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PROTON MAGNETIC RESONANCE INVESTIGATION OF THE COTACTICITY OF NON-LACTONIZED AND THE SEQUENCE DISTRIBUTIONS OF LACTONIZED (METHYL-METHACRYLATE–VINYL CHLORIDE) RADICAL COPOLYMERS

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Abstract—By PMR analysis, it has been found that in non-lactonized VC-rich (MMA–VC) radical copolymers, the frequencies of the α-Me resonances depend on the weight fractions of isolated MMA and MMA-MMA diads. By our assumption, the isolated MMA units should be preferentially coisotactic. In the lactonized (MMA–VC) copolymers, two new methoxy resonances lines have been observed and their relative intensities are proportional to the weight fractions of (MMA, VC) pentads and hexads.

INTRODUCTION

Proton Magnetic Resonance (PMR) has been used in many studies on methyl methacrylate copolymers. The methoxy resonance lines have been found to be sensitive to sequence lengths, mainly in (methyl methacrylate–styrene) [1,2] and (methyl methacrylate–acrylonitrile) [3] copolymers, while the methyl resonance frequencies were influenced by both sequence length and cotacticity [4].

More recently, (methyl methacrylate–vinyl chloride) copolymers P(MMA–VC) have been examined before [5] (by i.r. and PMR) and after cyclization [6,7] (by i.r. and pyrolysis). For non-lactonized copolymers, it has been shown that the α-methyl lines were of interest in both sequence distribution and cotacticity investigations, especially for the MMA centred triads [5].

The main difficulty in the PMR examination of the P(MMA–VC) copolymers is the partial intramolecular cyclization of the MMA–VC linkages even at moderately high temperature (~120° in bulk or in solution) and the lack of PMR resolution does not allow an easy analysis of the microstructure.

By complete lactonization, the copolymers are transformed into new (methyl methacrylate–α-methyl, γ-butyrolactone–vinyl chloride) terpolymers P(MMA–B–VC) which do not contain MMA–VC linkages. The obtained terpolymer samples (after lactonization in orthodichlorobenzene at 160–170°) could be easily studied by PMR at 140–150° with sufficiently good resolution.

This work is concerned, first, with the analysis of the cotacticity of a VC-rich non-lactonized copolymer, and second, with the examination of the new α-Me and OMe resonances of the lactonized copolymers; both sequence distribution and stereoconfiguration are considered.

EXPERIMENTAL

1. *Copolymers*

All copolymers were prepared from freshly distilled monomers. Radical copolymerization, in 1,2 dichloro-ethane at 60° with azobisisobutyronitrile as initiator, were stopped at low conversion (≤ 10 per cent). The copolymers obtained by precipitation in methanol were dried *in vacuo* at room temperature.

We used vapour phase chromatography (VPC) for kinetic studies [8]. The reactivity ratios calculated from Fineman–Ross and Lewis–Mayo plots were $r_{MMA} = 10{\cdot}6$ and $r_{VC} = 0{\cdot}14$. The copolymerization conditions and the characteristics of the copolymers are reported in Table 1.

2. *PMR spectroscopy and simulation*

All polymer solutions contained 6 per cent (w/v) of P(MMA–VC) in orthodichlorobenzene. The spectra of the non-lactonized copolymers were recorded at 100°, with hexamethyldisiloxane as internal reference (considered as $\tau = 10$ for convenience). Thereafter, the sample tube was heated at 160–170° in order to induce lactonization, the extent being checked by PMR using the methoxy/α-methyl intensity ratios.

The spectra of terpolymers were recorded at 140–150°. In some cases, peaks of the solvent have been used as internal reference in order to avoid undesirable ^{13}C—H resonances of hexamethyldisiloxane in the spectra of the α-methyl groups.

We used a Varian DA-60-IL spectrometer and, for MMA-poor copolymers which needed spectral accumulations, a Jeol JR-A1 spectrum accumulator. Non-resolved methoxy and α-methyl resonances were decomposed using a Dupont 310 Curve Resolver.

For the curve analysis, the resonances of the remaining methoxy groups—after complete lactonization—were easily reproduced with gaussian shape functions having 2·5–3·5 Hz at half height; for the α-methyl resonances, spectra were simulated with lorentzian shape functions with 2–3 Hz at half height.

