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ASSIGNMENTS FOR THE ^{1}H-NMR OF ALKOXY GROUPS IN SYNDIOTACTIC METHACRYLATE COPOLYMERS—I

METHYL METHACRYLATE-METHACRYLIC ACID COPOLYMERS AND METHYL METHACRYLATE-DIPHENYLMETHYL METHACRYLATE COPOLYMERS

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Abstract—Unusual assignments have been observed for the ^{1}H-NMR of alkoxy groups in syndiotactic methyl methacrylate-methacrylic acid (MMA-MAA) copolymers and methyl methacrylate-diphenylmethyl methacrylate (MMA-DPMMA) copolymers. Thereby, the alkoxy groups —OCH_3 and —$OCH<$ show a degenerate pentad assignment, in as much as the two monomer units nearest to the central monomer unit exert no differentiating influence on chemical shift, in contrast to the two next-to-nearest monomer units. By the use of copolymers possessing a tendency toward alternation with respect to compositional statistics, it is possible to distinguish between a degenerate pentad and a normal triad assignment. The reason for the degenerate pentad assignment is seen in specific conformations of the pentads, leading to the elimination of the differentiating influence on chemical shift for the two monomer units nearest to the central unit.

INTRODUCTION

As previously reported, the —OCH_3 ^{1}H-resonance of syndiotactic methyl methyacrylate-methacrylic acid (MMA-MAA) copolymers possesses a pentad assignment which is degenerate, since not the two nearest neighbour monomer units, but only the two next-to-nearest neighbour units exhibit a differentiating influence on the chemical shift of the —OCH_3 group in the central monomer unit [1, 2]. The same "next-to-nearest neighbour triad" assignment, i.e. degenerate pentad assignment, holds also for the —OCH_3 ^{1}H-resonance of the esterification products of the MMA-MAA copolymers with diphenyldiazomethane, i.e. for the derived syndiotactic methyl methacrylate-diphenylmethyl methacrylate (MMA-DPMMA) copolymers. To our knowledge, degenerate pentad assignments of this type have not been observed before.

The cause for the degenerate pentad assignment was seen in a specific set of conformations for the pentads. Hereby the "backbone" of the pentad was postulated to be in, or near an all-*trans*-conformation, this conformation being often assumed for syndiotactic vinyl homopolymers. The "backbone" conformation removes in the nearest neighbour monomer units the pendant —COOR groups, which differentiate between the two types of comonomer units, to a relatively large distance from the —COOR group of the central monomer unit. Also, the differentiating —COOR groups of the next-to-nearest monomer units are positioned relatively close to the —COOR group of the central unit. The all-*trans* "backbone" conformation of hexads is shown in a Natta projection in Fig. 1. As seen from Fig. 1, in addition, the α-CH_3 group, in contrast to the —COOR group, is surrounded in the all-*trans*-conformation by nearby positioned —COOR groups. Thus the chemical shift of the α-CH_3 groups will be mainly determined by the type of the nearest neighbour monomer units and a normal triad assignment prevails. It is likely that not only the backbone conformations, but also specific side chain conformations support the degenerate pentad assignment,

In this communication, the earlier findings on the —OCH_3 resonance of MMA-MAA and MMA-DPMMA copolymers are supported further and extended to copolymers possessing other compositional statistics. In addition, the —$OCH<$ resonance of the MMA-DPMMA copolymers is investigated. All copolymers have been prepared by polymer analogous reactions. Thereby each type of copolymer has been prepared to possess Bernoullian statistics, statistics showing a tendency toward alternation, and blocklike statistics.

While copolymers having Bernoullian statistics of the monomer units are often of great value for assigning the NMR-spectra of copolymers, these random copolymers cannot be used to differentiate between a degenerate compositional pentad assignment of the kind discussed and a normal triad assignment. For this differentiation, copolymers must be employed with statistics exhibiting either a tendency toward alternation, or a blocklike character. The differentiation can be more pronounced with those of alternating character [2].

EXPERIMENTAL

Syndiotactic poly(methacrylic acid) (s-PMAA) was obtained by low temperature radiation induced polymerization [3]. Starting from s-PMAA, the copolymers possessing Bernoullian and alternating statistics were prepared as shown in Fig. 2.

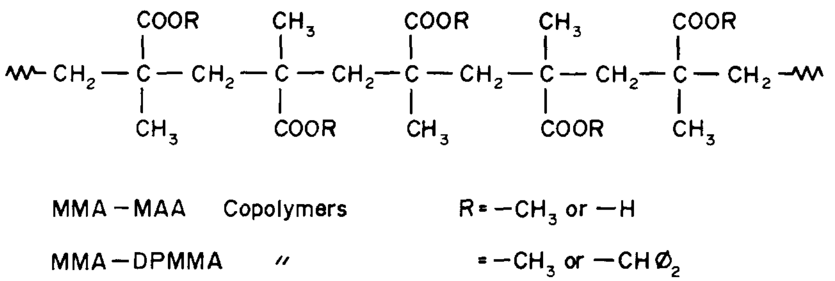

Fig. 1. Natta projection of syndiotactic hexads in MMA-MAA copolymers and MMA-DPMMA copolymers, in all-*trans* conformation.

Syndiotactic MMA-MAA copolymers of Bernoullian compositional statistics were obtained by esterification of s-PMAA by methanol in conc. H_2SO_4: 300 mg s-PMAA was dissolved in 8 ml conc. H_2SO_4 (95–97% by weight) and 1.6 ml CH_3OH added at 50° with stirring. After a period at 50°, the reaction was stopped by pouring slowly into 200 ml diethylether. After filtration, the polymer was redissolved in 1 N KOH, diluted with H_2O to 200 ml and precipitated by acidification with HCl. After heating to boiling, it was filtered and dried at 50° *in vacuo*. Typical reaction times were: 1.0 hr P(A) = 0.12, 2.25 hr P(A) = 0.19, 3.5 hr P(A) = 0.28, 6 hr P(A) = 0.34, 9 hr P(A) = 0.39, 48 hr P(A) = 0.48, 144 hr P(A) = 0.48 (A = MMA-unit). The MMA-MAA copolymers possessing a tendency toward alternation were obtained by esterification with methanol in the presence of dicyclohexylcarbodiimide (DCC) [4]. Syndiotactic MMA-DPMMA copolymers with Bernoullian or alternating statistics were prepared starting from the corresponding precursor MMA-MAA copolymers by complete esterification with diphenyldiazomethane according to known procedures [5, 6].

