^{13}C n.m.r. study of the graft copolymerization of a mixture of methyl methacrylate with ethyl acrylate on amylose*

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The study of the simultaneous grafting of ethyl acrylate with methyl methacrylate onto amylose with Ce(IV) ammonium nitrate as initiator was attempted. Grafting yields obtained using gravimetric and ^{13}C n.m.r. spectroscopic methods were compared and similar results were obtained. A study of the microstructure of the grafted products obtained involving either the quantitative determination of the grafted copolymer composition or the qualitative study of the sequence distribution and the stereochemical configuration of grafted copolymer sequences has been carried out. The α-methyl group carbon, the quaternary carbon and the carbonyl group carbon have been found to be sensitive to the relative stereochemical configuration of the chain segments.

(Keywords: amylose; graft copolymer; ^{13}C n.m.r.; starch; acrylic monomer; copolymerization)

INTRODUCTION

In recent years, grafting as a technique for modifying the chemical and physical properties of natural polymers has attracted much interest from both practical and fundamental points of view. It was assumed that a combination of synthetic macromolecules with natural macromolecules might yield compounds with properties combining the advantages of both materials, leading to increased mechanical stability and biological acceptability.

In our laboratories, a redox method with the Ce(IV) ion has been used to initiate the graft copolymerization of various acrylic monomers onto amylose (Am), and the reaction conditions and the characteristic grafting yields have been exhaustively studied[1,2]. However, information on the grafting characteristics of binary monomer mixtures on polysaccharides is scarce. Consequently, we decided to study the simultaneous grafting of two different monomers to see if the result would be to produce products with different physicochemical properties. Obviously, the estimation of the composition of the whole graft copolymer, the composition of the grafted side chain acrylic copolymer and the relative percentage of the acrylic side chains with respect to the natural polymeric backbone is important in the evaluation of the utility of such products. However, estimation of the composition of copolymer containing acrylate and methacrylate monomers is difficult using normal analytical techniques[3] because of the similarity of the constituents. N.m.r. spectroscopy, however, offers a simple and rapid evaluation[4] of the copolymer composition, and is a good technique to study the relative percentage of the synthetic side chain to the natural polymeric backbone[5].

In order to obtain the microstructure and the stereochemical configuration of monomer sequences in the grafted acrylic copolymer chains, this work presents an exhaustive analysis of the sequence distribution and stereochemistry of ethyl acrylate (EA)/methyl methacrylate (MMA) copolymers by ^{13}C n.m.r. spectroscopy. The assignments of the ^{13}C n.m.r. spectra have been carried out taking into consideration those of the spectra of the corresponding copolymers synthesized at low conversion.

EXPERIMENTAL

Materials

Amylose (amylose V, Avebe, The Netherlands) was used as supplied. The EA and MMA (both supplied by Merck) were washed with dilute alkali to remove the inhibitor, after which the monomers were distilled under an inert nitrogen atmosphere at reduced pressure. The initiator solution was prepared by dissolving Ce(IV) ammonium nitrate (5.482 g, Fluka) in 1 M nitric acid (100 cm^3). All other reagents were reagent grade and used as supplied.

Methods

Using the following monomer feed compositions: EA/MMA = 80/20, 60/40, 50/50, 40/60, 20/80 and 10/90, several Am-*g*-EA/MMA copolymers were synthesized. The reactions were carried out under nitrogen in a flask equipped with a magnetic stirrer and a reflux condenser, immersed in a constant temperature bath (30°C). Two lamps (40 W) were used to maintain a constant light irradiation since the reaction is affected by variation in irradiation[6].

The procedure was to disperse Am (2 g) in bidistilled

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* This paper is dedicated to the memory of Professors G. M. Guzman and M. Valero

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water (290 cm^3). The stirred mixture was deoxygenated by bubbling a slow stream of nitrogen for 30 min. Monomer mixture of known composition was then added (0.0469 mol). After 5 min, 0.1 N Ce(IV) ammonium nitrate solution (5 cm^3) in 1 M nitric acid was added. The mixture was allowed to react over 4 h. This period was used based upon previous studies[1,2] in which the different grafting yields reached almost constant values.

The products were separated by filtration and washed with dilute nitric acid and water. Then, the ungrafted Am was extracted with 0.5 M sodium hydroxide. All homopolymers produced were removed by Soxhlet extraction using tetrahydrofuran. The pure graft copolymers were identified using ^{13}C n.m.r. spectroscopy.