Table 1. Experimental conditions of the copolymerizations and characteristics of the copolymers

Sample	Monomer Feed			Copolymer composition MMA fraction		
P(MMA–VC)	MMA (mole)	VC (mole)	Solvent* (mole)	VPG†	PMR‡	FL§
1	0·0104	1·17	5·40	0·045	0·045	0·0
2	0·0305	1·29	5·43	0·135	0·150	0·15
3	0·068	1·31	5·63	0·24	0·20	0·15
4	0·09	1·10	5·50	0·30	0·27	0·20
5	0·102	1·105	5·40	0·41	0·36	0·25
6	0·197	1·45	5·23	0·55	0·56	0·45
7	0·21	1·40	5·45	0·64	0·61	0·45
8	0·35	1·056	5·50	0·75	0·70	0·64
9	0·50	0·63	5·57	0·90	0·90	0·82

* 1,2 Dichloro-ethane.
† Composition determined by vapour phase chromatography.
‡ Composition determined by proton magnetic resonance (see text).
§ Lactonized fraction of methyl methacrylate (see text).
MMA = methyl methacrylate; VC = vinyl chloride.

3. *Sequence distributions*

The sequence distributions were calculated from the monomer reactivity ratios and monomer feeds (IBM 1130), assuming no penultimate effect. The program used was that proposed by Harwood [9] with some minor modifications.

RESULTS AND DISCUSSION

1. *Lactonization ratios and composition of the copolymers*

At 100–110°, although there is bad spectral resolution (Fig. 1-I) quantitative determinations are possible. At higher temperature, the lactonization occurs and part of the MMA–VC linkages are cyclized, giving (B) units with the liberation of methyl chloride: the

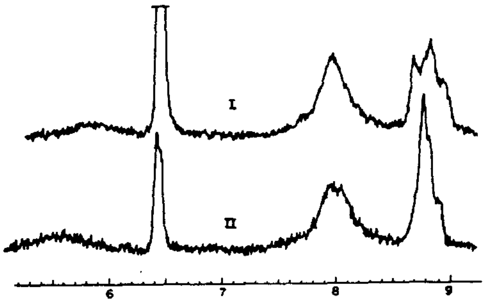


Fig. 1. PMR spectra at 60 MHz of a (methyl methacrylate–vinyl chloride) copolymer. (I) Non-lactonized copolymer (100–110°); (II) lactonized copolymer (140–150°).

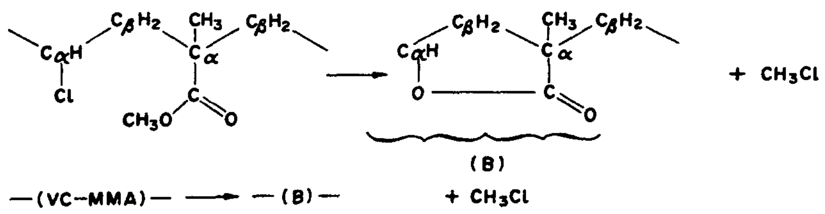


Table 2. Assignments of the resonances of the non-lactonized and lactonized (methyl methacrylate-vinyl chloride) copolymers [τ (HMDS) = 10 for convenience]

τ	P(MMA–VC)			P(MMA–B–VC)		
5·3–6·3	$-C_{\alpha}H$	(V)	(*a*)	$-C_{\alpha}H$	(V + B)	(a′)
6·4–6·5	–OMe	(M)	(*b*)	–OMe	(M)	(*b*′)
7·3–8·5	$>C_{\beta}H_2$	(M + V)	(*c*)	$>C_{\beta}H_2$	(V + M + B)	(*c*′)
8·5–9·1	$-CH_3$	(M)	(*d*)	$-CH_3$	(M + B)	(*d*′)

M = methyl methacrylate, V = vinyl chloride, B = α-methyl, γ-butyrolactone.

P(MMA) copolymer is transformed into P(MMA–B–VC) terpolymer (Fig. 1-II). The assignment of the P(MMA–VC) and P(MMA–B–VC) resonances is reported in Table 2. The non-lactonized fraction of MMA units and the composition of the copolymers could be easily calculated by the following relations:

$$\mathrm{FL} = 1 - \frac{(b')}{(d')}. \tag{1}$$

FL is the fraction of lactonized MMA units,

$$\mathrm{VC}\% = \frac{(a)}{(a) + (1/3)(b)}100 = \frac{(1/2)(c) - (1/3)(d)}{(1/2)(c)}100 \tag{2}$$

$$\mathrm{MMA}\% = \frac{(1/3)(b)}{(a) + (1/3)(b)}100 = \frac{(1/3)(d)}{(1/2)(c)}100. \tag{3}$$

(*a*), (*b*) .... are the relative intensities (Table 2).

Because the relative intensities of the three resonances (*a*), (*c*), (*d*) are not affected by the lactonization, (*a*), (*c*) and (*d*) can be replaced by (*a*′), (*c*′) and (*d*′) in the relations (2) and (3): the composition of the copolymers could be calculated at any extent of lactonization.

