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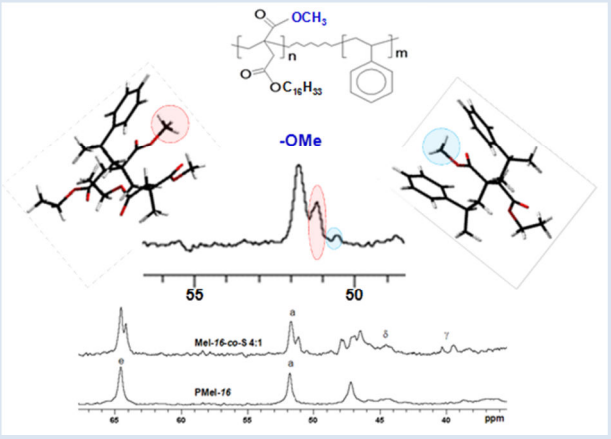
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NMR STUDY OF THE MICROSTRUCTURE OF METHYL-*N*-HEXADECYL ITACONATE WITH STYRENE COPOLYMERS

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ABSTRACT

A series of copolymers of styrene with methyl-*n*-hexadecylitaconates using different compositions in the feed have been prepared in bulk via radical at 60ºC with AIBN as initiator. In most of the cases the copolymers were obtained in good yields and the increase of one of the monomers in the feed mixture raises its amount in the copolymer and in some cases the copolymer composition is close to the feed ratio. The copolymers molecular structure was characterized by FTIR and a detailed study of NMR spectroscopy which included ^{1}H, ^{13}C and bidimentional experiments. The NMR studies indicate that the copolymers have a mainly random distribution of the monomeric units and the chemical shifts of the signals, especially the OCH_3 and OCH_2 are strongly influenced by the neighbor environment. ^{13}C NMR chemical shifts were also analyzed by simulation studies using ab initio Gauge-Independent Atomic Orbital (GIAO) calculations; we observed a good correlation between the experimental and calculated values.

Keywords: Alkyl itaconates, Styrene, Copolymers, NMR, Gauge-Independent Atomic Orbital (GIAO) method.

ESTUDIO DE LA MICROESTRUCTURA DE COPOLÍMEROS DE METIL-*N*-HEXADECIL ITACONATO CON ESTIRENO

RESUMEN

En este trabajo se preparó una serie de copolímeros de estireno con metil *n*-hexadecilitaconato con diferentes composiciones. Las polimerizaciones se llevaron a cabo por vía radical, en masa a 60ºC y AIBN como iniciador. En la mayoría de los casos los copolímeros se obtuvieron con buenos rendimientos y el incremento de cualquiera de los monómeros en la relación de alimentación incrementa su contenido en el copolímero, observándose en algunos casos que la composición del copolímero es bastante próxima a la relación usada en la alimentación. La estructura molecular de los copolímeros fue caracterizada mediante FTIR y un detallado estudio de RMN que incluyó ^{1}H, ^{13}C y experimentos bidimensionales. Los estudios de RMN indicaron que los copolímeros son básicamente al azar y que los desplazamientos químicos de muchas señales, y de modo particular las de los OCH_3 y OCH_2 correspondientes a las unidades de itaconato, están fuertemente influenciados por el entorno vecino. Los desplazamientos químicos de RMN-^{13}C fueron analizados mediante estudios de simulación, donde se empleó el método GIAO (por sus siglas en inglés Gauge-Independent Atomic Orbital), observándose una buena correlación entre los valores experimentales y los calculados.

Palabras Claves: Itaconatos de n-alquílo, Estireno, Copolímeros, RMN, método GIAO.

1. INTRODUCTION

The early works of Cowie related to the synthesis and the study of polyitaconates at the beginning of the 70's [1-4] inspired many researchers to investigate in this area and the interest for the study of these polymers have been continued until today. Most of the interest of these researches has been oriented to the study of their solid state and dissolution properties [4-11], as well as their thermal degradation [12-17]. The copolymerization of itaconates with vinyl monomers has also been studied [18-26].

