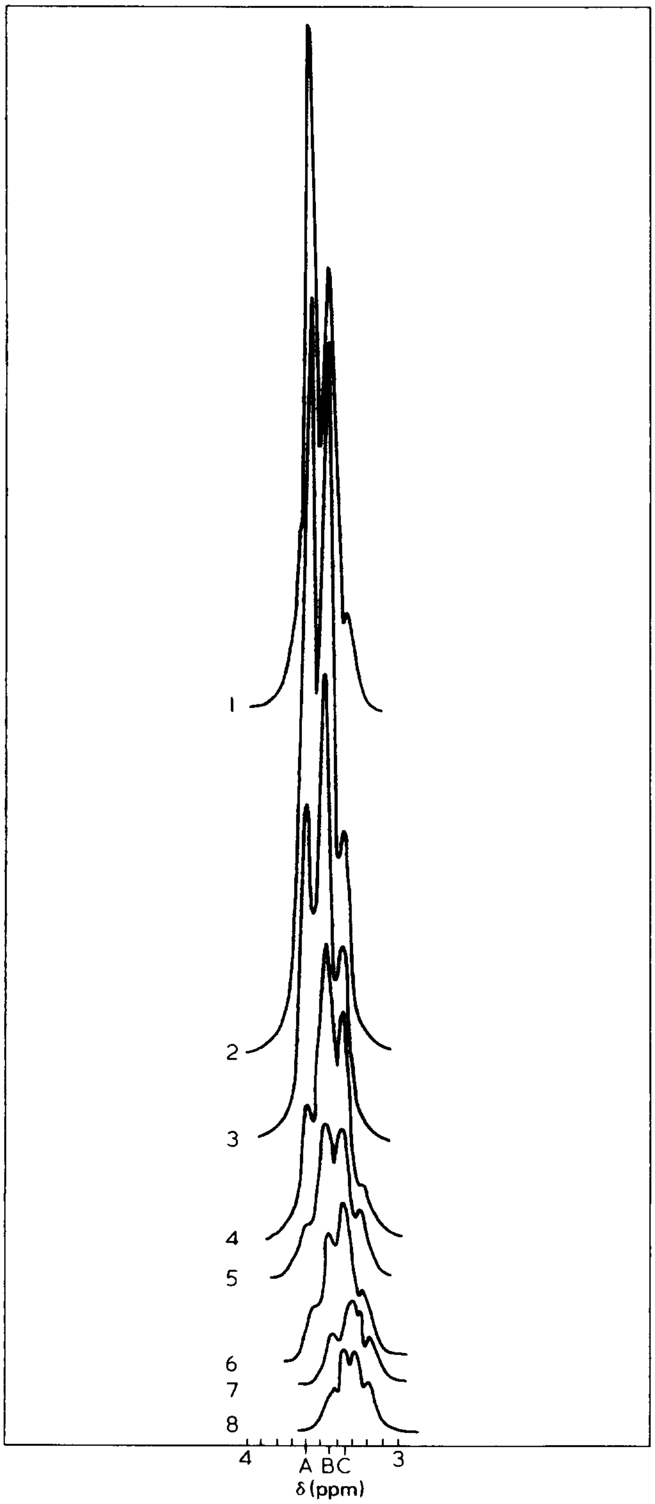

*Figure 3* OCH$_3$ signal of the MA–2VPy copolymers

*Figure 5* gives the comparison of the experimental and calculated aromatic signal fractions.

*α*CH$_3$ *signal in the* $^1$*H n.m.r. spectra.* The αCH$_3$ signal analysis gives microstructural information about the methyl methacrylate copolymers[8,9]. This signal has three parts assigned to isotactic, heterotactic and syndiotactic triads in poly(methyl methacrylate)[1]. The αCH$_3$ part of the spectrum for samples 9–16 is given in *Figure 6*.

In the spectrum of sample 9 there are the three signals of poly(methyl methacrylate) (1.25, 1.03 and 0.90 ppm) together with copolymer signals ($\delta \leqslant 0.90$ ppm). An attempt to assign these signals is based on the additivity of substitution and configurational effects[8].