The value of the cyclized MMA fractions are plotted versus MMA percentage in P(MMA–VC) (Table 1—Fig. 2). The solid curve is calculated from the theoretical relation established by Alfrey *et al.* [10]:

$$(1 - \mathrm{FL}) = [\cosh(P_{\mathrm{VM}} \times P_{\mathrm{MV}})^{1/2} - (P_{\mathrm{MV}}/P_{\mathrm{VM}})^{1/2} \times \sinh(P_{\mathrm{VM}}/P_{\mathrm{MV}})^{1/2}]^2.$$

(1–FL) is the non-lactonized MMA fraction, P_{MV} is the conditional probability that a VC unit is linked to a MMA-ended growing chain, and P_{VM}, the conditional probability that a MMA unit is linked to a VC-ended growing chain. P_{MV} and P_{VM} have been calculated from the reactivity ratios (kinetic data) and the monomer feed.

The experimental cyclized MMA fractions (FL) obtained from PMR measurements are in good agreement with the calculated values within experimental errors. Thus in dilute solution or in solid state (studied by thermogravimetry and vapour phase chromatography [11]) the thermal behaviour of the copolymers is nearly the same.

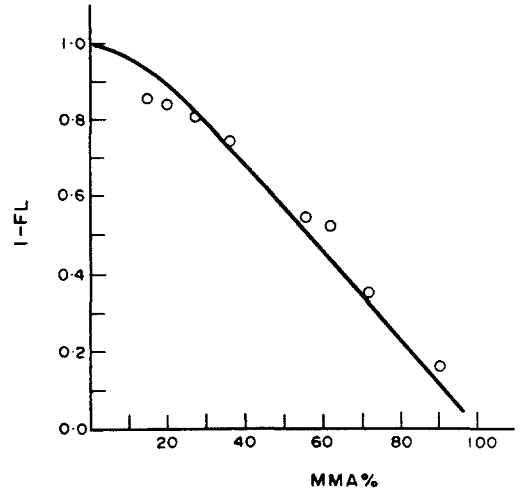
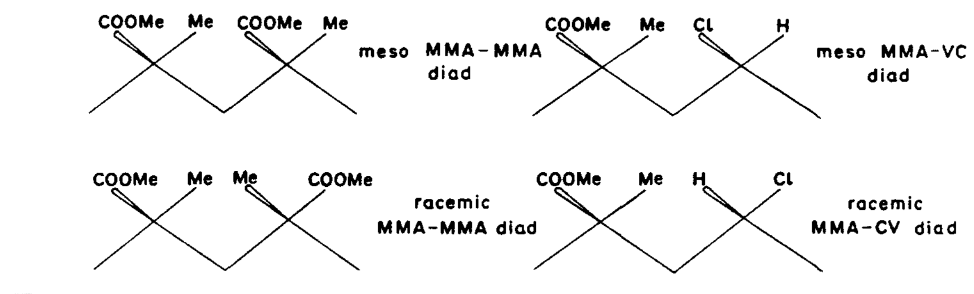


Fig. 2. Lactonized fraction of methyl methacrylate vs its percentages in the copolymers (lactonization in *ortho*-dichlorobenzene). Solid curve: calculated values assuming random cyclization.

2. *Configuration and sequence distribution of a VC-rich non-lactonized copolymer*

Prior to lactonization of the intersequences, the large OMe resonances (recorded at 100°, ~ 5 Hz at half height instead of 2·5 Hz for the OMe line of PMMA homopolymer recorded at 140°) (Fig. 1-I) seemed not to be influenced by the proximity of the VC comonomer (shoulders in the OMe spectrum could only be observed after lactonization), while the α-Me lines, which are already sensitive to the tacticity of the PMMA homosequences, became more complex and part of their resonances shifted downfield (cotacticity effect) (Fig. 1-I).



Because of the simplicity of their sequence distributions, the configuration analysis of VC-rich copolymer samples would be informative. In the particular case of *P*(MMA–VC) having 95·5 per cent of VC (Table 1), in which the weight fractions of isolated MMA units, MMA–MMA diads and longer MMA sequences are 0·63; 0·26 and 0·11 (from kinetic data), respectively, seven lines have been observed after the accumulation and curve decomposition of the α-Me spectrum (Fig. 3, II, III) recorded at 110–120°. Owing to the calcu-

