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# Selective INEPT as an NMR Tool for Studying Repeat Unit Distribution and Stereosequences in Poly(β-malic acid) Copolymers

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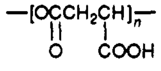
ABSTRACT: A one-dimensional NMR technique, namely, selective INEPT for selective insensitive nuclear enhancement by polarization transfer, recently developed for spectral assignment and structural characterization of organic compounds, has been used for peak assignments in poly(β-malic acid-*co*-benzyl malate) copolymers. By comparing the carbonyl NMR resonances of copolymers with different comonomer sequence distributions, it is confirmed that poly(β-malic acid-*co*-benzyl β-malate) copolymers which are obtained by heterogeneous $H_2$/Pd charcoal catalyzed partial hydrogenolysis of poly(benzyl β-malate) are block copolymers. Selective INEPT NMR has also been used to assign carbonyl carbon atom resonances of optically active stereopolymers of L-(*S*)- and D-(*R*)-benzyl malolactonates. Therefore, selective INEPT, which is used for the first time to make peak assignments in copolymers and stereocopolymers, appears to be a fruitful means of analyzing comonomer sequence distribution provided that repeating units are sensitive to closest neighbors.

## Introduction

The attention which is currently paid to poly(β-malic acid) (PMLA100), a polyester with pendant carboxyl groups, is increasing rapidly for several reasons.



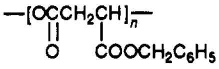
$-[\underset{\underset{O}{\|}}{OC}CH_2\underset{\underset{COOH}{|}}{CH}]_n-$

poly(β-malic acid) (PMLA100)

First, PMLA100 is a water-soluble polyelectrolyte derived from malic acid, a chiral hydroxy acid whose L enantiomer is an intermediate of the Krebs cycle. Accordingly, PMLA100 can be obtained either racemic or optically active.[1,2,5,9] Second, the presence of an aliphatic polyester backbone makes PMLA100 degradable in aqueous media and even in mammalian organisms.[2,3] Recently, PMLA100 has been found in microorganisms and recognized as an α-DNA polymerase inhibitor for some living cells although its exact role in the parent microorganisms is still unknown.[4] Last but not least, PMLA100 is the parent compound of a large family of functional polymers, copolymers and stereopolymers which can be made by direct copolymerization and/or by chemical modification.[5]

Poly(β-malic acid) has been synthesized in several steps from bromosuccinic acid,[6] aspartic acid enantiomers,[7] and malic acid enantiomers.[8] In any case, the last step is an $H_2$/Pd charcoal catalyzed hydrogenolysis of benzyl protecting groups present in poly(benzyl β-malate), PMLABe$_{100}$, a precursor obtained by ring-opening polymerization of benzyl malolactonate.[6]

When proper conditions are used, poly(β-malic acid-*co*-benzyl β-malate) can be recovered from the reaction medium by stopping the hydrogenolysis before completion.[9] Because the resulting copolymers exhibited unusual physicochemical properties, it has been suspected that catalytic hydrogenolysis by the Pd/charcoal method led to block copolymers. Proving the presence of long blocks of similar repeat units in a copolymer chain is always a difficult problem in polymer chain characterization. Our first approach was to show that hydrolysis of this copolymer yielded rather long oligomers made predominantly of benzyl β-malate repeating units.[10,11] In a second approach, we attempted to use high-field $^1$H and $^{13}$C NMR, which are known to be powerful tools for polymer chain structural analysis. However, this classical approach failed because of the lack of exploitable stereosensitivity.



$-[\underset{\underset{O}{\|}}{OC}CH_2\underset{\underset{COOCH_2C_6H_5}{|}}{CH}]_n-$

poly(benzyl β-malate) (PMLABe$_{100}$)

Recently, Bax[12] has described a new technique in one-dimensional NMR, namely, selective INEPT for selective insensitive nuclear enhancement by polarization transfer, which measures long-range heteronuclear connectivity and which has been used for the complete assignment of complex polycyclic aromatic hydrocarbons[13] and for the characterization of polysaccharide chains.[14]

In this paper, we wish to report the results of an attempt to use selective INEPT as a means of confirming the presence of blocks in copolymers obtained by partial hydrogenolysis of poly(benzyl β-malate).