Though the configurational effect has a smaller importance in the αCH$_3$ chemical shift, it is not to be neglected. Therefore, the higher field signal can be assigned to the $2_m 1_m 2$ triad ($m$ = meso configuration). The other triads can be assigned according to *Table 5*, where $s$ = the 2VPy substitution effect, $c1$ = the methoxy group configurational effect and $c2$ = the pyridine nucleus configurational effect. The values already known are marked by an asterisk. They determine:

$$c1 = 0.14 \text{ ppm}$$

$$c2 + s = 0.48 \text{ ppm}$$

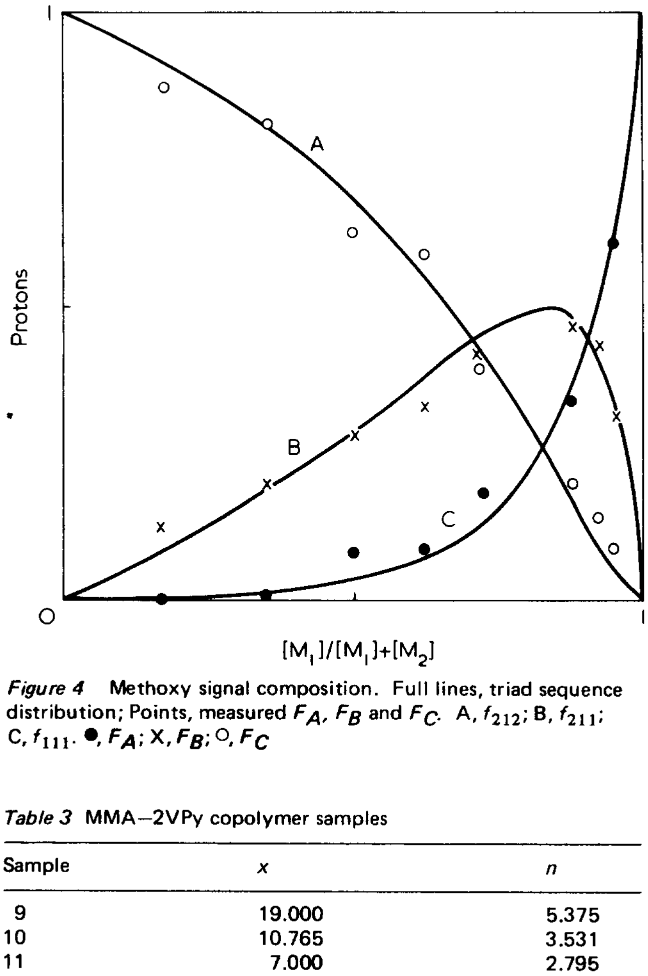

*Figure 4* Methoxy signal composition. Full lines, triad sequence distribution; Points, measured $F_A$, $F_B$ and $F_C$. A, $f_{212}$; B, $f_{211}$; C, $f_{111}$. ●, $F_A$; X, $F_B$; O, $F_C$

*Table 3* MMA–2VPy copolymer samples

| Sample | $x$ | $n$ |
|---|---|---|
| 9 | 19.000 | 5.375 |
| 10 | 10.765 | 3.531 |
| 11 | 7.000 | 2.795 |
| 12 | 3.000 | 1.371 |
| 13 | 1.670 | 0.854 |
| 14 | 1.000 | 0.556 |
| 15 | 0.492 | 0.392 |
| 16 | 0.205 | 0.160 |

*Table 4* Number of protons in the three parts of the aromatic zone

| | Part | | |
|---|---|---|---|
| Sequence | I | II | III |
| 222 | 1 | 1 | 1 |
| 221 | 1 | 1.5 | 0.5 |
| 121 | 1 | 2 | 0 |

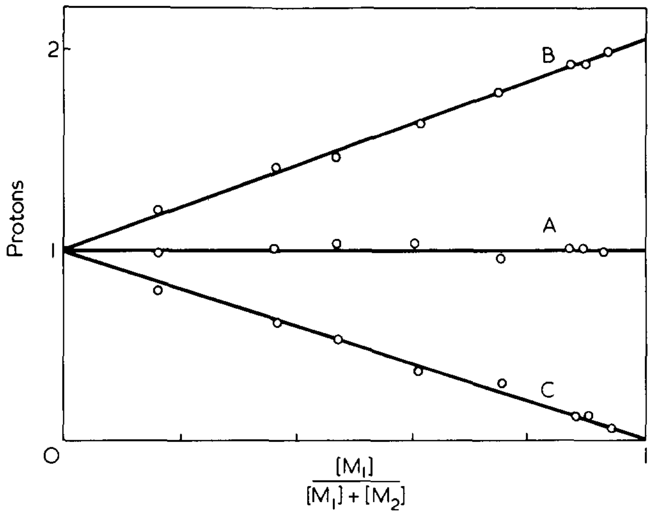

*Figure 5* Aromatic signal fractions. Full line, calculated; points, measured. A, I; B, II; C, III