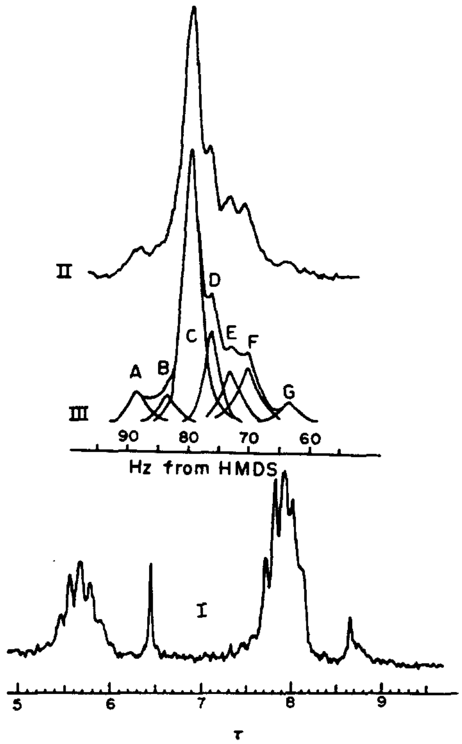


Fig. 3. PMR spectra at 60 MHz of a non-lactonized copolymer having 4·5 per cent of methyl methacrylate. (I) Normal spectrum; (II) accumulated spectrum of the α-methyl groups; (III) simulated spectrum of the α-methyl groups.

lated sequence distribution, the three lines at the low field side, A (89 Hz from HMDS), B (85 Hz) and C (80 Hz) should correspond to the isolated MMA units of *P*(MMA–VC)-I (sum of their intensities A + B + C = 0·60): the three possible cotactic triads of VC–$\underline{\text{MMA}}$–VC.

If we consider the relative chemical shifts of the α-H of polyvinylchloride (PVC):τ(SS) < τ (II), it seems reasonable to assume the same order for the α-Me chemical shifts of the isolated MMA units (Fig. 3):

$$\tau(S'S') = A < \tau(S'I') = \tau(I'S') = B < \tau(I'I') = C. \quad (5)$$

The centred unit of VC–$\underline{\text{VC}}$–VC and VC–$\underline{\text{MMA}}$–VC should experience the same magnetic influence from the two adjacent chlorine atoms. This assignment is not in agreement with that proposed by Johnston and Kopf [5] who, however, thought that the α-Me singlet of MMA–$\underline{\text{MMA}}$–VC (SI') is shifted upfield from MMA–$\underline{\text{MMA}}$–VC (SS'). If our assumptions are correct, the most favourable configuration appears to be meso I' (90 per cent of the VC–MMA–VC weight fraction—Table 3, Fig. 3).

For the same reason, we might have with D (77 Hz), E (74 Hz) and F (71 Hz) attributed to the three cotactic triads of VC–MMA–MMA (Table 3, fig. 3):

$$\tau(S'S) = D < \tau(S'I) = \tau(I'S) = E < \tau(I'I') = F. \quad (6)$$

In fact, E might be also due to the small contribution of MMA isotactic triads (II) (same chemical shift), having regard to the value of the long MMA sequence weight fraction (0·11). Finally, line G (64 Hz) should correspond to the MMA heterotactic (IS) triads. No other detectable signal corresponding to the MMA syndiotactic (SS) triads has been found at higher field. Thus, for the PMMA homosequences of the VC-rich copolymer P(MMA–VC)-I, we should not have the classical tactic triad distribution found in the radical PMMA homopolymers obtained at 60° (II = 0·03, IS + SI = 0·31, SS = 0·66).

If our attributions are correct and if the cyclization is negligible, it is of interest to note that in isolated MMA units 90 per cent of the cotactic diads are I', whereas I' only represents less than 50 per cent of the VC–MMA–MMA triads (Table 3). However, if there is some lactonization at 110–120°, the resonance line at 74 Hz (line D, Fig. 3), assigned to VC–$\underline{\text{MMA}}$–MMA (S'S) might be also due to the α-Me of the isolated B cycles of the lactonized copolymer (line H, Fig. 4). Just as the α-Me groups of VC–$\underline{\text{MMA}}$–MMA (I'S) and VC–$\underline{\text{B}}$–B. both resonate at 71 Hz. Moreover, all the relative

Table 3. Assignment of α-Me resonances of a non-lactonized VC-rich (methyl methacrylate–vinyl chloride) copolymer having 0·63, 0·26, 0·11 of isolated MMA, MMA–MMA diads and longer MMA sequences, respectively

Hz from HMDS	Triad	Assignment	Relative intensity
A = 89		S'S'	0·06 (0·09)
B = 85	—V$\underline{\text{M}}$V—	I'S' + S'I'	0·06 (0·09)
C = 80		I'I'	0·52 (0·82)
D = 77	—V$\underline{\text{M}}$M—	S'S'	0·13 (0·35)
E = 74	—V$\underline{\text{M}}$M— or —M$\underline{\text{M}}$M—	I'S + S'I = II	0·10 (0·27)
F = 71	—V$\underline{\text{M}}$M—	I'I	0·14 (0·38)
G = 64	—M$\underline{\text{M}}$M—	SI + IS	0·03

—MMA = M, VC = V.
α-Me groups of II, IS, SS resonate at 74, 67 and 60 Hz from HMDS, respectively, in orthodichlorobenzene at 140°.
(...) = Normalized relative intensities.