## Experimental Section

**Chemicals.** Racemic (PMLA$^{50}$Be$_{100}$) and optically active poly(benzyl β-malates) (PMLA$^x$Be$_{100}$, where $x$ is the enantiomeric excess in the monomer feed) were prepared from racemic and L-aspartic acid as described previously.[1]

Poly(methyl β-malate) was prepared by methylation of poly(β-malic acid) by the diazomethane method. Poly(β-malic acid) (50 mg) dissolved in dry acetone and an aliquot of a diazomethane ether solution were allowed to react at room temperature. Addition of diazomethane was continued until the solution became pale yellow. The solvent and the excess of diazomethane were then evaporated and $^{13}$C NMR in deuterated acetone showed that no free carboxyl groups remained after reaction.

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Partial and total hydrogenolysis of PMLA$^{x}$Be$_{100}$ leading to h-PMLA$^{50}$Be$_{x}$H$_{100-x}$ and to PMLA$^{50}$H$_{100}$ was carried out in a special hydrogenation apparatus described in ref 10. The Pd/charcoal catalyst was supplied by Janssen and used as received.

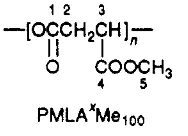
Cop-PMLA$^{50}$Be$_{100-y}$H$_{y}$ were prepared by partial esterification of PMLA$^{50}$H$_{100}$ with benzyl alcohol in acetone, using DCC as the coupling reagent.[9] Typically, 400 mg of PMLA$^{50}$H$_{100}$ was dissolved in dry acetone with a stoichiometric amount of DCC. The white precipitate which formed after 3 min was filtered and 250 mg of benzyl alcohol was added. The mixture was then allowed to stand for 12 h at room temperature. Finally, the solvent and the benzyl alcohol in excess were evaporated. The percentages of benzyl ester groups remaining in the resulting polymers were determined by $^{1}$H NMR.

Cop-PMLA$^{50}$Be$_{100-y}$Me$_{y}$ was obtained by allowing cop-PMLA$^{50}$Be$_{100-y}$H$_{y}$ to react with diazomethane in acetone at room temperature according to the procedure described above for the PMLA$^{50}$Me$_{100}$ homopolymer.

**NMR Spectra.** All compounds were dissolved in $CD_3COCD_3$, $CD_3Cl$, or $CD_2Cl_2$. $^{1}$H and $^{13}$C NMR spectra were recorded at 305 K, on Bruker WM-250-MHz or AM-300-MHz spectrometers using 5-mm sample tubes. $^{1}$H and $^{13}$C chemical shifts are reported in ppm from tetramethylsilane. The selective INEPT experiments have been described by Bax.[12,13] In our case, selective INEPT spectra were carried out with delays of $\Delta_1/2$ and $\Delta_2/2$ set to 37 and 18 ms, respectively, and the pulse width of the selective soft 90° $^{1}$H pulse was set to 10 ms ($\gamma H_2/2\pi = 25$ Hz). Calibration of this 90° pulse was done by optimizing the selective INEPT experiment for a nonspinning sample of 80% ethylbenzene in $CDCl_3$ and by incrementation of the attenuation. The optimum value was found for an attenuation of 36L. Broad-band decoupling was used during data acquisition. In the carbonyl area, a spectral width of 500 Hz and 8K data points (Hz/point = 0.12 Hz) were used for the acquisition. A line broadening of 1 Hz was applied before Fourier transformation in order to increase the signal-to-noise ratio for normal and selective INEPT spectra. Each of the selective INEPT and broad-band spectra of carbonyl areas resulted from 5120 scans.

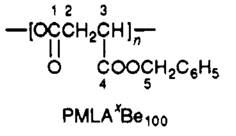
## Results and Discussion

**Assignments of Carbonyl Carbon Atom Resonances in Homopolymers.** Figures 1 and 2 show the normal (a) and the selective INEPT (b) spectra (carbonyl region) of the two homopolymer derivatives of racemic poly($\beta$-malic acid), namely, the methyl ester (PMLA$^{50}$Me$_{100}$) and the benzyl ester (PMLA$^{50}$Be$_{100}$), in deuterated acetone. In the PMLA$^{50}$Me$_{100}$ normal spectrum, five lines were observed: two pairs of partially overlapping ones under the experimental conditions (169.42–169.39 and 168.88–168.85 ppm) and a single line at 169.06 ppm. PMLA$^{50}$Be$_{100}$ had also five lines: a single one at 169.06 ppm and again two pairs of overlapping lines (168.88–168.85 and 168.79–168.76 ppm) (Figures 1a and 2a). Three of the five resonances observed for both polymers appeared at the same chemical shifts (169.09, 168.88, and 168.85 ppm).