In order to obtain acrylic copolymer chains free from Am, the graft copolymers (1 g) were hydrolysed with perchloric acid (60%, 1 cm^3) after swelling in glacial acetic acid (100 cm^3) for 1 h (ref. 5). The acrylic copolymer was recovered by precipitation in an ice–water bath.

N.m.r. measurements

^{13}C n.m.r. spectra were obtained on a Varian VXR300 MHz spectrometer, operating at 75.4 MHz. The conditions of operation were as follows: pulse width, 14 μs; acquisition time, 1 s; delay time, 3 s; spectral width, 16 000 Hz; 32 K data points for Fourier transformation. The spectra were produced using 20 000–50 000 transients.

The spectra of the graft copolymers were registered after swelling the sample in a mixture of d-dimethylsulphoxide and d-pyridine until a homogeneous gel was obtained. The spectra of the grafted acrylic copolymers were registered after dissolving the samples in d-chloroform. In both cases tetramethylsilane was used as an internal reference and ^{13}C n.m.r. measurements were carried out at 20–25°C.

RESULTS AND DISCUSSION

Gravimetric characterization

The yields of grafted and ungrafted acrylic copolymers were calculated from the weights of the polymer extracted and those of the hydrolysis products. The different data can be represented as: per cent grafting efficiency (%GE), per cent grafting (%G), per cent grafted acrylic copolymer (%Pol$_g$) and per cent total conversion (%TC).

$$\%GE = \frac{\text{Total weight of graft copolymer}}{\begin{array}{l}\text{Total weight of graft copolymer}\\ \quad + \text{total weight of ungrafted acrylic copolymer}\end{array}} \times 100 \qquad (1)$$

$$\%G = \frac{\begin{array}{l}\text{Total weight of graft copolymer}\\ \quad - \text{total weight of grafted Am}\end{array}}{\text{Total weight of grafted Am}} \times 100 \qquad (2)$$

$$\%Pol_g = \frac{\text{Total weight of grafted acrylic copolymer}}{\text{Total weight of monomers added}} \times 100 \qquad (3)$$

$$\%TC = \frac{\begin{array}{l}\text{Total weight of grafted and}\\ \quad \text{ungrafted acrylic copolymer}\end{array}}{\text{Total weight of monomers added}} \times 100 \qquad (4)$$

Table 1 shows the values of the above parmeters obtained with each feed composition. Comparison of the values obtained shows that the %GE values obtained from reactions in which mixtures of monomers are used are higher than those obtained for the pure monomers, with a maximum value of 89% for EA/MMA = 80/20.

Table 1 Grafting yields for the graft polymerization of EA/MMA onto Am

EA/MMA	%GE	%G Grav.[a]	%G ^{13}C[b]	%Pol$_g$	%TC
100/0	81	261	266	46	61
80/20	89	220	228	40	58
60/40	86	260	256	47	58
50/50	84	234	234	55	69
40/60	82	193	192	40	53
20/80	81	158	152	38	52
10/90	80	203	207	45	57
0/100	80	248	251	48	62

[a] Data obtained gravimetrically
[b] Data obtained from ^{13}C n.m.r.