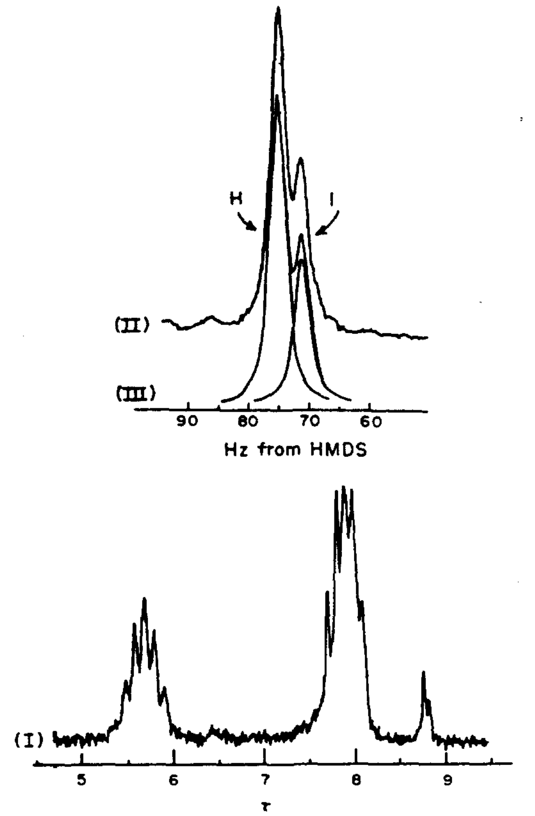


Fig. 4. PMR spectra at 60 MHz of a lactonized copolymer having 4·5 per cent of methyl methacrylate. (I) Normal spectrum; (II) accumulated spectrum of the α-methyl groups; (III) simulated spectrum of the α-methyl groups.

intensities of these α-Me lines should be affected by the probable difference in the lactonization rates between I′ and S′ cotactic diads.

These observed variations in the probabilities of the different cotactic placements in relation with the MMA sequence lengths should be useful in explaining the observed difference of the thermal behaviour of the copolymers. The lactonization activation energy of about 20 kcal mole^{-1} (calculated from PMR and thermogravimetry data) found for the VC-rich copolymer increases to 30 kcal mole^{-1} for the MMA-rich copolymer [12]. The low lactonization activation energy and the high concentration of I′ of isolated MMA units of the VC-rich copolymer (if the peak assignment of Fig. 3 and Table 3 is correct) suggest that I′ should lactonize more easily than S′. However, in VC-rich P(MMA–VC), traces of hydrochloric acid from dehydrochlorinated PVC homosequences may also promote cyclization.

For copolymers having more than 10 per cent of MMA, the lack of resolution in the α-Me spectra of the non-lactonized samples did not allow an easy analysis of microstructure.

3° *OMe and α-Me resonances after complete lactonization—sequence distributions*

(For convenience, MMA and VC will be represented by M and V, respectively, in the writing of sequences.)

After complete lactonization, the new OMe and α-Me peaks could be examined in relation with the M or (M,V) sequence distributions. The assignment of these new resonance lines is reported in Table 4.

Isolated M and MM diads. In the lactonized P(MMA–VC)-1 (Fig. 4–I), all the OMe groups disappear and only two main lorentzian lines could be observed in the α-Me accumulated spectrum: H(75 Hz) and I(71·4 Hz). Their relative intensities (H: 0·7 and I: 0·3) correspond to the weight fractions of isolated M (0·63) and MM (0·26) diads calculated from kinetic data. H and I could be reasonably assigned to the isolated B(—V$\underline{B}$V—) and BB (—V$\underline{B}$B— or —B$\underline{B}$V—)