The microstructure of polyitaconates has been studied by NMR spectroscopy and probably the first study on the tacticity of polyitaconates was performed by Horta, *et al*, in 1987 [27]. In this paper it was established that the carbonyl groups are sensitive to the stereochemistry when are evaluated by ^{13}C-NMR. Subsequent studies confirmed these results [8, 28], as well as -C**H$_2$**-COO protons are sensitive to the stereochemistry in ^{1}H NMR [9]. Solid state ^{13}C CP/MAS NMR has been used to study the crystallization of *n*-alkyl side chain in comb-like poly(*n*-alkyl-itaconate)s [8, 9]. Composition and structure of some copolymers of *n*-alkylitaconate and styrene have been studied by ^{13}C NMR [26, 29].

On the other hand, theoretical calculation of the chemical shielding tensors (CST) parameters by using ab initio techniques has become a powerful tool in the investigation of molecular structure. The ability to accurately evaluate and correlate the magnitude of the CST with variations in bond angles or the nearest-neighbor interactions has seen a number of recent applications in the investigation of molecular structure [30]. The gauge- independent atomic orbital (GIAO) method [31-33] at the Density Functional Theory (DFT) level is among the most popular and versatile methods available in the determination of the chemical shifts [34-39].

In this work we report the copolymerization and a detailed study of the microstructure by NMR of a series of random copolymers of methyl-*n*-hexadecyl itaconate (MeI-16) with styrene with various compositions. The ^{13}C NMR chemical shielding tensors for the methoxy group of the itaconate unit in this series of copolymers has been also analyzed using ab initio GIAO calculations and the results compared with the experimental ones.

2. EXPERIMENTAL PART

2.1 Materials

Styrene (Aldrich) was dried over CaH_2 and distilled under reduced pressure.

Itaconic acid (Aldrich 99.9 + %), 1-hexadecanol (Aldrich 99%) and other chemicals (analytical grade or better) were used without further purification.

2.2 Monomer synthesis

Mono-n-hexadecyl itaconate (MI-16) was synthesized by esterification of itaconic acid with the hexadecanol using acetyl chloride as catalyst [9]. Methyl-*n*-hexadecyl itaconate (MeI-16) was synthesized by methylation of the mono-n-hexadecyl itaconate (MI-16) with diazomethane following methods previously reported [6, 8-9].

2.3 Copolymerization

Copolymerization of MeI-16 with styrene was carried out in bulk at 60ºC under nitrogen atmosphere using AIBN (1% molar) during 48 hours. The molar ratio itaconate/styrene in the feed was varied as 1:0; 4:1; 2:1; 1:1; 1:2 and 0:1. The obtained copolymers were purified by dissolution in chloroform and precipitation with methanol. The purification process was repeated several times. In some cases it was necessary to boil the copolymers with methanol to eliminate traces of unreacted itaconate. Yields were determined gravimetrically based on the weight of the starting monomers.

2.4 Characterization

Infrared spectra were recorded on a Perkin-Elmer 2000 instrument from KBr discs samples or films prepared by casting.

NMR spectra were obtained with a Bruker Avance DRX 400 spectrometer at room temperature from samples dissolved in benzene-d_6.

2.5 Theoretical method

As a first approach to modeling the polymer structure, in this work we used a minimalist model, in which the general structure is represented by trimeric forms of itaconate (I) and styrene (S) combination units. The trimeric units were formed as follow:

III, IIS, and SIS

To determine the chemical shifts values, an accurate determination of the molecular geometry is

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necessary, that is why, the structures of all compounds, polymer fragments and tetramethylsilane (TMS), were optimized by using the hybrid density functional B3LYP method [9] and the 6-311G++(d,p) basis set. As well known, the chemical shift value is correlated with by the isotropic chemical shielding value (σ_{iso}), defined as [30]:

$$\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \qquad \text{(Eq. 1)}$$

where the σ_{ii} are the shielding tensor at the principal coordinates axes of the molecular system.