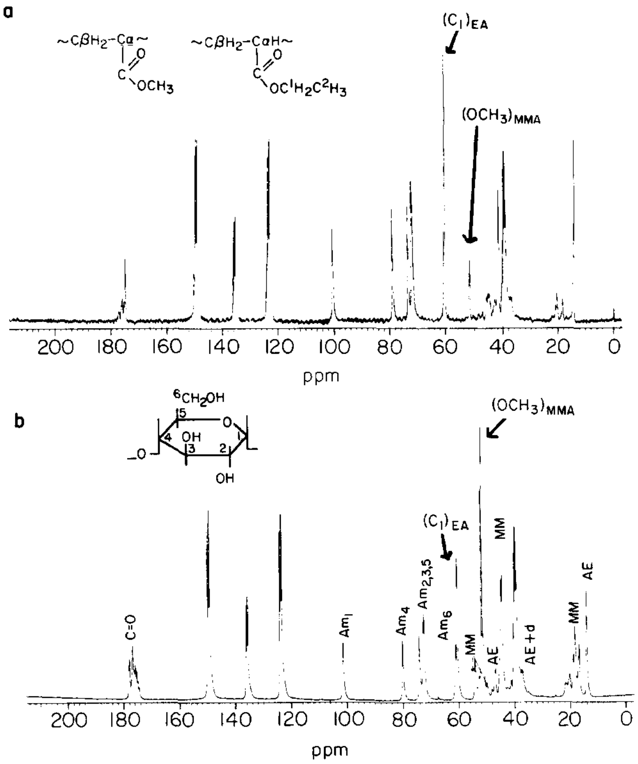

Figure 1 ^{13}C n.m.r. spectra of two graft copolymers of an EA/MMA mixture onto Am: (a) $F_{MMA} = 0.20$; (b) $F_{MMA} = 0.60$

In all cases, except for EA/MMA = 60/40, %G decreases with respect to the values obtained for the pure monomers; the same behaviour can be observed for the %Pol$_g$ values. Thus, we can say that under these reaction conditions the presence of another monomer leads to a decrease in the polymerization propagation rate.

^{13}C n.m.r. spectroscopy

Figure 1 shows ^{13}C n.m.r. of two Am-*g*-EA/MMA samples obtained from monomer feed compositions of 80/20 and 40/60, respectively. As we have reported in a previous paper[5], from these spectra we can calculate %G directly without previous degradation of the products, by comparing representative peaks of each component of the grafted product (Am, EA and MMA), but this is possible only if we take into account the spin-lattice relaxation time of each carbon type, and by registering the spectra under suitable conditions[8]. The %G values

Table 2 Comparison between monomer ratio EA/MMA in the feed and in the grafted copolymer

Feed composition (*F*)	Grafted polymer composition (*f*)
80/20	79/21
60/40	56/44
50/50	45/55
40/60	31/69
20/80	13/87

obtained gravimetrically and by ^{13}C n.m.r. agree to within an error of <2% as can be seen from *Table 1*. From these spectra the composition of the grafted polymer can also be calculated, taking a representative peak of both monomer units. In this case, the selected peaks were of the $-OCH_3$ carbon of the MMA unit and of the $-OCH_2-$ carbon of the EA unit, appearing at 51.76 and 60.50 ppm, respectively. Using this approach a correlation between the grafted copolymer composition and the feed composition was established (see *Table 2*).

It must be taken into account that these reactions were carried to total conversion, so that calculation of the reactivity ratios is of no value. However, it can be observed that there is a major proportion of methacrylate in the grafted copolymer as could be expected from the reactivity ratio ($r_{MMA}=2.03$, $r_{EA}=0.24$)[9], i.e. the side grafted chains are slightly richer in methacrylate units than in acrylate units.

Spectrometric ^{13}C n.m.r. characterization of the products allows the study of the microstructure of the grafted chains.

Grafted copolymer microstructure

To study the sequence distribution and stereoregularity of a copolymer it is necessary to know the reactivity ratios of both monomers at the conditions that the reactions were carried out. This is of no value in our case because of the high conversions obtained.

From a stereochemical point of view we assume that the configurational sequence distribution may be described according to Bernoullian statistics with the isotacticity and coisotacticity parameters σ_{MM}, σ_{MA}, σ_{AM} and σ_{AA}, as defined by Bovey[10,11] and Coleman[12], where σ_{MA} is the probability of generating a *meso* dyad between an 'M' (MMA) ending growing radical and an incoming 'A' (EA) monomer. We know values for $\sigma_{MM}=0.20$ and $\sigma_{AA}=0.44$, corresponding to the free radical polymerization of MMA and EA, respectively[13,14]. The coisotacticity parameters σ_{AM} and σ_{MA} are not directly accessible but it is reasonable to assume[15,16] that $\sigma_{MA}=\sigma_{AM}=\sigma^*$. This parameter must be determined from the analysis of the stereochemical configuration distribution derived from n.m.r. data. In our case, this calculation does not make any sense for the same reason expressed above for the reactivity parameters. Therefore only a qualitative study of the microstructure will be carried out, but taking into account the results obtained in a previous study for the same copolymer polymerized at low conversion[17].