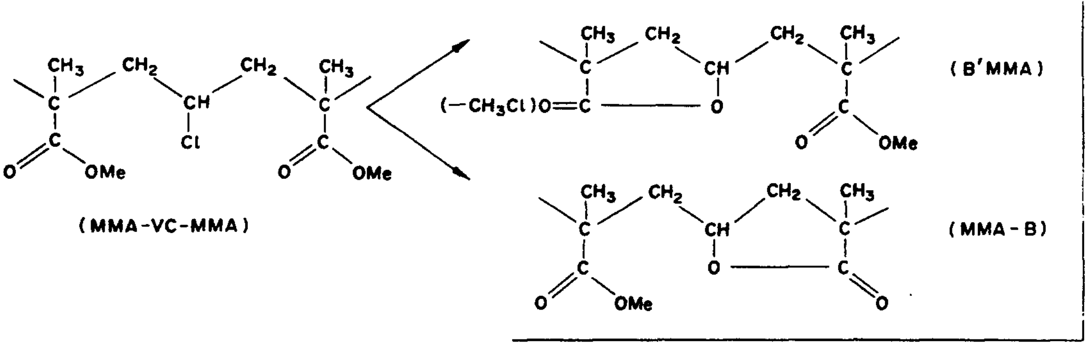
Table 4. Assignment of the α-methyl and methoxy resonances of the lactonized poly(methyl methacrylate–vinyl chloride) copolymer PMR spectra (MMA = M, VC = V)

Proton groups	Resonance lines in P(MMA–B–VC)	Hz (from HMDS)	Assignment of M sequences in P(MMA–B–VC)	Original M sequences in P(MMA–VC)
α-Me in P(MMA–VC)1	H	75	—B—	—M—
	I	71·4	—BB—	—MM—
OMe in P(MMA–VC)2 to P(MMA–VC)9	J	216·7	—B$\underline{M}$B— —B′$\underline{M}$B— or —B$\underline{M}$B′— —B′$\underline{M}$B′—	—VM$\underline{M}$MV— —MV$\underline{M}$MV— or —VM$\underline{M}$VM— —MV$\underline{M}$VM—
	K	215·2	—B$\underline{MM}$B— —B′$\underline{MM}$B— or —B$\underline{MM}$B′— —B′$\underline{MM}$B′—	—VM$\underline{MM}$MV— —MV$\underline{MM}$MV— or —VM$\underline{MM}$VM— —MV$\underline{MM}$VM—
	L	213	—BM$\underline{M}$MB—	Sequences longer than 3 MMA units
	M	210	—MM$\underline{M}$MM—	

diads of the P(MMA–B–V) terpolymer. If this assumption is correct, the resonance frequencies of the α-Me groups of B cycles should not be sensitive to the configuration effect.

(M, V) pentads and hexads. For higher concentration of MMA in the copolymers, part of the remaining OMe resonances are shifted downfield, and three or four gaussian lines (J, K, L, M) could be separated by simulation. The relative intensities of these lines depend on the composition of the P(MMA–B–VC) samples (Fig. 5). We have tentatively assigned these new OMe resonances, assuming that the downfield shift is due to the adjacent B cycles and neglecting the fact that, actually, the cyclization of MMA–VC linkages in —MVM— triads may give —B′M— or —MB— diads:

$$\tau(\text{—B}M\text{B—}) \simeq \tau(\text{—B}'M\text{B}'\text{—}) < \tau(\text{—B}M\text{M—})$$
$$\simeq \tau(\text{—B}'M\text{M—}) < \tau(\text{—M}M\text{M—})$$



With a view to confirm the PMR assignments of Table 4, the comparison between the relative intensities of the resonance lines J, M, L + M and the calculated distributions of the original (M,V) sequences could be instructive.

The normalized intensities of line J (—B$\underline{M}$B—, Table 4) are plotted versus MMA percentage in Fig. 6. The sums of the different (M,V) pentads [$\sum$p(M,V)] capable of giving isolated MMA units after complete lactonization are calculated from kinetic data (Fig. 6, dotted curve). If only the non-lactonized MMA fraction of $\sum$p(M,V) is taken into account, the obtained distribution (Fig. 6, solid curve) should correspond to the remaining OMe resonance J. Therefore, in assuming that the extent of lactonization given by Alfrey *et al.* [10] is verified for the set of $\sum$p(M,V), one might have:

non-lactonized MMA fraction of

$$\textstyle\sum p(M,V) = (1 - FL)\sum p(M,V). \qquad (7)$$

(l-FL) takes into account the non-lactonized centered MMA units of —VM$\underline{M}$MV— and the MMA units of the non-loctonized MMA–VC linkages (M^1_{NL}). The knowledge of the sequence distributions (kinetic data) allows quantitative determinations of the lactonizable MMA fraction in MMA–VC linkages (or run number as defined by Harwood and Ritchey [13]) according to the composition of the copolymers. On the other hand, the lactonized fraction (M^1_L) could be deduced from the curve of Fig. 2. Thus the non-lactonized one (M^1_{NL}) is given by:

$$M^1_{NL} = M^1 - M^1_L. \qquad (8)$$

The experimental distribution obtained from PMR measurements lies below the calculated (Fig. 6); this fact suggests that, after complete lactonization, part of the $\sum$p(M,V) does not give isolated MMA units. For example, one could have:

$$\text{M|VMMVM|C} \longrightarrow \text{MBMBV}$$

or

$$\text{M|VMMVM|V} \longrightarrow \text{B}'\text{MMBV} \qquad (9)$$
$$\text{P(MBV)}$$