$$-[\overset{1}{\underset{\|}{\underset{O}{}}}OC\overset{2}{C}H_2\overset{3}{C}H]_n- \quad \text{with } C^1{=}O \text{ and } \overset{4}{C}OO\overset{5}{C}H_3 \text{ on } C^3$$

PMLA$^{x}$Me$_{100}$



$$-[\overset{1}{C}(=O)O\overset{2}{C}H_2\overset{3}{C}H]_n- \quad \overset{4}{C}OO\overset{5}{C}H_2C_6H_5 \text{ on } C^3$$

PMLA$^{x}$Be$_{100}$

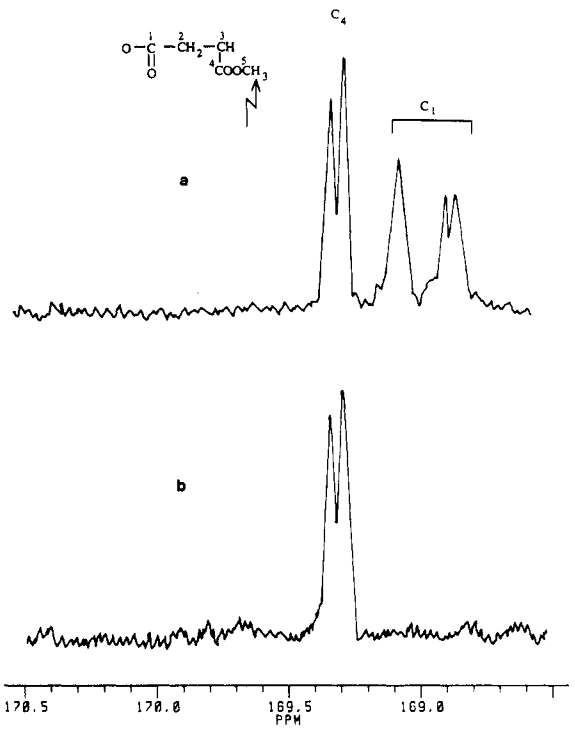


**Figure 1.** $^{13}$C NMR spectra (carbonyl carbon atom region) of PMLA$^{50}$Me$_{100}$ in deuterated acetone: (a) normal conditions (peaks at 169.40, 169.06, and 168.86 ppm); (b) after selective INEPT sequence (peak at 169.40 ppm), methyl groups being pulsed.

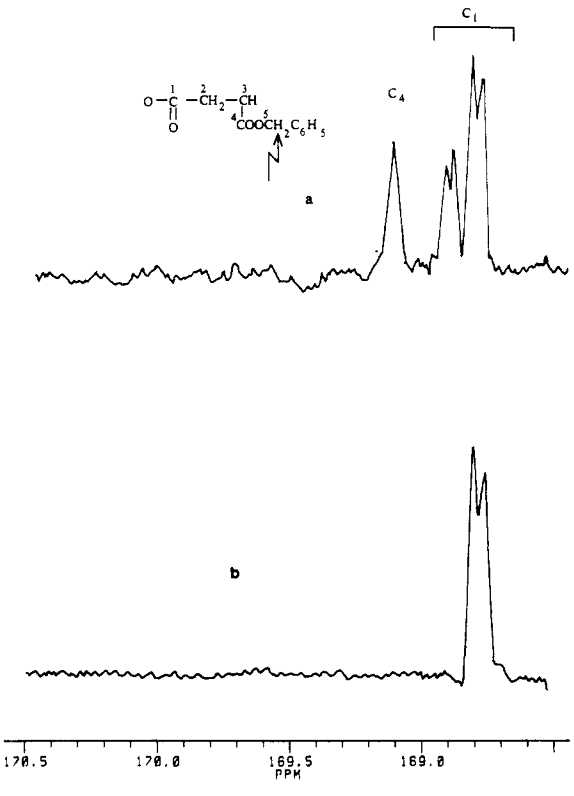


**Figure 2.** $^{13}$C NMR spectra (carbonyl carbon atom region) of PMLA$^{50}$Be$_{100}$ in deuterated acetone: (a) normal conditions (peaks at 169.06, 168.86, and 168.77 ppm); (b) after selective INEPT sequence (peak at 168.77 ppm), methylene groups of the benzyl substituent being pulsed.