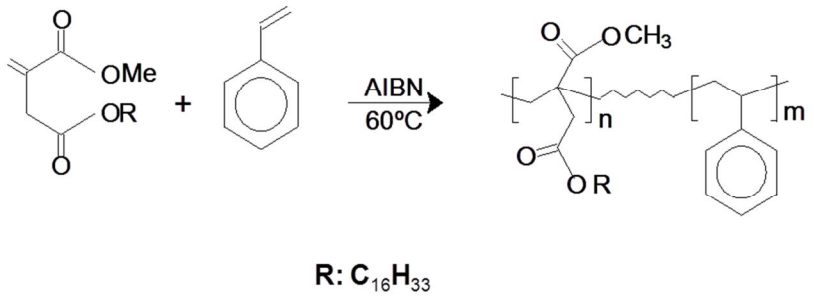
The calculated ^{13}C NMR chemical shifts values and the energy minimized structures for all structures were calculated using the GAUSSIAN 98 software [40]. The ^{13}C chemical shifts were calculated with GIAO method at the DFT level of theory were employed, in which the B3LYP functional and the 6-311G++(d,p) basis set were used.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of the copolymer series

In this work, the copolymerization between MeI-16 and styrene was carried out using the reaction conditions described above.

The reaction is represented in Scheme 1 and the results are shown in Table 1.



Scheme 1. Copolymerization reactions between methyl-*n*-hexadecyl itaconate and styrene.

Table 1. Results of the copolymerization of MeI-*16* with styrene[(a)].

MeI-16:S[(b)] (*mol:mol*)	*MeI-16:S*[(c)] (*mol:mol*)	*Yield*[(d)] (*%*)	$M_w \cdot 10^{-5}$[(e)] (*Da*)	M_w/M_n[(e)]	T_d[(f)] (*ºC*)
1:0	-	42.4	0.70	3.68	371
4:1	2.6:1	55.3	0.29	2.15	401
2:1	1.3:1	47.3	0.64	3.05	387
1:1	1:1.2	47.1	0.80	3.21	380
1:2	1:1.6	56.3	0.79	3.93	387
0:1	-	92.4	1.59	2.17	436

[(a)] In bulk at 60ºC during 48 hours under nitrogen atmosphere using AIBN (1% mol/mol). [(b)] Feed composition. [(c)] Copolymer composition measured by ^1H NMR. [(d)] Determined from total monomer amount. [(e)] From GPC masured in THF at 40ºC. [(f)] Decomposition temperature corresponding to the maximum of the DTGA curve.

As it is shown, all the copolymers were obtained with yields in the order of 50% and in most cases the weight-average molecular weight (M_w) near 70,000 Da. The increase of one of the monomers in the feed mixture raises its amount in the copolymer and in some cases the copolymer composition is close to the feed ratio. The Thermal stability of the copolymers, as recently reported by us, is intermediate between both homopolymers [41].

In Figure 1 are shown all the FTIR spectra of the

series of MeI-16-*co*-S together with those of poly(methyl-*n*-hexadecyl itaconate) (PMeI-16) and polystyrene (PS). The spectra of all copolymers were similar and exhibit the characteristic bands of both moieties and the only difference is due to the intensity of the bands.

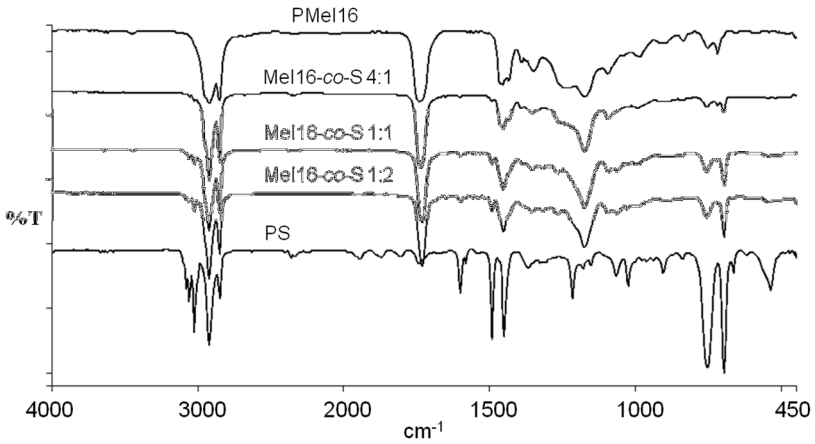


Figure 1. FTIR spectra of the series of MeI-16-*co*-S copolymers and of both homopolymers.