A different path to alternating and blocklike MMA-MAA and MMA-DPMMA copolymers started from syndiotactic poly(methylmethacrylate) (PMMA). The PMMA was prehydrolyzed for solubility in aqueous media to P(A) = 0.60, and then further hydrolyzed with a deficiency or an excess of base, as calculated on the MAA-units present. With a deficiency of base, blocklike copolymers, and with an excess of base, alternating coppolymers were obtained [7–9]. The MMA-MAA copolymers were also exhaustively esterified by diphenyldiazomethane [5, 6] to yield the corresponding MMA-DPMMA copolymers.

^{1}H-NMR spectra were recorded on a Varian HR 220 spectrometer in the c.w. mode at 220 MHz or a Bruker CXP-200 multinuclear FT spectrometer at 200 MHz. Typical recording conditions were: 200 MHz, 5% concentration of polymer (w/v), TMS as internal standard. Peak separation was carried out with a Dupont curve resolver, or alternately by hand drawing and planimeter.

RESULTS AND DISCUSSION

Figure 3 shows the partial ^{1}H-NMR spectra of the $-OCH_3$ and α-CH_3 groups of three MMA-MAA copolymers of different gross compositions, having com-

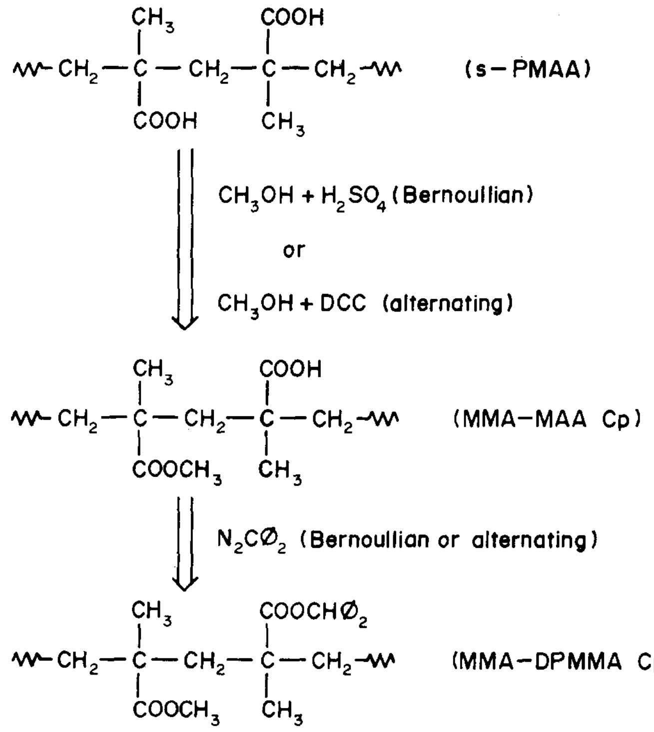

Fig. 2. Polymer analogous reactions leading to syndiotactic MMA-MAA and MMA-DPMMA copolymers, either of Bernoullian or of alternating compositional statistics.

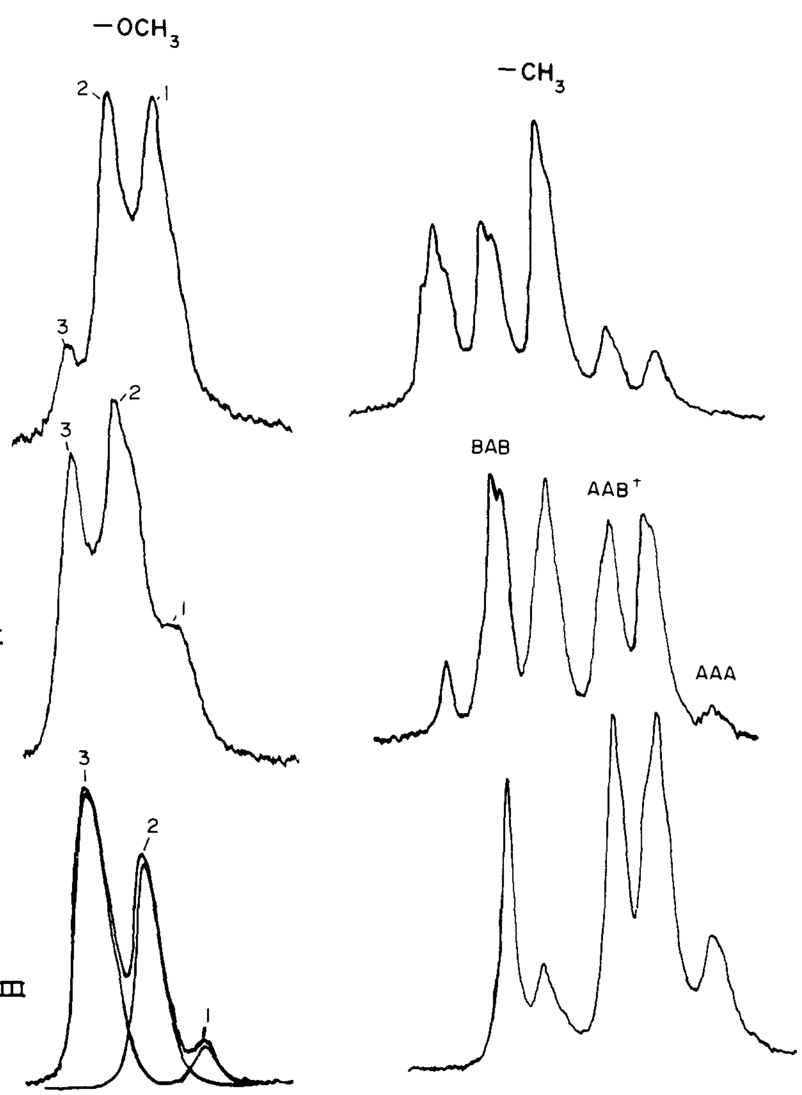

Fig. 3. ^{1}H-NMR partial spectra of the —OCH_3 (3.5–3.8 ppm) and the α-CH_3 (1.2–1.8 ppm) region for three MMA-MAA copolymers possessing a tendency toward alternation and prepared by DCC. Conversion [P(A)] increasing from trace **I** to **III**, assignment of A-centred triad as shown (A = MMA, B = MAA). Curve resolving demonstrated on the —OCH_3 resonance of trace **III**. Recording conditions: 220 MHz, pyridine·d_5, 100°.