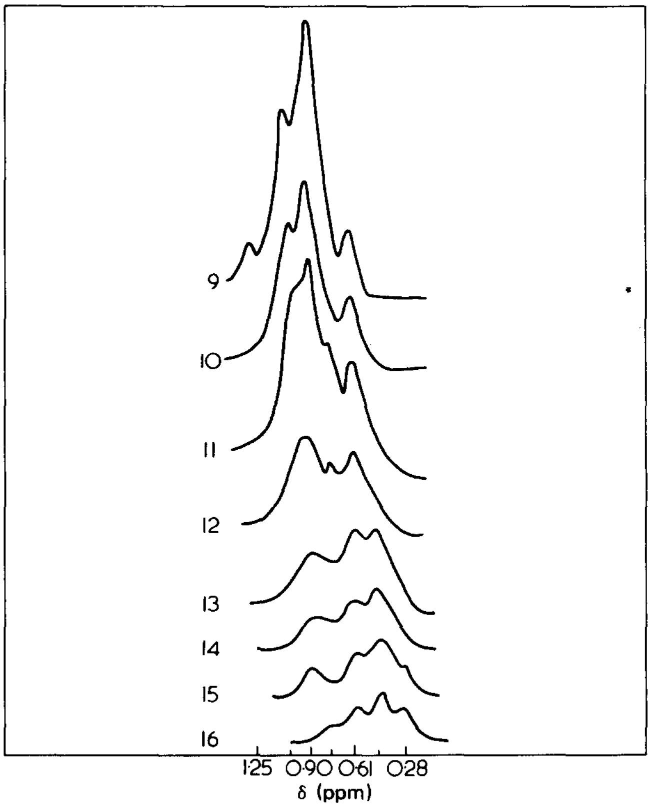

*Figure 6* $\alpha CH_3$ signal of the MMA–2VPy copolymers

A supplementary hypothesis can be made by assigning the 0.45 ppm signal to the $2_m1_r2$ triad. Then, all other chemical shifts in *Table 5* are obtained, together with:

$s$ = 0.32 ppm

$c2$ = 0.16 ppm

No other assignment can be made to satisfy the additivity rule.

In calculating the configurational parameter, $\sigma$ ($\sigma$ meaning the probability of coisotactic addition between the aromatic nucleus and the methoxy group), the probabilities for every triad can be written if:

$\sigma_{11}$ is the probability for a $1_m1$ diad $\quad \sigma_{11} = 0.23^{10}$

$\sigma_{12}$ is the probability for a $1_m2$ diad $\quad \sigma_{12} = 1 - \sigma$

The probabilities are given in *Table 6*.

The $\sigma$ value can be determined as the best fit between the experimental and calculated fractions for different values of $\sigma$. A satisfactory concordance was obtained for $\sigma = 0.5$, as can be seen from *Table 7*. Because signal separation between the 0.90 and 0.76 ppm gives relatively high errors, their sum is given in *Table 7*.

*Methoxy signal analysis.* Even from the appearance of the methoxy signal for the studied copolymers – *Figure 7* – it is clear that the Harwood–Ritchey and Ito–Yamashita treatments for the signal splitting are not sufficient. The signal is composed of many lines. The A part (from 3.25 to 3.58 ppm – as in the MMA-4VPy copolymers[4]) has three peaks:

$A_1$ – 3.54 ppm; $A_2$ – 3.42 ppm; $A_3$ – 3.30 ppm

Also, the $B$ part (2.85–3.25 ppm):

$B_1$ – 3.12 ppm; $B_2$ – 3.00 ppm; $B_3$ – 2.90 ppm

The $C$ part is overlapped by the main chain CH signal. The 2.80 ppm signal can be assigned to this part.