In the same manner, the relative intensities of line K, assigned to the MM diads in P(MMA–B–VC), are plotted vs MMA percentage (Fig. 7). These diads could originate from the (M,V) hexads [h(M,V)] reported in Table 4. The relative intensity of K is directly proportional to 2 $\sum$h(M,V), and the actual number of the non-lactonized MMA units is represented by the dotted curve (Fig. 7). If the lactonized MMA fractions of (M,V) pentads [(FL) $\sum$p(M,V) = difference between the two curves of Fig. 6] are taken into account, another more probable distribution of MM diads is obtained. This assumption is represented by the second probability of the cyclization reactions (9):

probable distribution of

$$\text{BMMB} = 2(1 - \text{FL})\textstyle\sum h(M,V) + (\text{FL})\sum p(M,V). \qquad (10)$$

The solid curve of Fig. 7 has been calculated from relation (10).

Agreement between experimental PMR and calculated distributions in P(MMA–B–VC) observed in Figs. 6 and 7 might be due to some compensation because:

(i) (M,V) pentads such as -VMMMV— and —MVMMV— could give MM diads after complete lactonization and,

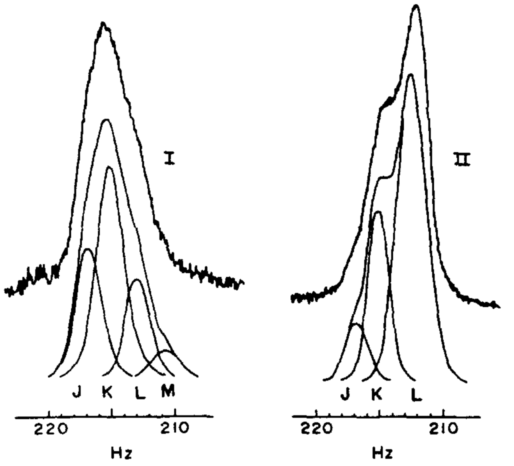


Fig. 5. OMe resonances of lactonized copolymers. (I) Experimental (upper, 64 scans accumulation) and simulated spectra of a copolymer having 27 per cent of methyl methacrylate; (II) experimental (upper, non-accumulated) and simulated spectra of a copolymer having 70 per cent of methyl methacrylate.

(ii) isolated MMA unit in the lactonized copolymer might originate from —MVMMMV— and —MVMMVM— hexads owing to the nature of the MMA–VC or VC–MMA diads configurations (I' or S').

Finally, long MMA sequences ($\geqslant$ triads) of P(MMA–B–VC) having OMe groups resonating at 210–213 Hz (lines L and M) correspond to the remaining non-lactonized MMA fractions. The sums of their relative intensities (L + M) are plotted vs MMA percentage in Fig. 8. For P(MMA–VC) having less than 70 per cent of MMA, line L (213 Hz) could be easily separated and assigned to the central MMA unit of —BMMMB— pentads of P(MMA–B–VC) (Table 4).

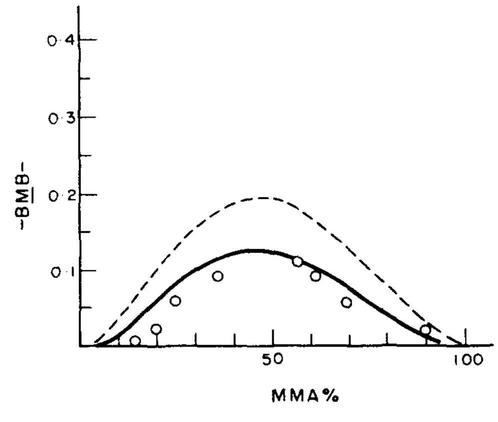


Fig. 6. Distribution of isolated MMA units in lactonized copolymers. (---) Sums of the fractions of (MMA, VC) pentads before lactonization; (——) same distribution if the lactonizable fraction is taken into account; (O) experimental intensities of line J at 216·7 Hz attributed to isolated MMA units in lactonized copolymers.