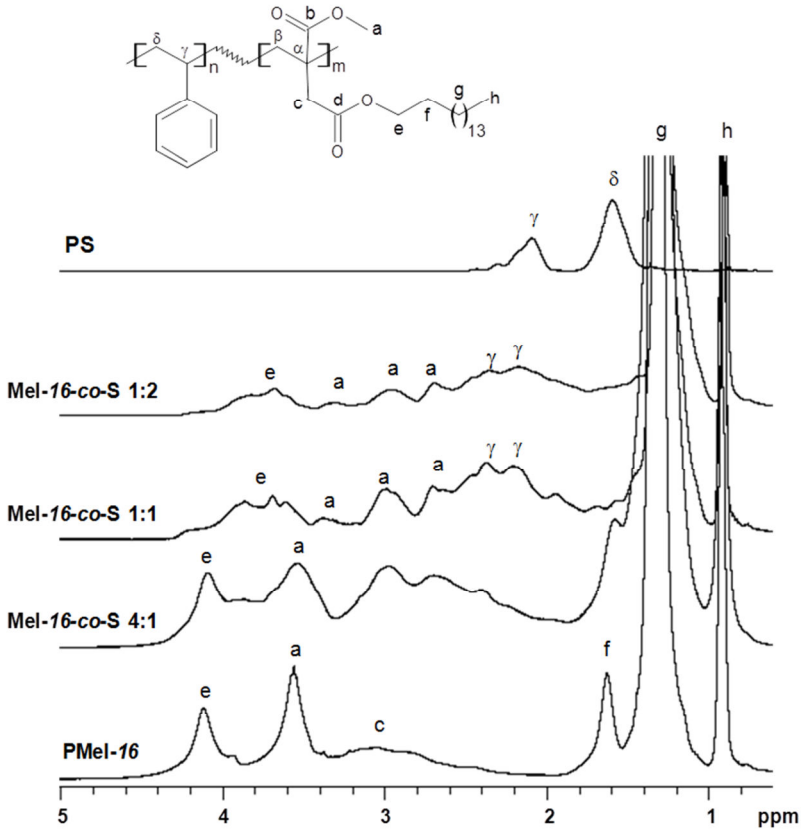


Figure 2. Expanded ^{1}H NMR spectra in the zone of 0 to 5 ppm for the PMeI-16-*co*-S copolymer series carried out in benzene-d_6 at 25ºC.

There it can be seen qualitatively that the most important bands of the styrene moiety, 3100-3000 cm^{-1} (stretching =C-H of the aromatic ring), 1602 cm^{-1} (symmetric ring stretch), 1500 cm^{-1} (ring stretch), 1450 cm^{-1} ("sideways" ring stretch) 760 cm^{-1} (out-of-plane ring C-H bending) and 700 cm^{-1} (out-of-plane ring bending), increase their intensities in comparison with those of the itaconate, as the amount of itaconate diminishes in the copolymers composition.

As in FTIR spectra, the intensity of the signals in the ^{1}H NMR spectra (Figure 2) changes following the composition. All the copolymers compositions are reported in Table 1 and were determined by ^{1}H NMR in the same way as we described in a previous paper [41].

With the aim of investigating the structure and the distribution of the monomers in the main chain of the copolymers, a detailed NMR study was performed with the whole series. In Figures 2 and 3 the ^{1}H and ^{13}C NMR spectra of all the copolymers synthesized in this work with the corresponding peak assignments and compared with poly(methyl-*n*-hexadecyl itaconate) (PMeI-16) and polystyrene (PS) are shown.