positional statistics with a tendency toward alternation and prepared by methanol and DCC. If for the —OCH_3 resonance a normal triad assignment were valid, as is in fact the case for the α-CH_3 resonance, there should exist a direct one-to-one correspondence of the peak areas for the three $-OCH_3$ peaks, when compared to the areas of the A-centred triads in the α-CH_3 resonance region (A = MMA-unit). However, no such correspondence can be detected over the range of composition. Surprisingly, with Bernoullian instead of alternating copolymers, this one-to-one correspondence can be observed such that the peaks 1, 2 and 3 of the —OCH_3 resonance have the same absolute integral intensity as the peaks BAB, AAB^+ and AAA in the α-CH_3 resonance, in this order. Moreover, when the spectrum of the homopolymer, syndiotactic PMMA, is compared, it is indicated that the homopolymeric sequence is in position 3. Therefore, the correct assigning of peaks to sequences must consider that in a Bernoullian copolymer the sought for sequences have the same probabilities as the normal triads. This is the case for "next-to-nearest neighbour triads", whose three monomer units are each separated by one unspecified monomer unit. In these pentads, the two monomer units nearest to the central unit remain undefined, because they show no influence on chemical shift.

Because the spectral resolution of the —OCH_3 ^{1}H-resonance is only modest, particularly for Bernoullian copolymers, the MMA-MAA copolymers were completely esterified by diphenyldiazomethane. In the derived MMA-DPMMA copolymers, the resolution of the —OCH_3 resonance is enhanced by the diphenylmethyl groups which act as an internal shift reagent.

In Fig. 4 the spectrum of an alternating MMA-MAA copolymer (trace **I**) is compared with its derived MMA-DPMMA copolymer (trace **II**). Obviously, the

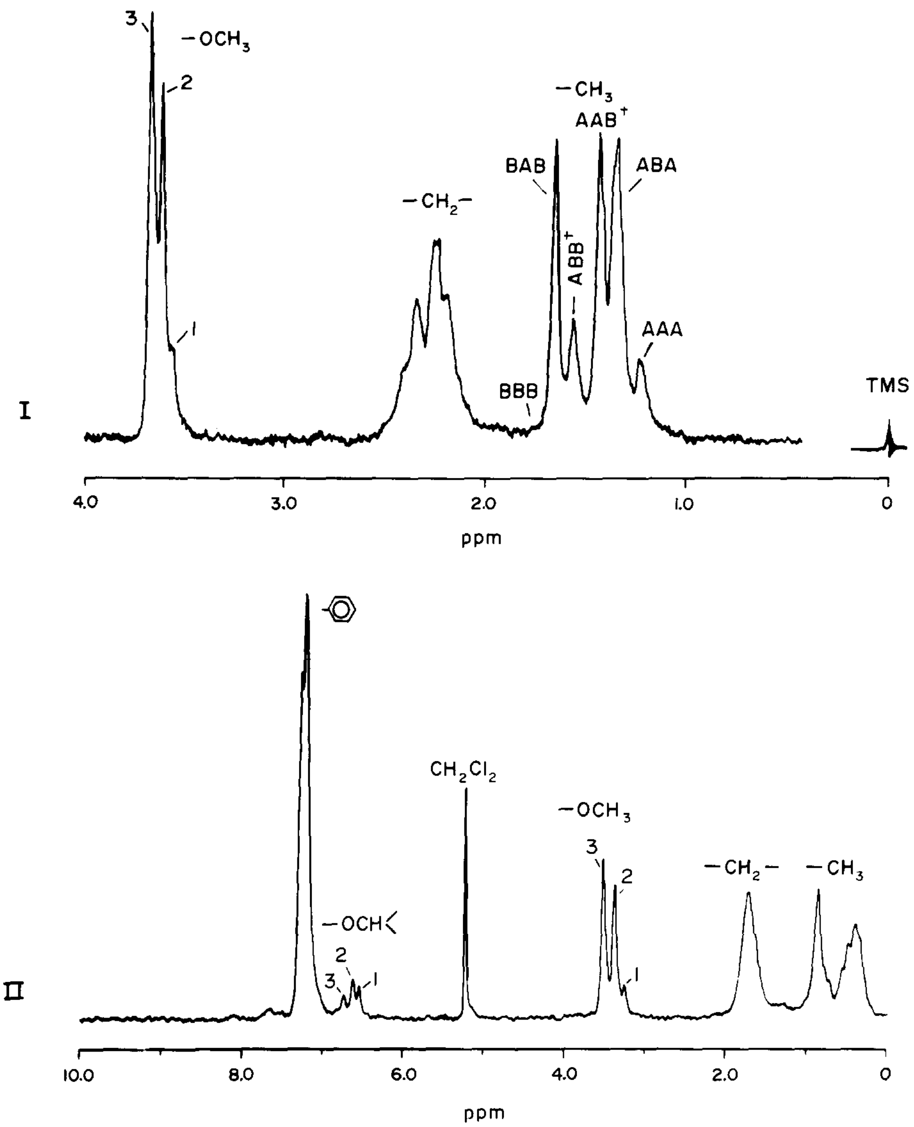

Fig. 4. ^{1}H-NMR survey spectra of a MMA-MAA copolymer of P(A) = 0.56 in pyridine·d_5 at 100° and of the derived MMA-DPMMA copolymer in $CDCl_3$ at 60° (A = MMA-unit). Two hundred and twenty megahertz, TMS or CH_2Cl_2 as internal standard.

resolution of the —OCH_3 resonance is enhanced and that of the α-CH_3 region greatly decreased in the MMA-DPMMA copolymers. In addition, the —OCH< resonance of the DPMMA-unit is seen to be resolved. The assignment for the —OCH_3 resonances in both copolymers can be expected to be the same because the relative peak areas appear already visually identical when the spectra of precursor and derived copolymers are compared. Figure 5 shows the comparison for five pairs of alternating copolymers. A result analogous to Figs 4 and 5 is obtained when Bernoullian copolymers are compared.