The normal spectra appeared significantly simplified when selective INEPT was applied (Figures 1b and 2b, respectively). In selective INEPT, sets of selective radiofrequency pulses are applied to preselected proton singlets. In the present cases, selective pulses were applied to $CH_3$ of methyl ester groups (3.73 ppm) or $CH_2$ of benzyl ester ones (5.33 ppm). The use of selective pulses was possible because resonances were resolved well enough.[11] Under these conditions and by setting in the pulse sequences $\Delta_1$ and $\Delta_2$ delays related to long-range C–H heteronuclear coupling constants of ca. 5 Hz, the pulse sequence can transfer proton magnetization to $^{13}$C nuclei which have a significant long-range scalar interaction with the selected protons. The detectable selective INEPT

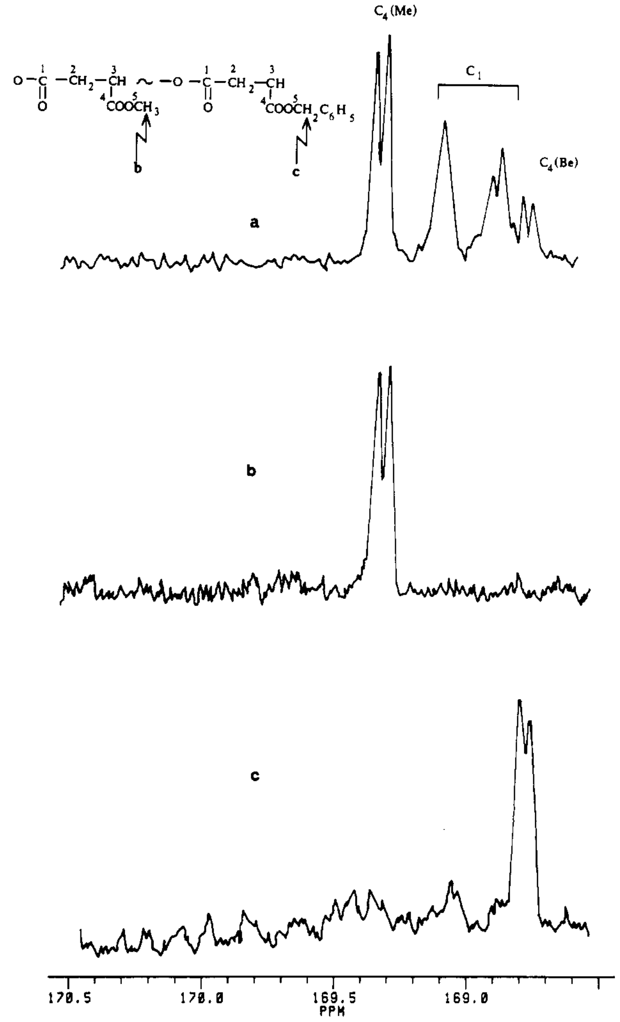


**Figure 3.** $^{13}C$ NMR spectra (carbonyl carbon atom region) of PMLA$^{50}$Me$_{22}$Be$_{78}$ in deuterated acetone: (a) normal conditions; (b) after selective INEPT sequence with $^1H$ selective pulse on $CH_2$; (c) after selective INEPT sequence with $^1H$ selective pulse on $CH_3$.

signal corresponded to C4 carbonyl carbon nuclei, determining three bonds connectivity by bridging one oxygen nucleus. Accordingly, the two lines observed in the selective INEPT spectra of PMLA$^{50}$Me$_{100}$ and PMLA$^{50}$-Be$_{100}$ located at 169.40 (Figure 1b) and 168.77 ppm (Figure 2b), respectively, can be definitely assigned to C4 carbon atoms. By comparison, peaks at 169.06 and 168.86 ppm (Figures 1a and 2a) correspond to stereosensitive carbonyl carbon atoms C1 located in the main chain (close to the chiral carbon atom C3 which is sensitive to triad effects[1]).

In a second stage, we have considered whether the selective INEPT NMR sequence can be extended to copolymers. Figure 3a shows the normal NMR spectrum of a poly($\beta$-malic acid ester) derivative containing 22% benzyl ester groups and 78% methyl groups in the side chains. Figures 3b and 3c show the selective INEPT spectra after applying $^1H$ selective pulses on $CH_3$ and on benzyl $CH_2$, respectively. Polarization transfer obviously simplified the spectrum shown in Figure 3a and revealed resonances of methyl ester units and benzyl ester units separately, depending on the preselected protonated carbon to which the pulse sequence was applied. Figure 3b shows the resonances of C4 carbonyl carbon atoms of methyl ester groups whereas Figure 3c shows the resonances of C4 carbonyl carbon atoms of benzyl ester groups present in the copolymer.