Under these conditions, the $OCH_3$ signal fractions are determined and are given in *Table 8*.

The Harwood–Ritchey and Ito–Yamashita equations are calculated, and the plots obtained are not really straight lines. The result of linearization by the Gauss method gives very scattered values, and it seems reasonable to assign

*Table 5* Assignment of the $\alpha CH_3$ signal

| Triad | Chemical shift calculation | Chemical shift value |
|---|---|---|
| $1_m1_m1$ | 1.25 | 1.25* |
| $1_m1_r1$ | $1.25 - c1$ | 1.03* |
| $1_r1_r1$ | $1.25 - 2c1$ | 0.90* |
| $1_m1_m2$ | $1.25 - s - c2$ | 0.76 |
| $1_r1_m2$ | $1.25 - c1 - s - c2$ | 0.61 |
| $1_m1_r2$ | $1.25 - s$ | 0.90 |
| $1_r1_r2$ | $1.25 - s - c1$ | 0.76 |
| $2_m1_m2$ | $1.25 - 2s - 2c2$ | 0.28* |
| $2_m1_r2$ | $1.25 - 2s - c2$ | 0.45 |
| $2_r1_r2$ | $1.25 - 2s$ | 0.61 |

*Table 6* The $\alpha CH_3$ signal composition

| Chemical shift (ppm) | Probability |
|---|---|
| 1.25 | $\sigma_{11}^2 f_{111}$ |
| 1.03 | $2\sigma_{11}(1 - \sigma_{11})f_{111}$ |
| 0.90 | $(1 - \sigma_{11})^2 f_{111} + \sigma_{11} f_{112}$ |
| 0.76 | $[\sigma_{11}(1 - \sigma) + \sigma(1 - \sigma_{11})] f_{112}$ |
| 0.61 | $(1 - \sigma_{11})(1 - \sigma) f_{112} + \sigma^2 f_{212}$ |
| 0.45 | $2\sigma(1 - \sigma) f_{212}$ |
| 0.28 | $(1 - \sigma)^2 f_{212}$ |

*Table 7* $\alpha CH_3$ signal composition calculated for $\sigma$ = 0.5 and measured

| | Chemical shift | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1.25 ppm | | 1.03 ppm | | 0.90 + 0.76 ppm | | 0.61 ppm | | 0.45 ppm | | 0.28 ppm | |
| Sample | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. |
| 9 | 0.036 | 0.054 | 0.242 | 0.225 | 0.582 | 0.636 | 0.119 | 0.085 | 0.015 | 0 | 0.008 | 0 |
| 10 | 0.030 | 0.028 | 0.197 | 0.200 | 0.564 | 0.550 | 0.162 | 0.171 | 0.032 | 0.051 | 0.016 | 0 |
| 11 | 0.025 | 0.010 | 0.168 | 0.180 | 0.545 | 0.527 | 0.189 | 0.220 | 0.048 | 0.063 | 0.024 | 0 |
| 12 | 0.012 | 0 | 0.079 | 0.108 | 0.438 | 0.456 | 0.262 | 0.290 | 0.140 | 0.146 | 0.070 | 0 |
| 13 | 0.005 | 0 | 0.036 | 0.045 | 0.329 | 0.356 | 0.284 | 0.321 | 0.231 | 0.207 | 0.116 | 0.070 |
| 14 | 0.002 | 0 | 0.016 | 0.010 | 0.230 | 0.232 | 0.284 | 0.295 | 0.312 | 0.330 | 0.156 | 0.133 |
| 15 | 0.001 | 0 | 0.008 | 0 | 0.167 | 0.195 | 0.279 | 0.296 | 0.365 | 0.383 | 0.183 | 0.126 |
| 16 | 0.000 | 0 | 0.001 | 0 | 0.070 | 0.120 | 0.265 | 0.230 | 0.468 | 0.440 | 0.223 | 0.210 |