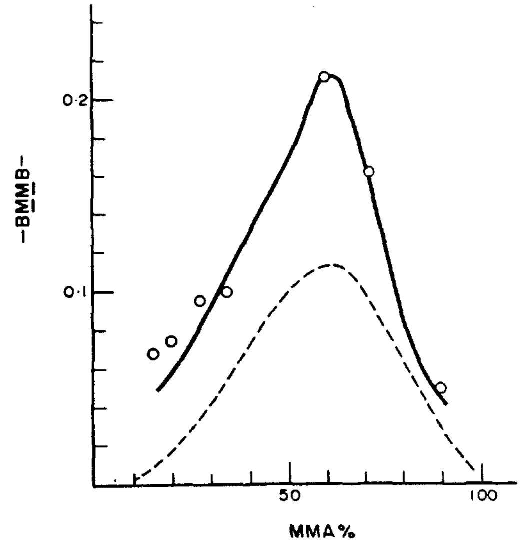


Fig. 7. Distribution of MMA–MMA diads in lactonized copolymers. (---) Variation of $2(1 - FL)\sum h(M, V)$ vs MMA percentage; (——) variation of $2(1 - FL)\sum h(M, V) + (FL)\sum p(M, V)$ vs MMA percentage; (O) experimental intensity of line K at 215·2 Hz attributed to —BMMMB—.

Although there is relatively good agreement between experimental and calculated sequence distributions of Figs. 6–8, the proposed solution may not be unique.

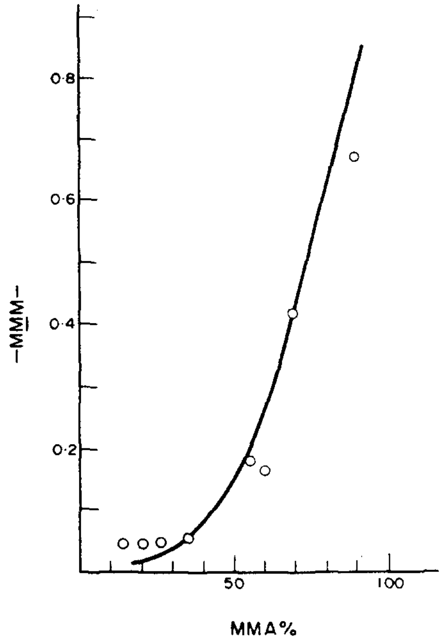


Fig. 8. Distribution of long MMA sequences after complete lactonization. (——) Calculated curve for MMA sequences longer than 3 units; (O) experimental intensities of (L + M) at 213 and 210 Hz attributed to —BMMMMB— and —MMM—.

CONCLUSION

The microstructure of non-lactonized P(MMA–VC) has been studied for VC-rich copolymers, and it seems that the most favourable stereoconfiguration for isolated MMA units in VC–MMA triads should be coisotactic.

The examination of the completely lactonized P(MMA–VC) by PMR should reflect the sequence distribution of the original radical copolymers. The assignment proposed for the new α-Me and OMe resonance lines seems to be confirmed by the distributions of isolated MMA units, MMA–MMA diads, (MMA, VC) pentads and hexads, taking into account theoretical as well experimental (PMR measurements) lactonizable MMA fractions, although the hypothesis may appear to be oversimplified. These agreements suggest that the gaussian peak shape of the OMe resonance lines might be due to the small difference in electronic surroundings experienced by the OMe groups in —BM— or —B′M— diads. The tacticity and cotacticity effect on the chemical shift of OMe should not be discernible at 60 MHz.

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Résumé—L'analyse par RMP des groupements α-méthyles des copolymères (MAM–CV) riches en CV a permis de relier les résonances des protons méthyliques à la distribution des unités MAM isolés et des diades MAM–MAM. La configuration des unités MAM isolés serait préférentiellement coisotactique. Après lactonisation complète des alternances, la résonance des protons méthoxy se démultiplie et les intensités partielles de ces raies méthoxy dépendent de la distribution des pentades et hexades (MAM, CV).

Zusammenfassung—Mithilfe der Protonenresonanzspektroskopie wurde gefunden, daß in radikalisch hergestellten Copolymeren aus MMA und VC, die reich an VC und nicht lactonisiert sind, die Frequenzen der α-Methyl-Resonanzen abhängen vom Gewichtsanteil isolierter MMA-Einheiten und MMA-Diaden. Nach unserer Auffassung sind die isolierten MMA-Einheiten überwiegend coisotaktisch angeordnet. In lactonisierten MMA-VC-Copolymeren wurden zwei neue Methoxy-Resonanzlinien aufgefunden, deren relative Intensitäten dem Gewichtsanteil von MMA-VC-Pentaden und -Hexaden proportional sind.