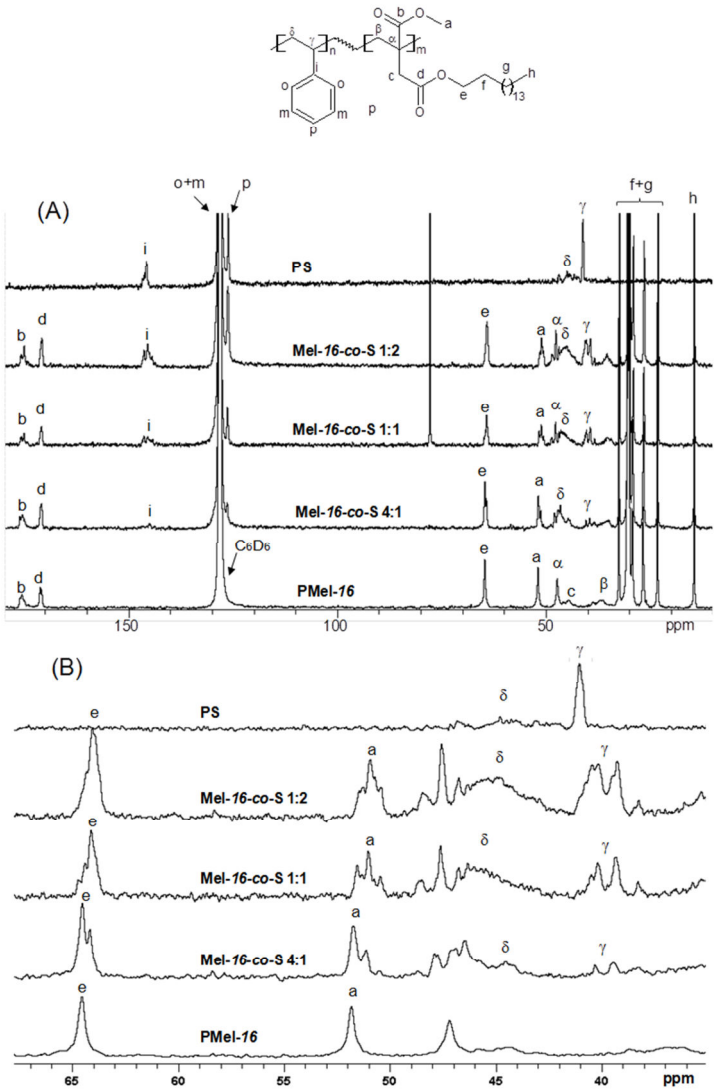


Figure 3. (A) ^{13}C NMR spectra with the corresponding peak assignments for the PMeI-16-*co*-S copolymer series carried out in benzene-d_6 at 25ºC. (B) Expanded ^{13}C NMR spectra of the PMeI-16-*co*-S copolymer series on the zone of 35 to 70 ppm.

There it can be appreciated that the signals of OCH_3 (a) and OCH_2 (e), are not only shifted to high field in comparison with the corresponding signal of the homopolymer, but also are highly split and broadened. This split rises with the increase of the styrene proportion in the copolymer. In the case of the OCH_3 (a) at least three types of protons at 3.32, 2.96 and 2.71 ppm can be observed, whereas for the OCH_2 (e) the signal experiments a broadening between 4.25 and 3.5 ppm. The corresponding signals in the ^{13}C NMR spectra (51.9 ppm for OCH_3 (a) and 64.5 for OCH_2 (e)) show a similar behavior as may be appreciated in Figure 3 (Figure 3B shows the expanded zone between 35 and 65 ppm for a better view). For example, in the case of the OCH_3(a) the singlet that appears at 52 ppm in the homopolymer splits at least in three signals at 51.7, 51.0 and 50.5 ppm as will be explained later. This fact not only indicates that the copolymerization was successfully carried out, but also suggests that the units of styrene and itaconate are randomly distributed in the copolymer chain as we have reported recently [29].

The assignment of both, proton and carbon signals, were done by the HMQC bidimensional spectra. Figure 4 shows the HMQC spectra of the MeI-16-*co*-S 1:2 copolymer with the corresponding cross–peak of the signals. There is a clear interaction between the 2.71 and 2.96 ppm signals in the ^{1}H NMR with those that appears centered at 51 ppm in the ^{13}C NMR assigned to the OCH_3 carbon. It is noticeable that the interaction between the signals of the OCH_3 (a) at about 3.55 ppm in the ^{1}H NMR and 51.9 ppm in the ^{13}C NMR in the homopolymer is not observed in the copolymers. Finally the broad signal that appears between 3.5 and 4.0 ppm shows a very strong interaction with the signal at 64.5 ppm in the ^{13}C NMR confirming that the former corresponds to the OCH_2 (e).