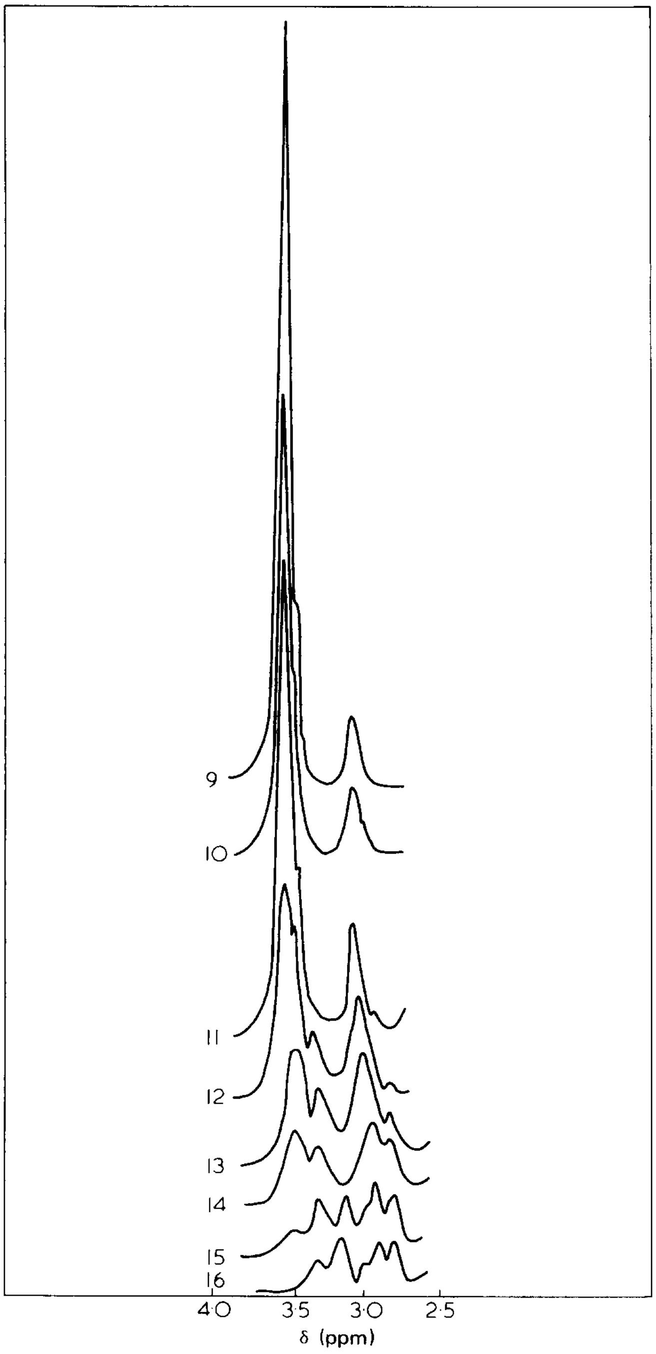

*Figure 7* Methoxy signal in the MMA–2VPy copolymers

*Table 8* Methoxy signal fractions

| Sample | $F_A$ | $F_B$ | $F_C$ |
|---|---|---|---|
| 9 | 0.851 | 0.149 | 0 |
| 10 | 0.773 | 0.227 | 0 |
| 11 | 0.702 | 0.270 | 0.028 |
| 12 | 0.500 | 0.405 | 0.095 |
| 13 | 0.384 | 0.490 | 0.126 |
| 14 | 0.285 | 0.530 | 0.185 |
| 15 | 0.232 | 0.532 | 0.236 |
| 16 | 0.150 | 0.495 | 0.355 |

methoxy signal splitting to influence of the pentad. The most realistic hypothesis seems to be as follows. Two 2VPy units from the ends of a pentad sequence and on the same side as the central methoxy group have the same screening effect as one 2VPy unit in the next-neighbouring group and on the same side of the methoxy group. Thus, pentad assignment of the methoxy signal can be made as in *Table 9*. The equations are:

$$F_A = f_{11111} + f_{21111} + (1-\sigma)(f_{21121} + f_{12111} + f_{22111}) + $$

$$+ (1-\sigma)^2(f_{12121} + f_{22121}) + (1-\sigma^2) f_{21112} + $$

$$+ [(1-\sigma)^2 + \sigma_{22}\sigma(1-\sigma)] f_{22112} + $$

$$+ (1-\sigma)^2\sigma_{22}(2-\sigma_{22}) f_{22122}$$

$$F_B = \sigma(f_{21121} + f_{12111} + f_{22111}) + \sigma^2 f_{21112} + $$

$$+ 2\sigma(1-\sigma)(f_{12121} + f_{22121}) + \sigma(2-\sigma-\sigma_{22}) f_{22112} + $$