Using the data obtained from the copolymerization of EA and MMA carried out at low conversion and based upon these spectra a high similarity between the splitting of the bands corresponding to the low conversion copolymers and the bands corresponding to the copolymers obtained from the hydrolysis of the graft copolymers (high conversion) has been observed. We will demonstrate that this similarity is good enough to be used for the basis of studying the microstructure of the grafted chains from a qualitative point of view.

The ^{13}C n.m.r. spectra of the grafted acrylic samples prepared from different feed compositions are shown in *Figure 2*. The assignments of the resonance peaks have been made on the basis of results of the off-resonance decoupling and by comparison with spectra of analogous

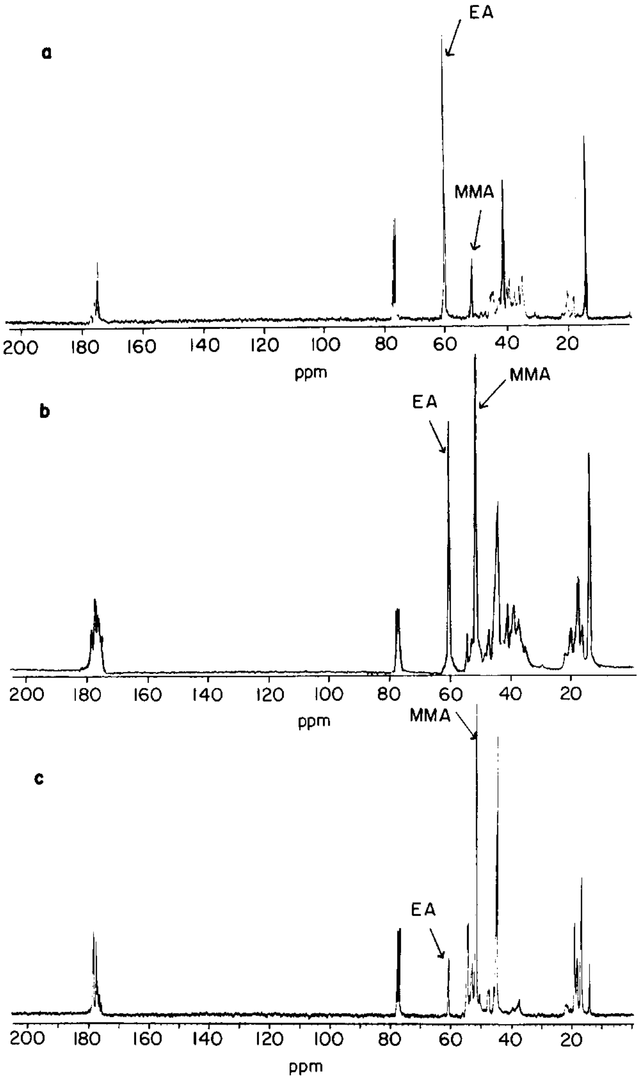

Figure 2 ^{13}C n.m.r. spectra of several acrylic copolymers isolated from their grafted copolymers onto Am: (a) $F_{MMA}=0.20$; (b) $F_{MMA}=0.50$; (c) $F_{MMA}=0.80$

Table 3 ^{13}C n.m.r. chemical shifts of EA/MMA copolymer with d-chloroform as solvent

Chemical shift (ppm)	Assignment
174–179	C=O (EA, MMA)
76–78	d-Chloroform
60.60	C_1 (EA)
52–54	C_β (MMA)
43–46	C_α (MMA)
51.76	$-OCH_3$ (MMA)
33–38	C_β (EA)
15–22	$(CH_3)^\alpha$ (MMA)
14.05	C_2 (EA)