Evaluation of the —OCH_3 region of alternating MMA-DPMMA copolymers for sequence probabilities and comparing the data to the triad probabilities obtained from the α-CH_3 resonance of the precursor MMA-MAA copolymers, results in the large discrepancies seen in Fig. 6. The triad data [○, △, □] cannot be made to fit the sequence data of the —OCH_3 region [●, ▲, ■] in whatever triad assignment is chosen for the —OCH_3 region. In Fig. 6, AAA → peak 3, AAB† → peak 2 and BAB → peak 1 has been chosen, because of the one-to-one correspondence in Bernoullian copolymers. As pointed out, no such discrepancies are observed if the —OCH_3 region of Bernoullian MMA-DPMMA copolymers is evaluated and compared with the triad data of the precursor MMA-MAA copolymer.

In order to verify the degenerate pentad assignment, the probabilities of the degenerate pentads P(XXX‡) must be known:

$$\begin{aligned} P(AAA‡) &= P(AAAAA) + P(AAABA) \\ &\quad + P(ABAAA) + P(ABABA) \\ &= P(AAAAA) + P(AAABA†) \\ &\quad + P(ABABA) \end{aligned} \qquad (1)$$

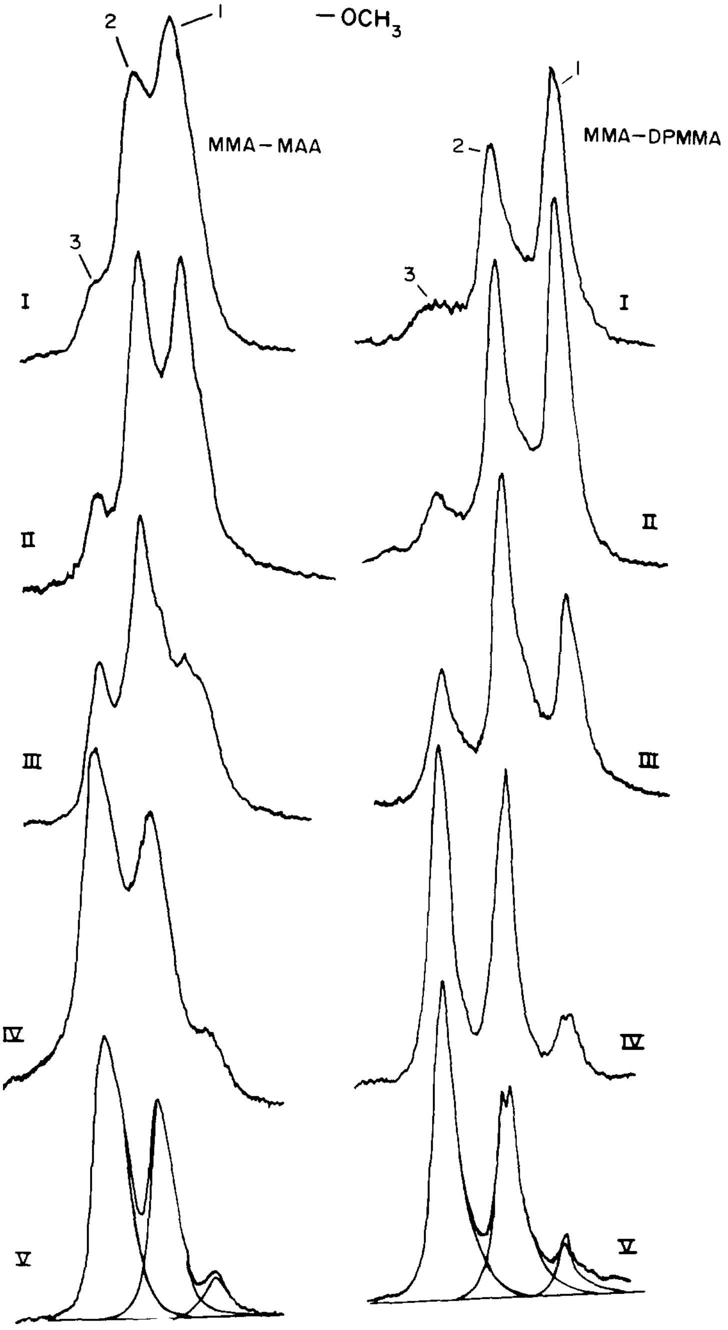

Fig. 5. The —OCH_3 ^1H-resonance in alternating syndiotactic MMA-MAA copolymers and of the MMA–DPMMA copolymers derived therefrom. The gross compositions of the copolymers were: P(A) = 0.29 traces **I**, P(A) = 0.31 traces **II**, P(A) = 0.39 traces **III**, P(A) = 0.56 traces **IV**, and P(A) = 0.62 traces **V** (A = MMA-unit). Recording conditions: MMA-MAA cp, 250 Hz spectral width, 220 MHz, pyridine·d_5, 100°; MMA-DPMMA cp, 500 Hz spectral width, 220 MHz, $CDCl_3$, 60°.

$$\begin{aligned} P(AAB\dagger\ddagger) &= P(AAB\ddagger) + P(BAA\ddagger) \\ &= P(AAAAB\dagger) + P(AAABB\dagger) \\ &\quad + P(ABAAB\dagger) + P(ABABB\dagger) \qquad (2) \\ P(BAB\ddagger) &= P(BAAAB) + P(BAABB\dagger) \\ &\quad + P(BBABB). \qquad (3) \end{aligned}$$

Here † indicates that both the forward and the reverse forms of the sequence are included and ‡ the degenerate pentad. It would be convenient if the pentad probabilities in Eqns 1 to 3 could be directly determined from the α-CH_3 resonance of the MMA-MAA copolymers. Toward this end, the external shift reagent acridine was employed in pyridine solution. A pentad splitting of the triads can indeed by observed, as seen in Fig. 7 where the chemical shifts are plotted vs mole % acridine in pyridine. However, the resolution between pentads was still unsatisfactory and also strong overlapping occurred between α-CH_3 and β-CH_2-resonance regions. The results with quinoline–pyridine mixtures were still less satisfactory. It was

