Nuclear Magnetic Resonance Investigations of Sequence Distribution and Tacticity in Methyl Methacrylate–Vinyl Chloride Copolymers

N. W. Johnston* and P. W. Kopf

Union Carbide Corporation, Research and Development Department, Bound Brook, New Jersey 08805. *Received October 4, 1971*

ABSTRACT: Proton nuclear magnetic resonance spectroscopy has been used in a detailed study of free-radical-initiated methyl methacrylate–vinyl chloride copolymers. The nmr spectra of the α-CH_3 region show as many as five peaks whose intensities change markedly with composition and polymerization temperature. These results are interpreted in terms of both triad sequence distribution and triad tacticity.

Nuclear magnetic resonance spectroscopy has been used in a considerable number of studies on methyl methacrylate copolymers. These studies have pointed out that the methoxy resonance area in such polymers as methyl methacrylate–styrene and methyl methacrylate–substituted styrenes can be analyzed by considering the sequence distribution of the polymer in terms of triads or pentads[1-3] and for some copolymers in terms of sequence distribution plus stereochemistry considerations.[3-4] In these copolymer systems, the α-methyl resonance area has been analyzed in terms of sequence distribution only. Guillot, *et al.*, have made some qualitative assignments based on sequence distribution and stereochemistry in methyl methacrylate–acrylonitrile copolymers.[5] They, however, concluded that this copolymer did not have sufficiently resolved peaks for further analysis and that the system showed evidence for penultimate effects.

In an effort to obtain information about the microstructure of methyl methacrylate–vinyl chloride (MMA–VCl) copolymers, we have studied the α-methyl region of the nmr spectra of a series of copolymers. The entire nmr spectrum of a MMA–VCl copolymer (Figure 1) shows the α-methyl region to have appreciable structure, while the methoxy region shows essentially none.

The sequence distributions of polymers of this type have been studied extensively through cyclization reactions and no evidence has been found for any penultimate effects.[6-9] The results of our nmr study on the α-methyl region of the MMA–VCl copolymers would indicate that both the sequence distribution and the stereochemistry of the various MMA centered triads affect the observed spectrum.

Experimental Section

Preparation of Polymers. All polymers were prepared in a nitrogen atmosphere from freshly distilled or purified monomers.

Polymers 1–8 were prepared in 2-butanone at 55° using 0.4 wt % *tert*-butyl peroxypivalate as initiator. Polymer 9 was prepared in bulk at −35° using 0.1 wt % tri-*n*-butylboron as initiator. Polymer 10 was prepared in bulk at −70° using 0.1 wt % tri-*n*-butylboron as initiator.

Conversions were kept low and all polymers were isolated by pouring the polymerization mixture into a large excess of methanol. The polymers were reprecipitated several times from 2-butanone solutions by additions of the solutions to methanol. The samples were dried *in vacuo* and copolymer compositions determined by C, H, and Cl analysis. Monomer feeds, polymer compositions, and conversions for all polymers studied are shown in Table I. Reactivity ratios of 0.044/11.2 for VCl/MMA prepared at 55° were determined in previous work[6] and verified in this work.

Nmr Spectra. Nmr spectra were obtained on a Varian HA-100D-15 100-MHz spectrometer using the field-sweep mode and hexamethyldisilane as the internal lock. Sample tubes of 10-mm diameter were used in obtaining spectra of solutions of 10% polymer in *o*-dichlorobenzene at 100°. Each experimental spectrum was separately stored on a Varian C-1024 spectrum accumulator. The appropriate interface with a teletype permitted a digitized spectrum to be obtained on paper tape. The digitized spectra were then read into an IBM-1130 computer. Using a computer program which permitted Gaussian and Lorenztian peak shape functions, the area of each peak was obtained by fitting the experimental spectrum with a theoretical spectrum for a minimum standard deviation. Not all peaks in a particular spectrum necessarily were given the same line width or peak shape function; however, these characteristics of a particular peak were consistent from spectrum to spectrum. The α-methyl peak areas of all spectra are listed in Table II, and the experimental nmr spectra of six of the samples made at 55° are shown in Figure 2. The peaks are labeled A–E with increasing magnetic field and the total areas have been normalized.