$$+ (1-\sigma)[(1+\sigma) - 2\sigma_{22} + (1+\sigma)\sigma_{22}^2] f_{22122}$$

$$F_C = \sigma^2(f_{12121} + f_{22121}) + \sigma_{22}\sigma^2 f_{22112} + $$

$$+ [\sigma^2 + 2\sigma_{22}(1-\sigma_{22})\sigma(1-\sigma)] f_{22122}$$

Using $\sigma_{22} = 0.22$[12] and $\sigma$ = 0.5 determined from the $\alpha CH_3$ signal, the methoxy signal fractions of *Figure 8* are obtained. The experimental values better satisfy the pentad assignment.

Comparing the line intensities for the methoxy signal and pentad fractions of the same composition, we can assign the lines as follows:

*Table 9* Pentad assignment of the methoxy signal

| Part of signal | Pentad | Cinfigurational probability |
|---|---|---|
| A | 11111 | 1 |
| | 21111 | 1 |
| | $2_r1_m1_m1_r2$ | $(1-\sigma)^2$ |
| | $2_m1_m1_m1_r2$ | $2\sigma(1-\sigma)$ |
| | $2_r1_m1_r21$ | $(1-\sigma)^2$ |
| | $2_m1_m1_r21$ | $\sigma(1-\sigma)$ |
| | $12_r111$ | $1-\sigma$ |
| | $2_m2_r111$ | $\sigma_{22}(1-\sigma)$ |
| | $2_r2_r111$ | $(1-\sigma_{22})(1-\sigma)$ |
| | $12_r1_r21$ | $(1-\sigma)^2$ |
| | $2_m2_r1_m1_r2$ | $\sigma_{22}(1-\sigma)^2$ |
| | $2_r2_r1_m1_r2$ | $(1-\sigma_{22})(1-\sigma)^2$ |
| | $2_m2_r1_m1_m2$ | $\sigma_{22}\sigma(1-\sigma)$ |
| | $2_m2_r1_r21$ | $\sigma_{22}(1-\sigma)^2$ |
| | $2_r2_r1_r21$ | $(1-\sigma_{22})(1-\sigma)^2$ |
| | $2_m2_r1_r2_m2$ | $\sigma_{22}^2(1-\sigma)^2$ |
| | $2_r2_r1_r2_m2$ | $2\sigma_{22}(1-\sigma)^2(1-\sigma_{22})$ |
| B | $2_m1_m1_m1_m2$ | $\sigma^2$ |
| | $2_r1_m1_m21$ | $\sigma(1-\sigma)$ |
| | $2_m1_m1_m21$ | $\sigma^2$ |
| | $12_m111$ | $\sigma$ |
| | $2_r2_m111$ | $(1-\sigma_{22})\sigma$ |
| | $2_m2_m111$ | $\sigma_{22}\sigma$ |
| | $12_m1_r21$ | $2\sigma(1-\sigma)$ |
| | $2_r2_m1_m1_r2$ | $(1-\sigma_{22})\sigma(1-\sigma)$ |
| | $2_m2_m1_m1_r2$ | $\sigma_{22}\sigma(1-\sigma)$ |
| | $2_r2_r1_m1_m2$ | $(1-\sigma_{22})\sigma(1-\sigma)$ |
| | $2_r2_m1_m1_m2$ | $(1-\sigma_{22})\sigma^2$ |
| | $2_r2_m1_r21$ | $(1-\sigma_{22})\sigma(1-\sigma)$ |
| | $2_m2_r1_m21$ | $\sigma_{22}\sigma(1-\sigma)$ |
| | $2_m2_m1_r21$ | $\sigma_{22}\sigma(1-\sigma)$ |
| | $2_r2_r1_m21$ | $(1-\sigma_{22})\sigma(1-\sigma)$ |
| | $2_r2_m1_r2_m2$ | $\sigma_{22}(1-\sigma_{22})\sigma(1-\sigma)$ |
| | $2_m2_m1_r2_m2$ | $2\sigma_{22}^2\sigma(1-\sigma)$ |
| | $2_r2_r1_m2_r2$ | $2(1-\sigma_{22})^2\sigma(1-\sigma)$ |
| | $2_r2_r1_r2_r2$ | $(1-\sigma_{22})^2(1-\sigma)^2$ |
| C | $12_m1_m21$ | $\sigma^2$ |
| | $2_m2_m1_m1_m2$ | $\sigma_{22}\sigma^2$ |
| | $2_r2_m1_m21$ | $(1-\sigma_{22})\sigma^2$ |
| | $2_m2_m1_m21$ | $\sigma_{22}\sigma^2$ |
| | $2_r2_m1_m2_r2$ | $(1-\sigma_{22})^2\sigma^2$ |
| | $2_m2_m1_m2_r2$ | $2\sigma_{22}(1-\sigma_{22})\sigma^2$ |
| | $2_m2_m1_r2_r2$ | $2\sigma_{22}(1-\sigma_{22})\sigma(1-\sigma)$ |
| | $2_m2_m1_m2_m2$ | $\sigma_{22}^2\sigma^2$ |