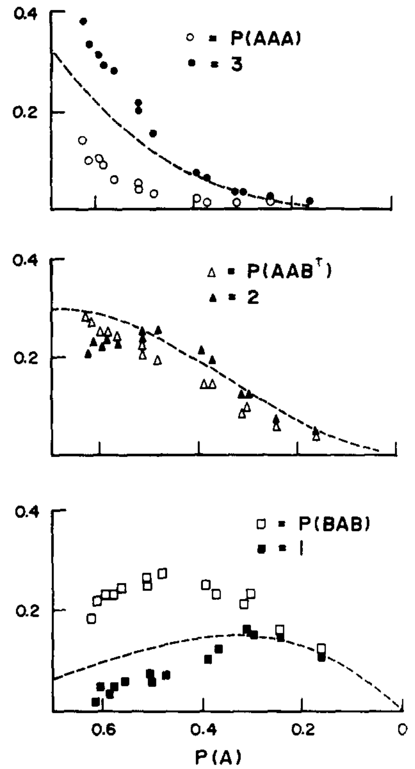

Fig. 6. Sequence probabilities obtained from the —OCH_3 resonance of alternating MMA-DPMMA copolymers [● = peak 3; ▲ = peak 2; ■ = peak 1], compared with the triad probabilities evaluated from the α-CH_3 resonance of the precursor MMA-MAA copolymers. Calculated Bernoullian triad probabilities shown as curves [----].

therefore necessary to approximate the pentad probabilities by conditional probabilities of first or second order, both being derived from the experimentally determined triad probabilities of the α-CH_3 resonances of MMA-MAA copolymers. Using the pentad probability P(BAABB†) as an example

$$\begin{aligned} P(BAABB\dagger) &= P(AAB\dagger)P(A/B)P(B/B) \\ &= P(AAB\dagger)P(AA/B)P(AB/B) \qquad (4) \end{aligned}$$

whereby, for instance

$$\begin{aligned} P(A/B) &= \frac{P(AB)}{P(A)} = \frac{P(ABA) + 0.5\,P(ABB\dagger)}{P(A)} \\ &= \frac{0.5\,P(AAB\dagger) + P(BAB)}{P(A)} \qquad (5) \end{aligned}$$

or

$$\begin{aligned} P(AA/B) &= \frac{0.5\,P(AAB\dagger)}{P(AA)} \\ &= \frac{0.5\,P(AAB\dagger)}{P(AAA) + 0.5\,P(AAB\dagger)}. \qquad (6) \end{aligned}$$

It has been shown earlier that, for MMA-MAA copolymers prepared by DCC [10] and for alternating and blocklike MMA-MAA copolymers prepared by hydrolysis with deficiency or excess of base [11], the conditional probabilities of first order already suffice for reasonable accuracy. Nevertheless, conditional probabilities of second order have been applied for the calculation of pentad probabilities. The degenerate pentad probabilities were than obtained by Eqns 1 to 3. In Fig. 8 the degenerate pentad probabilities P(XXX‡) are plotted [○, △, □] for alternating copolymers prepared by DCC. As opposed to the triad probabilities, the degenerate pentad probabilities agree with the experimental sequence probabilities of peaks 1 to 3 in the —OCH_3 region of MMA-DPMMA copolymers [■, ▲, ●], if ■ = peak 1, ▲ = peak 2 and ● = peak 3 (the numbering of the peaks is from high to low field as in Figs 3–5). The experimental triad probabilities are also shown (curves) and demonstrate the large difference between degenerate pentad and triad probabilities for alternating copolymers. Employing alternating copolymers prepared by hydrolysis of PMMA with an excess of base, an analogous result as in Fig. 8 is obtained (not shown). The calculated degenerate pentad probabilities agree with the experimental —OCH_3 probabilities of the derived MMA-DPMMA copolymers, while the experimental triad probabilities are situated far outside the range of experimental error.

When Bernoullian copolymers are employed, the calculated probabilities of degenerate pentads, the calculated Bernoullian triads, the experimental probabilities of sequences of the —OCH_3 resonance, and the experimental probabilities of triads of the α-CH_3

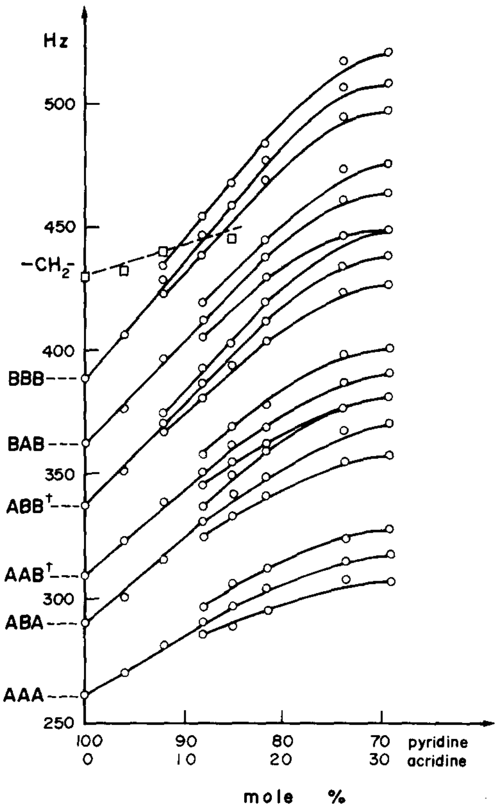

Fig. 7. Shift of triad peak positions and splitting into pentads in the α-CH_3 ^{1}H-resonance of MMA-MAA copolymers when acridine in pyridine is used as an external shift reagent. The α-CH_3 resonance is overlapping at higher acridine contents with the β-CH_2 region; [□] is the border of the β-CH_2-resonance to high field. Two hundred and twenty megahertz, 100°, TMS.