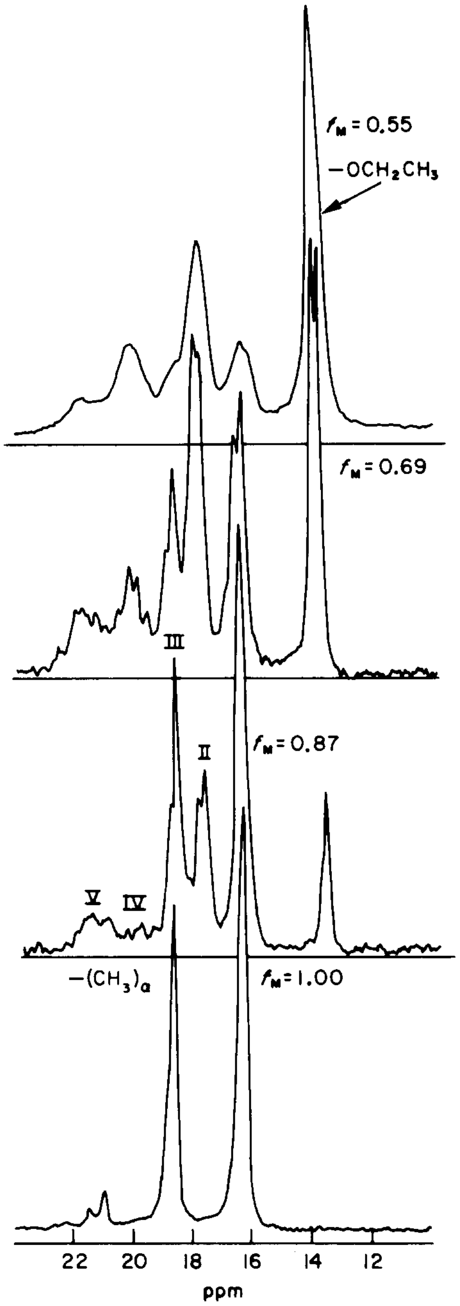

Figure 3 Expanded ^{13}C n.m.r. pattern of the $-(CH_3)_\alpha$ resonance signals of EA/MMA copolymers

chemical groups taken from the literature[18–22]. These assignments are listed in *Table 3*.

It is known that the ^{13}C n.m.r. resonance signals of the carbonyl carbon of poly(ethyl acrylate)s[13] in general do not give information regarding the stereochemical configuration of monomer sequences. However, the backbone methylene carbon splits into a signal assigned to a tactic diad or tetrad distribution. However, we have seen[14] in the ^{13}C n.m.r. spectrum of poly(methyl methacrylate) (PMMA) that $-C{=}O$, $-(CH_3)_\alpha$ and the quaternary carbon split into signals that can be assigned to a tactic triad or pentad distribution. Consequently, in order to describe the microstructure and the stereochemical configuration we have concentrated on the resolution of the $-(CH_3)_\alpha$ and quaternary carbon of M centred sequences and the carbonyl group of both M and A centred sequences.

$-(CH_3)_\alpha$ resonance signals. Figure 3 shows the expansion of the resonance signals assigned to the $-(CH_3)_\alpha$ carbon of MMA units. A careful analysis of the signal between 16 ppm and 24 ppm allows us to define five resonance bands (I, II, III, IV, V) whose intensities change drastically with the composition of the copolymer samples. These signals have been analysed on the basis of MMA centred signals, taking into account the configurational effect on the chemical shift of the $-(CH_3)_\alpha$ carbon of the MMA centred units.

By observing the spectra in *Figure 3*, it can be easily appreciated that peaks I (16.37 ppm), II (18.63 ppm) and V (21.24 ppm) correspond to the chemical shifts of (*rr*), (*mr* or *rm*) and (*mm*) triads of PMMA. Consequently with this and with our observations of the spectra registered from the low conversion copolymer samples[15], we have assigned these peaks to the same kind of MMM triads in the high conversion copolymer chains. Also, as in the low conversion spectra, the intensities of signals II (17.89 ppm) and IV (20.21 ppm) increase with increasing EA mole fraction. We again assign these signals to MMA or AMM and AMA triads independently of their stereochemistry.

Quaternary carbon resonance signals. Figure 4 shows expansions of the quaternary carbon of the MMA units in the copolymers obtained at various feed compositions. This figure shows splitting into three peaks whose intensities change with the composition of the copolymer. By comparison of the resonance signals of this carbon with that in the PMMA spectrum[22] we can clearly assert that they correspond to the M centred triads independently of the composition but with the following stereochemical configuration:

syndiotactic triads (*rr*)	$\delta = 44.44$ ppm
heterotactic triads (*mr* or *rm*)	$\delta = 44.79$ ppm
isotactic triads (*mm*)	$\delta = 45.43$ ppm

Carbonyl carbon resonance signals. Figure 5 shows the expansion of the carbonyl carbon resonance signal for the three samples of EA/MMA copolymer synthesized from different monomer feeds. Seven different signals (I–VII) can be easily seen. Their intensities change drastically with composition. Assignment of these signals has been carried out in terms of M and A centred triads on the basis of the different chemical shifts of the carbonyl groups for PMMA (*Figure 5*) and for poly(ethyl acrylate) (174.46 ppm).