$$A_1 \quad f_{11111}+f_{21111}$$

$$A_2 \quad (1-\sigma)(f_{21121}+f_{12111}+f_{22111})+(1-\sigma)^2(f_{12121}+ \\ +f_{22121})+(1-\sigma^2)f_{21112}$$

$$A_3 \quad [(1-\sigma)^2+\sigma_{22}\sigma(1-\sigma)]\,f_{22112}+ \\ +(1-\sigma)^2\sigma_{22}(2-\sigma_{22})f_{22122}$$

$$B_1 \quad (1-\sigma)[(1+\sigma)-2\sigma_{22}+(1+\sigma)\sigma_{22}^2]\,f_{22122}$$

$$B_2 \quad \sigma(f_{21121}+f_{12111}+f_{22111})+\sigma^2 f_{21112}$$

$$B_3 \quad 2\sigma(1-\sigma)(f_{12121}+f_{22121})+\sigma(2-\sigma-\sigma_{22})f_{22112}$$

$$C_1 \quad [\sigma^2+2\sigma_{22}(1-\sigma_{22})\sigma(1-\sigma)]\,f_{22122}$$

## DISCUSSION

The MA–2VPy and MMA–2VPy systems can be characterized by the terminal model of copolymerization, the preferred monomer being 2VPy in all cases ($r_1 < 1$, $r_2 > 1$).

The configurational characterization given from the $^1$H n.m.r. spectra needs some discussion, because of ambiguous spectral assignments. First, the spectrum resolution is better than for the MMA–4VPy[4] and MA–4VPy[13] systems. The aromatic and $\alpha CH_3$ signals are resolved, but especially the methoxy signal, which becomes much more difficult to assign. The aromatic signal is determined mainly by the triad sequences, but the slight high-field shift when increasing the 2VPy content (*Figure 1*) suggests a configurational influence as well. The $\alpha CH_3$ signal is sensitive to substitution and configuration. The values in *Table 5* indicate a large substituent influence ($s = 2c2$), which can be explained by the relative proximity of the aromatic group (5 bonds) compared with the distance between aromatic and methoxy group (7 bonds). The $OCH_3$ group is placed in the centre of the aromatic screening cone, while the $\alpha CH_3$ group is at the periphery. This is the reason for interpreting the $OCH_3$ signal splitting in terms of the configurational effect, neglecting the effects of substitution.

In order to obtain an unambiguous assignment, an attempt was made to synthesize the alternating radical copolymers MA–2VPy and MMA–2VPy by $ZnCl_2$ complexation[14]. Owing to the great polarity of nitrogen, 2VPy complexed with $ZnCl_2$ more strongly than the acrylic monomer, and copolymers could not be obtained.