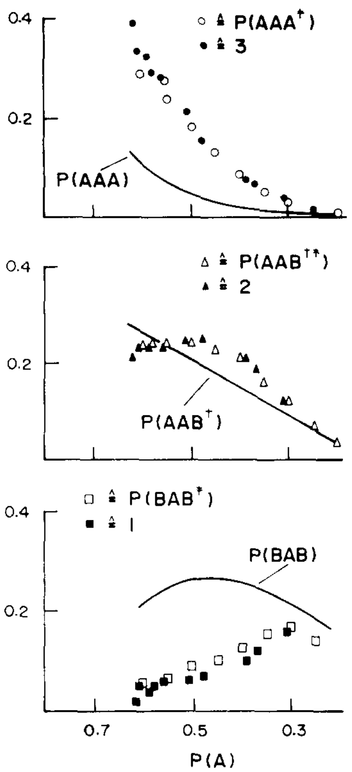

Fig. 8. Calculated probabilities of degenerate pentads P(XXX‡) [○, △, □]. Experimental probabilities of sequences from the —OCH_3 resonance of derived alternating MMA-DPMMA copolymers [● = peak 3; ▲ = peak 2; ■ = peak 1; peak numbering from high to low field, as in Figs 3–5]. Experimental triad probabilities from the α-CH_3 regions of precursor MMA-MAA copolymers [—].

region, should all agree. This is the case, as shown in Fig. 9b. The experimental probabilities for the —OCH_3 resonance in derived MMA-DPMMA copolymers [○] and for the triads in the α-CH_3 region of MMA-MAA copolymers [△] are situated close to the curve calculated for degenerate pentads [----]. Thus the Bernoullian copolymers cannot be used to distinguish between a degenerate pentad and a triad assignment, as follows already from the definition of Bernoullian statistics.

The agreement between the experimental probabilities determined from the —OCH_3 resonance in derived MMA-DPMMA [○] and in the precursor MMA-MAA copolymers [□] is the feature of Fig. 9a, which has been obtained for alternating copolymers prepared by DCC. In Fig. 9, both for the Bernoullian and alternating copolymers, the probabilities of the degenerate pentads have been calculated by conditional probabilities of first order.

Using blocklike copolymers, it should again be possible to differentiate between a degenerate pentad and a triad assignment. However, the difference between the probabilities for degenerate pentads and triads becomes first larger and then smaller with increasing blockiness, when departing from random statistics. Very long blocks lead to the almost exclusive presence of all-A- or all-B-sequences. The probabilities for the all-A-sequences then become nearly the same, as is the case for the all-B-sequences. Fortunately, the blocklike character for the MMA-MAA copolymers prepared by hydrolysis is only moderate [11]. In Fig. 10 the calculated probabilities for degenerate pentads [⊗, ◬, ⊠] agree with the experimental probabilities of the —OCH_3 resonance in derived MMA-DPMMA copolymers [●, ▲, ■]. The experimental triad probabilities [—] are however

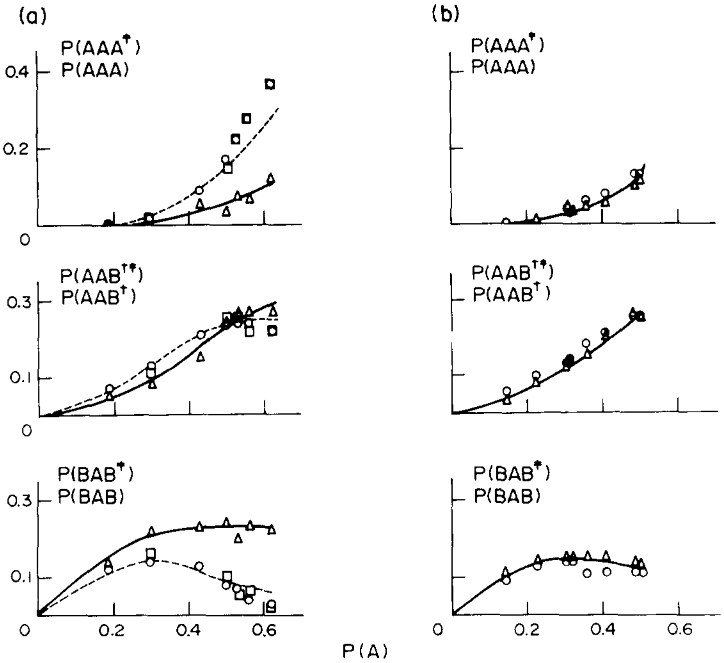

Fig. 9. Calculated probabilities of degenerate pentads P(XXX‡) [----]. Experimental probabilities of sequences from the —OCH_3 resonance of precursor MMA-MAA and derived MMA-DPMMA copolymers (□ = MMA-MAA cp; ○ = MMA-DPMMA cp]. Experimental probabilities of triads of precursor MMA-MAA copolymers [△ and ——]. (a) alternating, (b) Bernoullian copolymers.

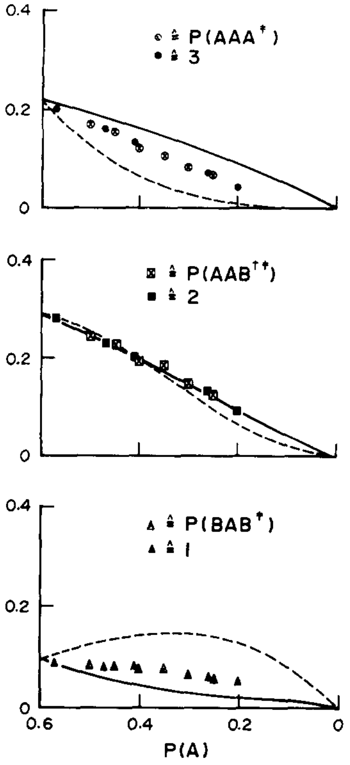

Fig. 10. Calculated probabilities of degenerate pentads P(XXX‡) [⊗, ◬, ⊠], experimental probabilities of sequences from the —OCH$_3$ resonance of derived MMA-DPMMA copolymers [●, ▲, ■], experimental triad probabilities of precursor MMA-MAA copolymers [——], and calculated Bernoullian triad probabilities [----].

not very far removed from the degenerate pentad probabilities, rendering the differentiation between the two less certain. The extent of blockiness in the copolymers can be judged from the distance of the experimental triad probabilities from the calculated Bernoullian values [----].

Since the results on alternating, Bernoullian, and blocklike copolymers support the degenerate pentad assignment for the —OCH$_3$ group situated in the MMA monomer unit, both in MMA-MAA and MMA-DPMMA copolymers, one may now also consider the —OCH< group of the DPMMA monomer unit in the MMA-DPMMA copolymers. In Fig. 11 this resonance is shown for an alternating (trace **I**) and a Bernoullian (trace **II**) MMA-DPMMA copolymer, together with a syndiotactic DPMMA homopolymer (trace **III**). Comparison of the position of the single peak of the homopolymer with the copolymers indicates that the sequence BBB (B = DPMMA-unit) is located in position 1, whereby it is *a priori* undecided whether that sequence BBB is a triad or a degenerate pentad.