Table 4 EA/MMA copolymer carbonyl group assignments

Signal number	Chemical shift (ppm)	Copolymer sequence	
		Composition	Configuration
I	177.89	MMM	(*rr*)
II	176.76	MMM	(*mr*), (*rm*)
		MMA	(*rm*), (*rr*)
		AMM	(*mr*), (*rr*)
III	176.36	MAM	–
IV	175.82	MMM	(*mm*)
		MMA	(*mr*)
		AMM	(*rm*)
		AMA	(*mm*), (*mr*, *rm*)
V	175.46	AAM	–
		MAA	–
VI	174.84	AMA	(*rr*)
VII	174.41	AAA	–

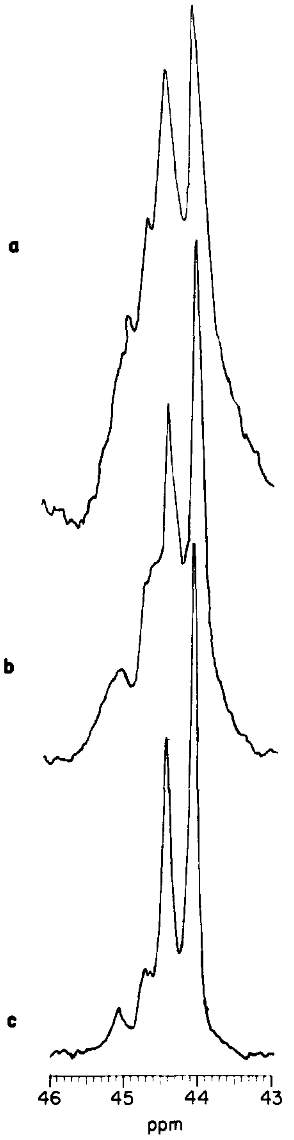

Figure 4 Expanded ^{13}C n.m.r. pattern of the quaternary carbon resonance signals of the EA/MMA copolymers: (a) $F_{MMA}=0.50$; (b) $F_{MMA}=0.60$; (c) $F_{MMA}=0.80$

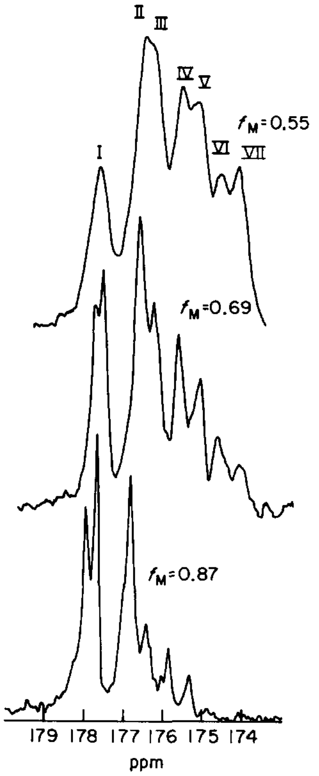

Figure 5 Expanded ^{13}C n.m.r. pattern of the carbonyl resonance signals of M and A centred sequences

We consider that the EA centred triads are not sensitive to the configuration, whereas the MMA centred triads may be sensitive to the stereochemical configuration of triad sequences. These observations allow us to suggest the same assignment (*Table 4*) as was indicated in the carbonyl study of the copolymers symthesized at low conversion.

CONCLUSIONS

1. The copolymers have been characterized gravimetrically and spectroscopically, and good agreement has been found between the results.
2. From the point of view of acrylic grafted chains ^{13}C n.m.r. spectroscopy has enabled us to show that MMA is more reactive than EA under our reaction conditions, as in other radical polymerizations.
3. The microstructures of acrylic copolymers grafted onto Am are the same as those copolymers synthesized at low conversion. The quaternary carbon and α-methyl group carbon signals are sensitive to the relative stereochemical configuration of the chain segments, in terms of MMA centred triads, being independent of composition in the quaternary carbon signal case. However, the carbonyl group signal is sensitive to the relative stereochemical configuration of the chain segments, in terms of MMA centred triads, giving even pentads; it is not sensitive to the stereochemical configuration in terms of EA centred triads.

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