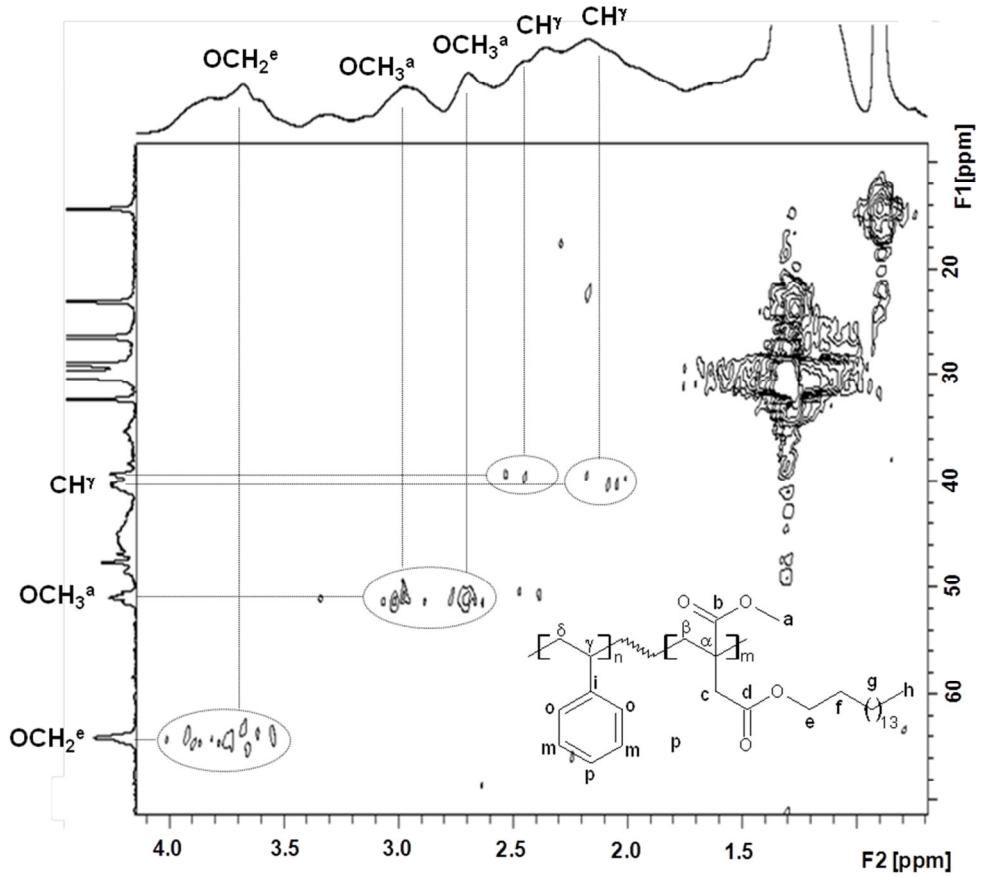


Figure 4. HMQC spectrum of the MeI-*16-co*-S 4:1 copolymer carried out in benzene at 25ºC.

If a simple model of a triad is used to explain the microstructure, the signals in the homopolymer would correspond to a sequence of itaconate-itaconate-itaconate (III). When a small amount of styrene is incorporated in the polymer, two new signals of less intensity at 51.0 and 64.0 ppm appear in the ^{13}C NMR together with the formers (Figure 3 b). Both signals may be considered as corresponding to an itaconate-itaconate-styrene (IIS) sequence. For the OCH_3, another very week peak at 50.5 ppm, attributed to a SIS sequence is also observed. With the increase of the styrene content in the copolymer these new signals raise in relation to the original ones. The splitting and the broadening of these signals are due to a change of the chemical environment produced when an itaconate unit is adjacent to a styrene one; the shift to higher field is probably due to the itaconate´s OCH_3 or OCH_2 groups are located inside the protection cone of the aromatic ring of the styrene unit as may be observed in Figure 5. The structures shown in Figure 5 were generated by theoretical calculations of chemical shielding with ab initio methods and will be discussed later. For example, for the methoxy group, the signal that appears at 51.0 ppm is due to the itaconate unit which is located in the center of a IIS where the OCH_3 group is oriented toward the aromatic ring, as shown in Figure 5 A; whereas the signal at 50.5 ppm is due to a situation where the OCH_3 group of the itaconate in a SIS triad is adjacent to two aromatic rings as may be seen in Figure 5B. The signal centered at 64.0 ppm becomes broader with the increase of the styrene content in the copolymer, probably for the same reasons, the OCH_2 group of the itaconate is oriented towards the phenyl ring in the IIS and SIS triads.