The comparison of the —OCH< resonances of derived MMA-DPMMA copolymers to the resonances of the B-centred triads in the α-CH$_3$ region of precursor MMA-MAA copolymers, both of alternating character, is seen in Fig. 12. Obviously, there is no one-to-one correlation between P(1), P(2), P(3) on the one side and P(BBB), P(ABB†), P(ABA) on the other. The quantitative data are presented in Fig. 13, a plot which is analogous to that of Fig. 6. It is not possible to fit the triad data [○, △, □] to the —OCH< data [●, ▲, ■]. If the same pairing of normalized areas of peaks 1, 2 and 3 to P(BBB), P(ABB†) and P(ABA), respectively, as in Fig. 13 is used for Bernoullian MMA-DPMMA copolymers, a fit is achieved, however. This is demonstrated by Table 1, in which the areas of the —OCH< resonance P(1), P(2) and P(3), are compared with the triad data of the α-CH$_3$ group and the calculated Bernoullian triads.

The degenerate pentad probabilities have been obtained by

$$\text{P(BBB‡)} = \text{P(BBBBB)} + \text{P(BABBB†)} + \text{P(BABAB)} \qquad (7)$$

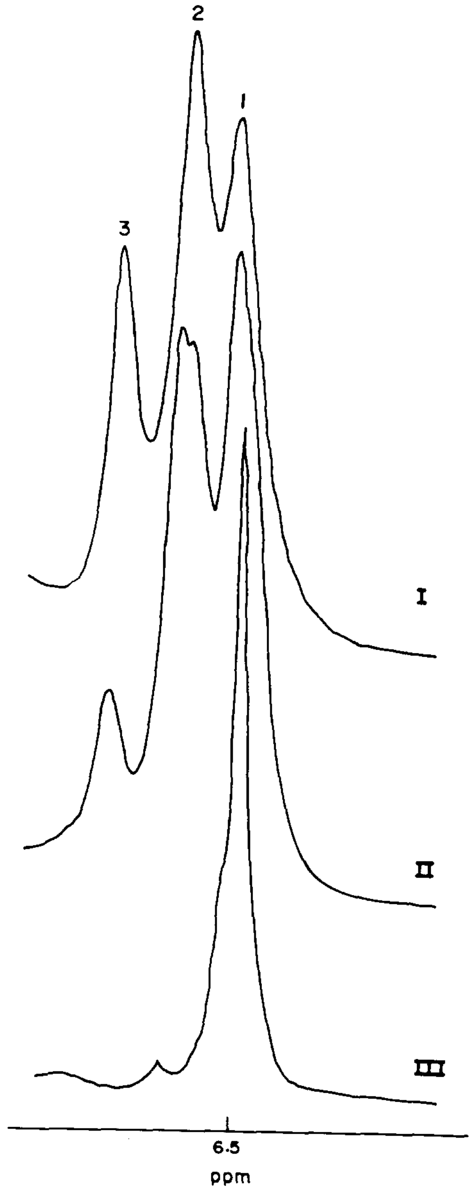

Fig. 11. —OCH<^{1}H resonance region of an alternating MMA-DPMMA copolymer of P(A) = 0.44 (trace **I**), of a Bernoullian MMA-DPMMA copolymer, P(A) = 0.33 (trace **II**), and of a DPMMA homopolymer, P(A) = 0.0 (trace **III**) (A = MMA-unit). 300, MHz CDCl$_3$, 60°, TMS.

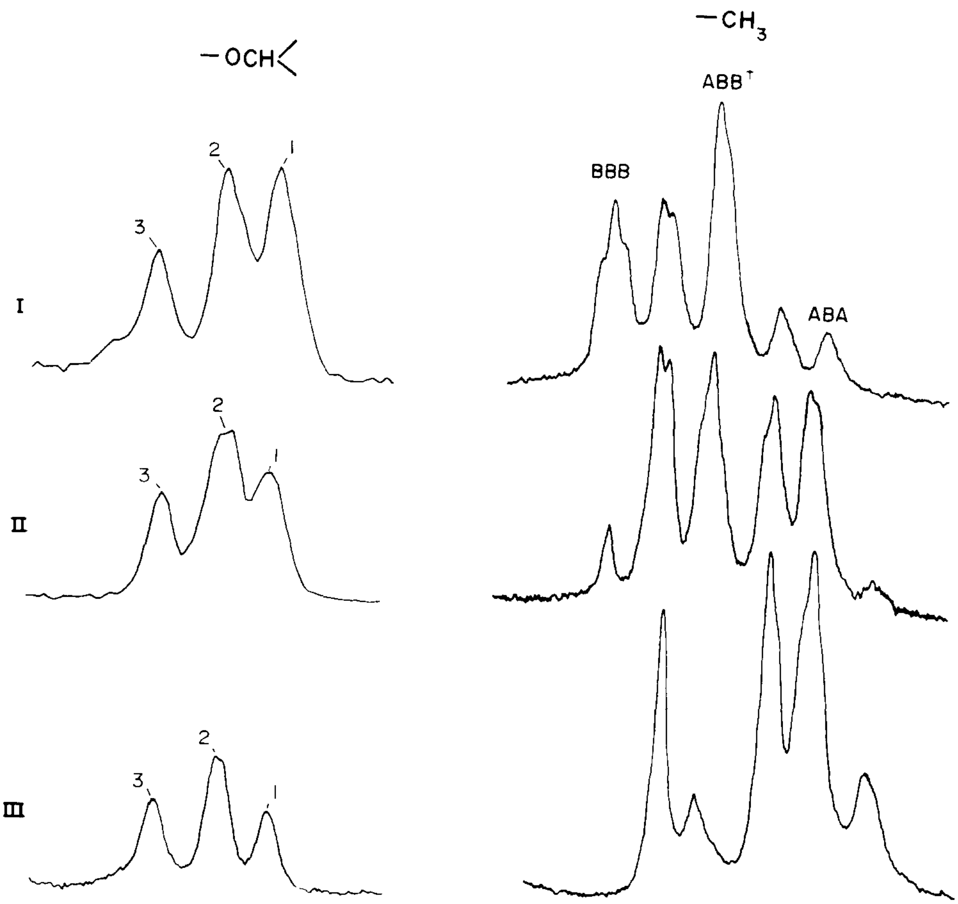

Fig. 12. ^{1}H-NMR partial spectra of the —OCH< and the α-CH$_3$ region for three alternating MMA-DPMMA and MMA-MAA copolymers. Conversion increasing from trace **I** to **III**, assignment of B-centred triads as shown (A = MMA). Two hundred and twenty megahertz, CDCl$_3$, 60°.