Results and Discussion

Theoretical Considerations. Sequence distributions were predicted from reactivity ratios using computer programs discussed in a previous paper.[10] These programs predict the sequence distributions in terms of triads, pentads, and run numbers. The run number,[11] *R*, is defined as the average number of uninterrupted monomer sequences which occurs in a copolymer chain per 100 monomer units. The run number is, therefore, an expression related to all sequence distributions in a copolymer.

Sequence Distribution from Nmr Results. Figure 3A shows the predicted triad distributions for MMA–VCl *vs.* mole fraction of MMA for copolymers made at 55°. Figure 3A should be compared with Figure 3B, which shows the relative

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(1) J. H. Harwood and W. M. Ritchey, *J. Polym. Sci., Part B*, **3**, 419 (1965).
(2) F. A. Bovey, *ibid., Part B*, **62**, 197 (1962).
(3) H. J. Harwood, A. K. Shaw, R. E. Bockrath, and W. M. Ritchey, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **8**, 227 (1969).
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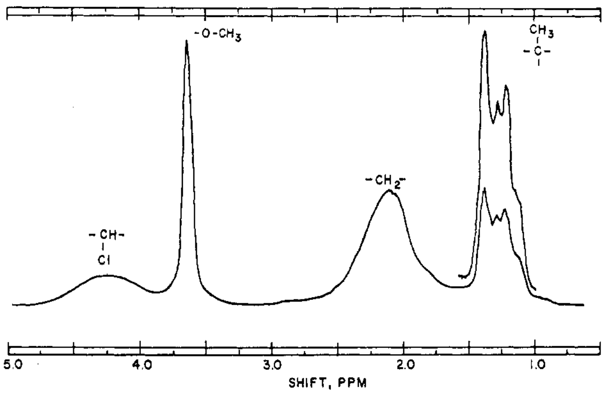


Figure 1. Nmr spectrum (100 MHz) of a 45/55 mol % MMA-VCl copolymer.

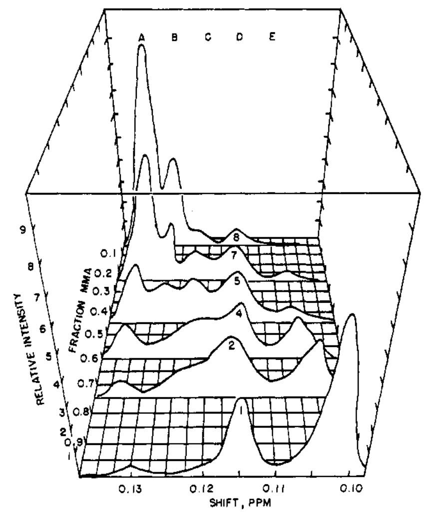


Figure 2. Nmr spectra of the α-CH$_3$ region in MMA-VCl copolymers. The area of each spectrum is normalized.

TABLE I

FEED-POLYMER COMPOSITIONS

Polymer no.	Mol % MMA Feed	Mol % MMA Polymer	% conversion
1	100.0	100.0	29.0
2	20.0	76.3	1.0
3	15.0	70.2	2.0
4	10.0	62.1	0.5
5	6.0	44.6	6.4
6	5.0	37.2	10.2
7	2.5	24.1	8.0
8	0.5	5.8	6.5
9	0.5	8.5	1.3
10	0.5	12.0	0.2

experimental areas for all five α-methyl peaks *vs.* mole fraction of MMA for copolymers 1-8. Comparing these figures, the reasoning used in making triad assignments to the various peaks can be followed.

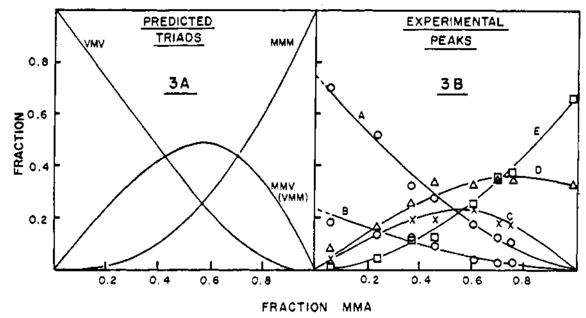


Figure 3. Predicted triad distributions (3A) and experimental peak areas (3B) *vs.* fraction of MMA in the polymer.