The configurational parameters obtained ($\sigma = 1$ for MA–2VPy and $\sigma = 0.5$ for MMA–2VPy) agree with the hypothesis of steric determination of the alternating addition configuration[2,11]. It also seems probable that the attractive interaction between pyridine and the acrylic group, which determines the coisotactic placement preference[2], is higher than that of benzene and acrylic group (compare $\sigma = 0.8$ for MA–styrene[2] with $\sigma = 0.98$ for MA–4VPy[13] and $\sigma = 1$ for MA–2VPy). This fact can be explained by the higher donor character of the pyridine nucleus. The higher $\sigma$

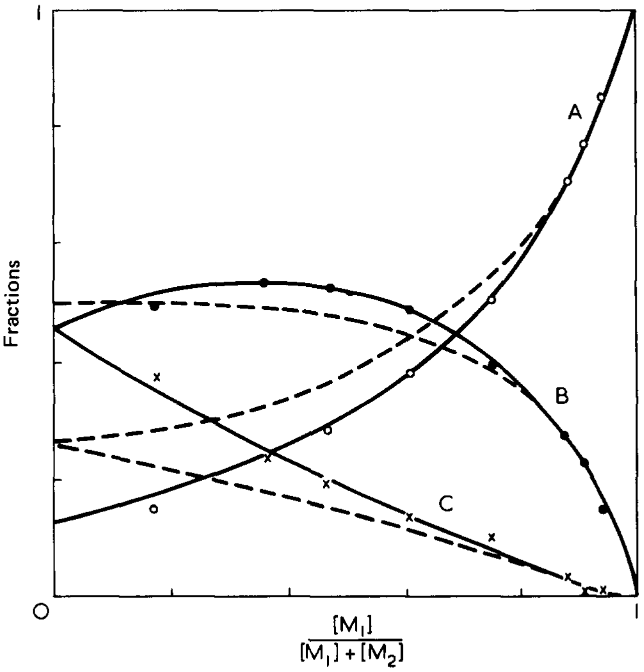

*Figure 8* Methoxy signal splitting in the MMA–2VPy copolymers. Full curves, calculated using pentad assignment; dotted curves, calculated by triads and $\sigma = 0.5$; points, experimental determined. A, $F_A$; B, $F_B$; C, $F_C$

values for pyridine-containing systems suggest therefore the influence of the polarity also on the alternating addition configuration[16].

The methoxy signal in the $^1H$ n.m.r. spectra of the MMA–2VPy copolymers cannot be interpreted in terms of triad, as in the MMA–4VPy copolymers[4]. The 'penultimate' unit influence on this signal was also observed in *p*-chlorostyrene–MMA[3] and phenyl methacrylate–MMA[15] copolymers. The assignment is not out of discussion, however, because if the higher field shift is the result of the aromatic group screening effect, the differences in the chemical shift of the three parts of the signal (0.15–0.2 ppm for the MA copolymers and 0.5 ppm for the MMA copolymers) cannot be explained.

## CONCLUSION

The systems studied can be characterized by a terminal model of copolymerization. In the $^1H$ n.m.r. spectra at 60 MHz, the aromatic and $\alpha CH_3$ protons signals are sensitive to triad influence. The $OCH_3$ signal in MA–2VPy copolymers can also be explained by triad sequences. The $OCH_3$ signal in MMA–2VPy copolymers is split by 'penultimate' unit influence – pentad sequences. The analysis of all signals gives an alternating addition between MA and 2VPy entirely 'coisotactic', while in MMA–2VPy it is perfectly random.

## EXPERIMENTAL

Copolymers were synthesized in benzene solution at 60°C under argon atmosphere with AIBN as initiator. The conversion was kept below 5%, as determined by n.m.r. The samples were purified by reprecipitation in benzene-petroleum ether system and then dried *in vacuo*.

The n.m.r. spectra were obtained in $CDCl_3$ solution at 60°C on a Jeol C-60HL spectrometer operating at 60 MHz. The copolymer composition was determined from the integral curves, drawn 5–10 times, until the error was below 0.5%. For the MA–2VPy copolymers the ratios of saturated to the aromatic areas and the $OCH_3$ area to the H6 aromatic area were utilized. For the MMA–2VPy the ratios were the saturated to the aromatic area and the $\alpha CH_3$ to the H6 aromatic area.

The least squares error straight lines were calculated by the Gauss method on a JEC-6 computer.

The aromatic, $\alpha CH_3$ and $OCH_3$ from MA signal fractions were determined by elemental curve decomposition[17], cutting and weighing the copies. The $OCH_3$ signal from MMA was decomposed using the spectrum integral for the parts A and B and part C was determined by difference.

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