$$P(ABB\dagger\ddagger) = P(ABBBB\dagger) + P(AABBB\dagger) + P(ABBAB\dagger) + P(AABAB\dagger) \quad (8)$$

$$P(ABA\ddagger) = P(ABBBA) + P(AABBA\dagger) + P(AABAA) \quad (9)$$

wherein the pentad probabilities have been calculated by equations of the type of Eqns 4 to 6, using conditional probabilities of second order. In Fig. 14, the degenerate pentad probabilities [○, △, □] have been plotted together with the P(1), P(2) and P(3) [●, ▲, ■]. Both sets of points show reasonable agree-

Table 1. Relative areas, normalized to P(B) (B = DPMMA-unit), P(1), P(2) and P(3), of the peaks in the —OCH< resonance region of Bernoullian MMA-DPMMA copolymers (left three columns), probabilities of B-centred triads determined from the α-CH$_3$ resonance of the precursor MMA-MAA copolymers (middle three columns) and the calculated Bernoullian triad probabilities (right three columns)

MMA-DPMMA Cp —OCH<			MMA-MAA Cp α-CH$_3$			Bernoullian		
P(1)	P(2)	P(3)	P(BBB)	P(ABB†)	P(ABA)	P(BBB)	P(ABB†)	P(ABA†)
0.33	0.28	0.08	0.34	0.27	0.08	0.33	0.29	0.06
0.30	0.30	0.07	0.32	0.28	0.08	0.31	0.30	0.07
0.21	0.34	0.09	0.26	0.29	0.09	0.26	0.29	0.08
0.15	0.30	0.13	0.20	0.28	0.10	0.20	0.28	0.10
0.10	0.27	0.14	0.11	0.26	0.13	0.13	0.25	0.13
0.07	0.26	0.17	0.11	0.24	0.14	0.12	0.24	0.13

B = MAA-unit in MMA-MAA copolymers, or DPMMA-unit in MMA-DPMMA copolymers.

P(1) + P(2) + P(3) = P(B).

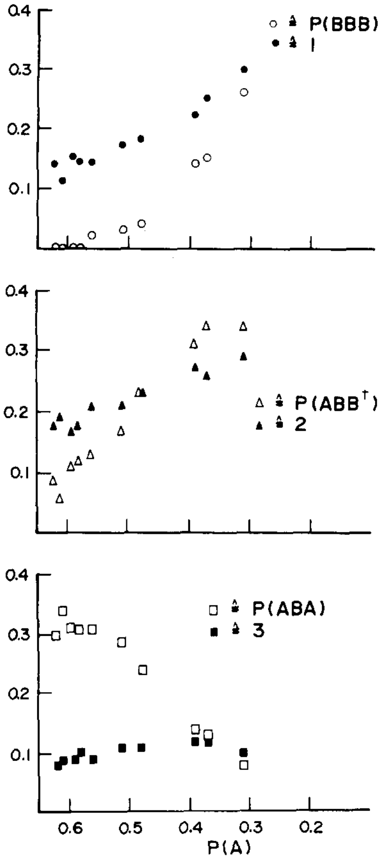

Fig. 13. Comparison of the sequence probabilities obtained from the —OCH< resonance of alternating MMA-DPMMA copolymers [● = peak 1; ▲ = peak 2, ■ = peak 3, as counted from high to low field] with the triad probabilities evaluated from the α-CH_3 resonance of the precursor MMA-MAA copolymers [○, △, □].

ment, somewhat larger deviations may be due to disturbances from spinning side bands of the aromatic resonance which is close to the —OCH< region. The sets deviate strongly from the triad probabilities of the α-CH_3 resonance [——]. Thus a degenerate pentad assignment is not only valid for the —OCH_3 group in the MMA-units, but also for the —OCH< group in the DPMMA-units, as in fact may be expected for the all-*trans* conformation depicted in Fig. 1. The assignments for the —OCH_3 and —OCH< resonance of MMA-DPMMA copolymer given previously on the basis of Bernoullian copolymers alone [6] must therefore be corrected such that for the normal triads the corresponding degenerate pentads are written: AAA → AAA‡, AAB† → AAB‡, BAB → BAB‡ etc.

It must be concluded that the ^{1}H-NMR of the alkoxy groups in syndiotactic MMA-MAA and MMA-DPMMA copolymers can be described by degenerate pentad assignments. Other syndiotactic methacrylate copolymers may show similar behaviour. The reason for this so far unobserved unusual influence of sequences on chemical shift is seen in preferred conformations of the syndiotactic sequences. Hereby the preferred conformations are likely to be the all-*trans* "backbone", or conformations close to this all-*trans* chain, corroborating the all-*trans* conformation of syndiotactic vinyl polymers by chemical shift.

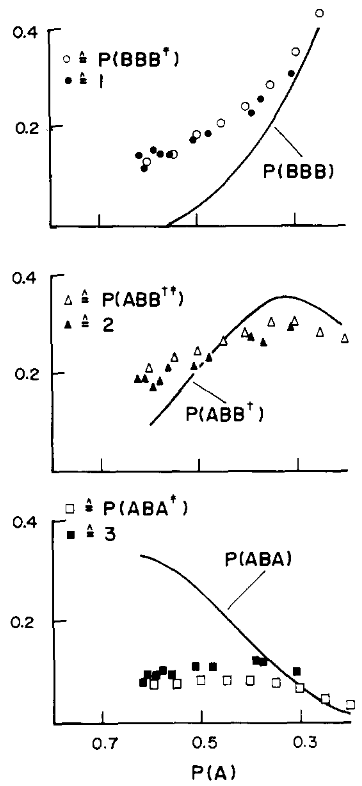

Fig. 14. Calculated probabilities of degenerate pentads P(XXX‡) [○, △, □]; experimental probabilities of sequences from the —OCH< resonance of derived alternating MMA-DPMMA copolymers [● = peak 1; ▲ = peak 2; ■ = peak 3; peak numbering from high to low field as in Fig. 11], and experimental triad probabilities from the α-CH_3 region of precursor MMA-MAA copolymers [——].

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