TABLE II

AREAS OF α-METHYL NMR PEAKS

Spectrum no.	Mol % MMA	α-Methyl peak % A	% B	% C	% D	% E
1	100.0				32	65
2	76.3	10	2	17	34	37
3	70.2	12	2	18	34	34
4	62.1	17	3	23	32	25
5	44.6	27	9	19	33	12
6	37.2	32	12	19	25	12
7	24.1	50	16	13	18	3
8	5.8	69	21	3	7	0
9	8.5	54	15	16	12	3
10	12.0	60	14	14	12	0

Peaks A and B in Figure 3B decrease as MMA content increases in much the same manner as for VMV (vinyl chloride-methyl methacrylate-vinyl chloride) in 3A. Therefore, peaks A and B are assigned as VMV triads. Peak C increases and decreases as the MMV (VMM) line does; therefore, peak C is assigned to MMV triads. Peak D increases in the same manner as an MMV triad but does not decrease at high MMA content. It is concluded that peak D contains both MMM and MMV triads. Peak E is actually a doublet at high MMA content; thus it must have contributions from both MMM and MMV triads. The assignments for each peak are listed in Table V.

The assignments of C, D, and E may be verified by plotting

$$F_{\mathrm{PEAK}}/F_{\mathrm{MMM}} = X + YF_{\mathrm{MMV}}/F_{\mathrm{MMM}} \qquad (1)$$

where F_{PEAK} is the relative area of each peak and F_{MMM} and F_{MMV} are predicted triad distributions.[3] The slope (Y) is then the fraction of MMV in that peak and the intercept (X) is the fraction of MMM. If the assignments are correct, the slopes and intercepts for the plots of C, D, and E should both total 1.0 and the plots should be linear. The plots for copolymers 2-8 are shown in Figure 4 and are found to meet the above criteria.

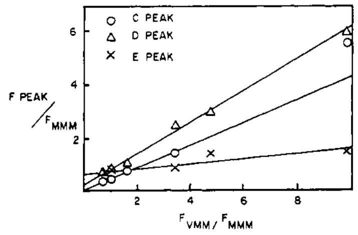


Figure 4. Verifications of triad assignments for copolymers 2-8.

Peaks A and B are assigned to VMV triads, so that the fractional area of A and B expressed in terms of the total area of the α-methyl region should equal the F_{VMV} in the copolymer. The following relationships may, therefore, be used to calculate the run number, R

$$F_{\mathrm{VMV}} = \text{area } (A + B)/\text{total } \alpha\text{-methyl area} \qquad (2)$$

$$F_{\mathrm{VMV}} = P_{\mathrm{MV}}^2 \qquad (3)$$

$$P_{\mathrm{MV}} = R/2M \tag{4}$$

$$R = 2M[\text{area } (A + B)/\text{total } \alpha\text{-methyl area}]^{1/2} \tag{5}$$

where M is the mole per cent MMA in the polymer. Run numbers calculated from experimental data are compared with predicted run numbers in Table III. The agreement between experimental and predicted run numbers is good for most copolymers, and as expected the best comparisons are found for copolymers with high VMV content.

TABLE III
COMPARISON OF RUN NUMBERS

Polymer no.	Mol % MMA	R_{exptl}[a]	R_{pred}[b]	σ_{MV}[c]
1	100			
2	76	53	41	*d*
3	70	52	49	*d*
4	62	55	55	*d*
5	45	54	58	0.50
6	37	49	54	0.52
7	24	39	40	0.49
8	6	11	11	0.48
9	9	14		0.47
10	12	21		0.44

[a] R_{exptl} determined from nmr data. [b] R_{pred} predicted from feed–conversion–reactivity ratio data. [c] MV dyad tacticity calculated from $[A/(A + B)]^{1/2}$. [d] Areas of peaks A and B not sufficiently defined to be accurate.