To corroborate these facts, we carried out some theoretical calculations of chemical shielding with ab initio methods employing optimized conformations obtained by using the hybrid density functional B3LYP method and the 6-311G++ (d,p) basis set. As we mentioned above, from these calculations two energy minimized structures shown in Figure 5 were generated. The first one corresponding to the IIS situation in which an itaconate unit is between a styrene and other itaconate unit (Figure 5A). The second is due to a SIS situation where an itaconate unit is between two styrene units (Figure 5B). For both situations is clear that the methoxy group of the itaconate unit is located inside the protection cone of the aromatic ring of the neighbor styrene unit as suggested by NMR experiments.

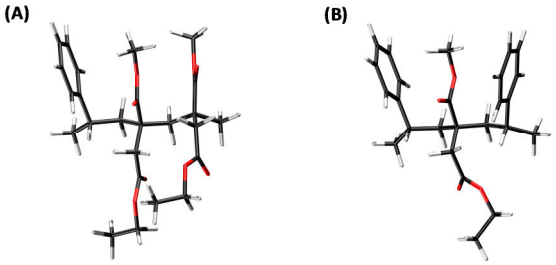


Figure 5. Simulated structures of two different conformations adopted by the MeI-16-*co*-S showing the relative orientations of OCH_3 respect to the aromatic ring. (A) OCH_3 next to an aromatic ring in a sequence IIS. (B) OCH_3 between two aromatic rings in a sequence SIS.

The calculated ^{13}C NMR chemical shifts for the methoxy groups of the above structures are given in Table 2. In order to compare the predicted values with experimental results, we subtract the calculated σ_{iso} values from that of the TMS molecule modeled.

As may be seen in Table 2, the calculated chemical shift values for the methoxy group agree adequately with those obtained experimentally, corroborating the presence of IIS and SIS sequences in the copolymer chain. It can be inferred that these results are also applicable to those observed chemical shift of the OCH_2 group.

Table 2. Isotropic chemical shielding values for the methoxy group in ^{13}C NMR compared with experimental data.

Structure	*Calculated ^{13}C NMR shift (in ppm)*[(a)]	*Observed ^{13}C NMR shift (in ppm)*[(b)]
S-I-S	50.8	50.5
I-I-S	51.6[(c)]	51.0
I-I-S	52.4[(d)]	-
I-I-I	52.9	51.9[(e)]

[(a)] Calculated with GIAO method at the DFT level of theory, in which the B3LYP functional and the 6-311G++(d,p) basis set were used. [(b)] Carried out in benzene-d_6 at 25ºC. [(c)] Shift of the methoxy group of the Itaconate at the middle. [(d)] Shift of the methoxy of the Itaconate of the extreme. [(e)] Chemical shift measured for the homopolymer 51.9 ppm.

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The shift of both signals to higher field occurs as mentioned when the methoxy or methyleneoxy groups are on the same side of the ring and the group remains in the protection cone of the ring. There is clear that the effect on the OCH_3 is greater than on the OCH_2 because the former is closer to the benzene ring.

The additional signals located between the described ones would correspond to intermediate situations, but it is necessary to conduct more conformational studies on molecular stability to corroborate this fact.

The styrene ring also influences the second methylene of the itaconate side chain (f in Figure 2) shifting this signal in the ^{1}H NMR to higher field, overlapping it over interior protons (g). This situation was observed in the COSY spectrum (not shown here).