Tacticities from Nmr Results. The fact that more than one peak is observed for both the VMV and MMV triads cannot be explained in terms of penultimate effects or distributions other than triads. Other distributions such as tetrads or pentads do not fit the experimental data and no evidence has been found for penultimate effects in previous work.[6–9]

The multiple peaks for VMV and MMV can, however, be explained in terms of the tacticities of the triads. (MMM triads, *e.g.*, pure PMMA, show resolved nmr peaks from each type of tacticity.) We assume that peak B corresponds to only one VMV tacticity as it contains less than 25% of the total area assigned to VMV triads. If the relative amount of this tacticity is given by $\sigma_{\mathrm{MV}}{}^2$ where σ_{MV} is the probability of the corresponding dyad tacticity and A and B are the fractional areas of the respective peaks, we may use eq 6 to calculate σ_{MV}. Table III shows the value of σ_{MV} calculated for

$$\sigma_{\mathrm{MV}} = [B/(A + B)]^{1/2} \tag{6}$$

each composition. The mean value for σ_{MV} in samples 5, 6, 7, and 8 is very near 0.50. The value of σ_{MV} appreciably different from 0.50 indicates a preference for a particular dyad tacticity, generally for steric reasons. For example, the coisotactic MV dyad (Table IV) is expected to be sterically less favorable than the cosyndiotactic MV dyad. At lower polymerization temperatures, σ_{MV} may change enough so that peak B may be definitely assigned to either the coisotactic or cosyndiotactic VMV triad. Thus, copolymers 9 and 10 were synthesized. As shown in Table III, σ_{MV} is 0.47 at −35° and 0.44 at −70°. Thus, peak B may be assigned to the least sterically favored triad, VMV (II). Peak A then must contain VMV (IS, SI) and VMV (SS) triads. (See examples in Table IV.)

TABLE IV
TACTICITY ILLUSTRATIONS

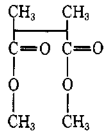
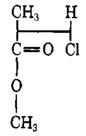
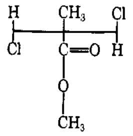
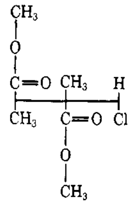
Dyad or triad	Designation	Structure	Probability
MM	Isotactic (I)		σ_{MM}
MV	Coisotactic (I)		σ_{MV}
VMV	(IS)		$\sigma_{\mathrm{MV}}(1 - \sigma_{\mathrm{MV}})$
MMV	(SI)		$(1 - \sigma_{\mathrm{MM}})\sigma_{\mathrm{MV}}$

TABLE V
SUMMARY OF SEQUENCE DISTRIBUTION AND TACTICITY PREDICTIONS AND ASSIGNMENTS

Peak	Shift, ppm[a]	Assignment	Relative Triad Tacticity[b] Predicted	Found
A	1.35	VMV (IS)		0.75
		VMV (SI)		
		VMV (SS)		
B	1.31	VMV (II)		0.25
C	1.25	MMV (SS)	0.40	0.38
D	1.18	MMV (SI)	0.40	0.56
		MMV (IS)	0.10	
		MMM (IS)		0.32
E	1.07	MMV (II)	0.10	0.08
		MMM (SS)		0.64

[a] Downfield from HMDS, 10% solutions in ODCB at 100°. [b] At 55°.

The value of σ_{MM}, the probability that an MM dyad formed at 55° is isotactic, may be obtained from the distribution of triad tacticities in pure PMMA.[12] In sample 1 (PMMA), the ratio of iso- to hetero- to syndiotactic triads is 4:31:65, giving a σ_{MM} value of 0.20.

A knowledge of σ_{MV} and σ_{MM} permits a prediction of the distribution of the four tacticities in MMV triads. Table V shows the predicted amount of each triad tacticity from the products of the various dyad tacticities. Since σ_{MV} is so near 0.5 for polymers made at 55°, we must rely on the low-temperature polymers when assigning the particular MMV tacticities that contribute to peaks C, D, and E.

In copolymers 7, 8, 9, and 10 the contribution of MMM

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(12) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).

heterotactic triads to peak D is extremely small. Thus, peaks C and D for these copolymers are essentially made up of purely MMV triad tacticities, and the relative intensities of C to D are independent of the reactivity ratios. For samples 7 and 8, peak C is less than peak D, while for samples 9 and 10, peak D is less than peak C. At lower polymerization temperatures, peak C increases at the expense of D; therefore, C must correspond to the more sterically favored tacticity, namely, MMV (SS). Peak D contains the MMV (IS) contribution.