The itaconate units also have an effect over the styrene signals in ^{13}C and ^{1}H NMR. The methyne carbon of the styrene unit (γ) also undergoes splitting in two main signals centered at 40.3 y 39.3 ppm in the ^{13}C NMR as may be observed in Figure 3. When the copolymer has a high styrene content (MeI-16-*co*-S 1:2), the signal centered in 40.3 ppm is broad, slightly split in two peaks at 40.5 and 40.2 ppm and is more intense than that located at 39.3 ppm. The splitting of the low field signal is possible due to the presence of the sequences SSS and SSI, while that appearing at 39.3 ppm is probably caused by the ISI triad. When the itaconate content increases, the signal at 40.5 ppm decreases in relation to the others and is not even present for MeI-16-*co*-S 4:1 copolymer. This fact allows to assign this peak to the SSS sequence and the relative increase of the signal at 39.3 ppm confirms that it is due to the ISI sequence.

The CH proton (γ) is also shifted to low field and split in at least two broad signals at 2.2 and 2.4 ppm in the ^{1}H NMR spectra. In the HMQC spectra (Figure 4) the correlation of the signals undoubtedly confirm that the low field signal corresponds to the ISI sequence, whereas the other must correspond to the SSI and SSS sequences. These signals overlap the broad CH_2-COO (c) signal.

The presence of styrene units also affects the multiplicity and intensity of carbonyl signals (b) and (d), this effect being more prominent in the former one due to its proximity to the aromatic ring as may be seen in the expanded ^{13}C NMR spectrum in the zone between 170 and 177 ppm shown in Figure 6.

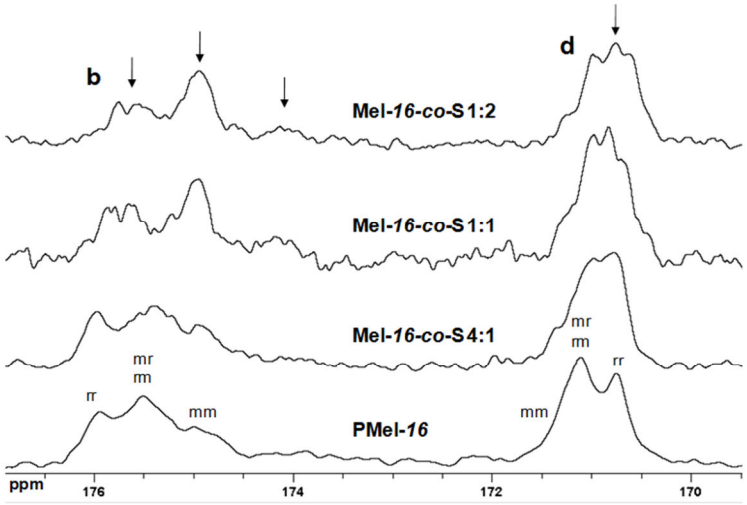


Figure 6. Expanded ^{13}C NMR spectra of the PMeI-16-*co*-S copolymer series from 170 to 177 ppm. The new peaks in the copolymers are indicated with arrows (see text).

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For the copolymers with high content of styrene, the signal of the vinyl carbonyl (b) shows significant changes. The peak corresponding to the syndiotactic triad that appears at 176 ppm, suffers a slight shift to higher field accompanied with splitting, likewise the heterotactic and syndiotactic signals also shifted at 175 and 174 ppm respectively. The interaction at three bonds between the MeO protons that appears at 2.7 and 3.0 ppm with the signal at 175 ppm and the one at 3.3 ppm with the carbon signal at 176 ppm are observed in the HMBC spectrum, confirming that these shifts are due to the presence of IIS and SIS sequences in the copolymer. This is consistent with the appearance of a peak at 170.5 ppm carbonyl ester (d).

From these results, it is clear that the chemical shift is not only influenced by the stereochemistry but also by the composition, it is important to remember that the carbonyl signals, in the homopolymer, are very sensitive to stereochemistry factors in ^{13}C-NMR. Finally, the random distribution of the constitutional units in the copolymers is also confirmed by all these results.

4. CONCLUSIONS

The results obtained here allow us to conclude that the poly (methyl-*n*-hexadecyl itaconate-*co*-styrene) copolymers obtained are mainly random. The chemical shifts of the main groups present in both units of the copolymer are strongly influenced not only by the composition and electronic factors of the surrounding but also by the stereochemistry. The experimental chemical shifts of the methoxy groups in ^{13}C NMR were in a very good agreement with those calculated by theoretical model which allow to suggest that structures optimized by the theoretical method are present in the polymeric structure.

5. ACKNOWLEDGMENTS

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