Experimentally, the relative amount of MMV triads in peaks C, D, and E may be obtained from the slopes and intercepts obtained from Figure 4. A distribution very close to the experimental distribution may be obtained when the triads are grouped and arranged as shown in Table V.

It is not possible to determine within our experimental accuracy which of the MMV (IS) and MMV (II) triads contributes to peaks D and E exactly. We have established, however, that the MMV (SI) peak is shifted upfield from MMV (SS). Thus, we tentatively assign MMV (IS) to peak D and MMV (II) to peak E. Table V summarizes all the sequence distribution and tacticity assignments made.

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Copolymerization with Depropagation. VII.[1a] Coisotacticities in the Free-Radical Copolymerization of α-Methylstyrene and Methyl Methacrylate between Their Ceiling Temperatures

M. Izu,[1b,c] K. F. O'Driscoll,*[1c] R. J. Hill,[1d] M. J. Quinn,[1d] and H. J. Harwood[1d]

University of Waterloo, Waterloo, Ontario, Canada, and the Institute of Polymer Science, University of Akron, Akron, Ohio 44304. *Received September 3, 1971*

ABSTRACT: Nuclear magnetic resonance spectra have been studied for copolymers of α-methylstyrene and methyl methacrylate polymerized at temperatures from 0 to 147°. Analysis of the methoxy resonance patterns in terms of a previously published reversible copolymerization model yielded information on the coisotacticities of the copolymers. From an Arrhenius plot, the difference in enthalpy of activation for a coisotactic placement relative to that for a cosyndiotactic placement, $\Delta(\Delta H^{\ddagger})$, was determined to be 1.8 ± 0.5 kcal/mol, while $\Delta(\Delta S^{\ddagger})$ was found to be 3.6 ± 1.4 eu.

The monomers α-methylstyrene and methyl methacrylate have relatively low ceiling temperatures of 61 and 164°, respectively.[2] Therefore, the effects of depropagation must be considered when copolymerizations involving these monomers are conducted at about 100° or higher. In a previous paper,[3] we showed that the effect of reaction temperature on the copolymer composition curve could be interpreted quantitatively in terms of the kinetics for the dyad reversible copolymerization model.[4] In this paper, we report studies on the nmr spectra of the copolymers formed under conditions where depropagation occurs. We have analyzed the methoxy resonance patterns of the copolymers by applying our reversible copolymerization model[3] and have determined, according to the scheme proposed by Ito and Yamashita,[5] the coisotacticities of copolymers prepared at various temperatures.

Experimental Section

Free radical copolymerizations were carried out in bulk by the procedures described in the previous paper.[3] Nmr spectra (60 MHz) of copolymers in CCl_4 solution (10 wt % or less polymer) were measured at 90%. Copolymer compositions were determined from the proportions of aromatic proton resonance observed in the spectra. The methoxy resonance patterns were evaluated in the standard manner.[6] Resonance areas were determined by planimetry.

Results and Discussion

The methoxy proton resonance of α-methylstyrene-(S)-methyl methacrylate (M) copolymers is observed as two or three resonances occurring over the δ 3.0–4.0 ppm range. According to the interpretation of Ito and Yamashita,[5] the resonance observed at 3.3–3.9 ppm (designated X) is due to methoxy protons centered in *all* MM*M triads and in (SM*M + MM*S) and SMS triads having *only* racemic (cosyndiotactic) M–S placements. The resonance observed at 2.9–3.3 ppm (designated Y) is attributed to methoxy protons centered in (SM*M + MM*S) and SM*S triads having *one* meso (coisotactic) M–S placement. The methoxy proton resonance observed at the highest field area, 2.5–2.9 ppm (designated Z), is attributed to methoxy protons centered in SMS triads having *two* meso (coisotactic) M–S placements. If σ represents the probability that a given M–S placement is meso (coisotactic) and if P_{MS} represents the conditional probability that an M unit is followed by an S unit in the copolymer, the fractions of methoxy resonance observed in

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[1] (a) Part VI: M. Izu and K. F. O'Driscoll, *Polym. J.*, **1**, 27 (1970); (b) on leave from the Department of Hydrocarbon Chemistry, Kyoto University, Kyoto, Japan; (c) University of Waterloo; (d) University of Akron.

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