The selective INEPT NMR sequence was also used to detect C1 and C4 resonances in the case of PMLA$^x$Be$_{100}$ optically active stereocopolymers, where $x$ is in the range $50 \leq x < 100$ and reflects the enantiomeric composition of the monomer feed and thus the configurational composition of the stereocopolymer chains. Figures 4a and 4b present the normal NMR spectra of racemic PMLA$^{50}$-Be$_{100}$ and of optically active PMLA$^{98}$Be$_{100}$ chains of the latter being almost configurationally isotactic. Dissolution of PMLA$^{98}$Be$_{100}$ required the use of hot deuterated chloroform.[2] The racemic PMLA$^{50}$Be$_{100}$ stereocopolymer gave rise to a rather complex NMR spectrum with multiple peaks in the 168–170 ppm region because of the stereosensitivity of the C1 and C4 carbonyl carbon atoms. In contrast, the optically active PMLA$^{98}$Be$_{100}$ led to a simpler spectrum composed of two narrow resonances corresponding to C1 and C4 carbon atoms only because of isotacticity. Selective INEPT was used to sharpen the assignments. Figure 4d shows the selective INEPT spectrum of PMLA$^{50}$Be$_{100}$ after $^1H$ selective pulse application to benzylic $CH_2$ protons. Under these conditions, the NMR spectrum of PMLA$^{50}$Be$_{100}$ was simplified and exhibited one group of peaks only located between 168.6 and 168.7 ppm assignable to C4 carbon atoms located in pendant side-chain ester bonds. Therefore, the peaks located at lower fields (168.7$_5$–168.9 ppm), which did not appear after selective INEPT, can be assigned to C1 carbon atoms of the main chain. Integrations after inverse gated decoupling (Figure 4a) showed similar line shapes for the two groups of peaks in agreement with the presence of one C1 and one C4 carbon atoms in each repeat units.

Further information on the relationship between stereosensitivity and peak splittings was obtained from selective INEPT spectra of stereocopolymers. Indeed, when $x$ increased, the peaks centered at 168.9 ppm (integration = 1/2 carbon atom) decreased and were no longer present for $x = 98$. Accordingly, these peaks can be assigned to the effects of syndio and heterosyndio configurational sequences on the C1 resonances as they are not present in isotactic polymers. On the other hand, the peaks located in the 168.7–168.8 ppm region (1/2 carbon atom too) turned to one peak only located at 168.76 ppm in the case of isotactic PMLA$^{98}$Be$_{100}$. Therefore, this peak was assigned to C1 carbon atoms in a isotactic environment. Similarly, only one peak remained in the C4 part of the spectrum. This peak, which is located at 168.68 ppm, was assigned to isotactic sequences.

**Repeat Unit Distribution in Partially Benzylated Poly($\beta$-malic acid).** Selective INEPT sequence was finally applied to poly($\beta$-malic acid) and to four partially benzylated derivatives of different origins in an attempt to show the presence of blocks in those obtained by partial hydrogenolysis of PMLA$^{50}$Be$_{100}$ as compared with derivatives obtained by partial coupling. For this experiment, two copolymers, which were prepared by coupling of benzyl alcohol to PMLA$^{50}$H$_{100}$ by using the dicyclohexylcarbodiimide (DCC) method, were compared with two copolymers of close gross compositions, which were obtained by partial hydrogenolysis.

Two copolymers were prepared according to method a, namely, cop-PMLA$^{50}$Be$_{22}$H$_{78}$ and cop-PMLA$^{50}$Be$_{35}$H$_{65}$, and two according to method b, namely, h-PMLA$^{50}$Be$_{25}$H$_{75}$ and h-PMLA$^{50}$Be$_{22}$H$_{78}$. Normal and selective INEPT NMR were performed for these four copolymers and the resulting spectra were compared to that given by a simple mixture of PMLA$^{50}$Be$_{100}$ and PMLA$^{50}$H$_{100}$ in a 2:1 ratio (mole/mole). Deuterated acetone was used as the common solvent as we were dealing with racemic main chains. Figure

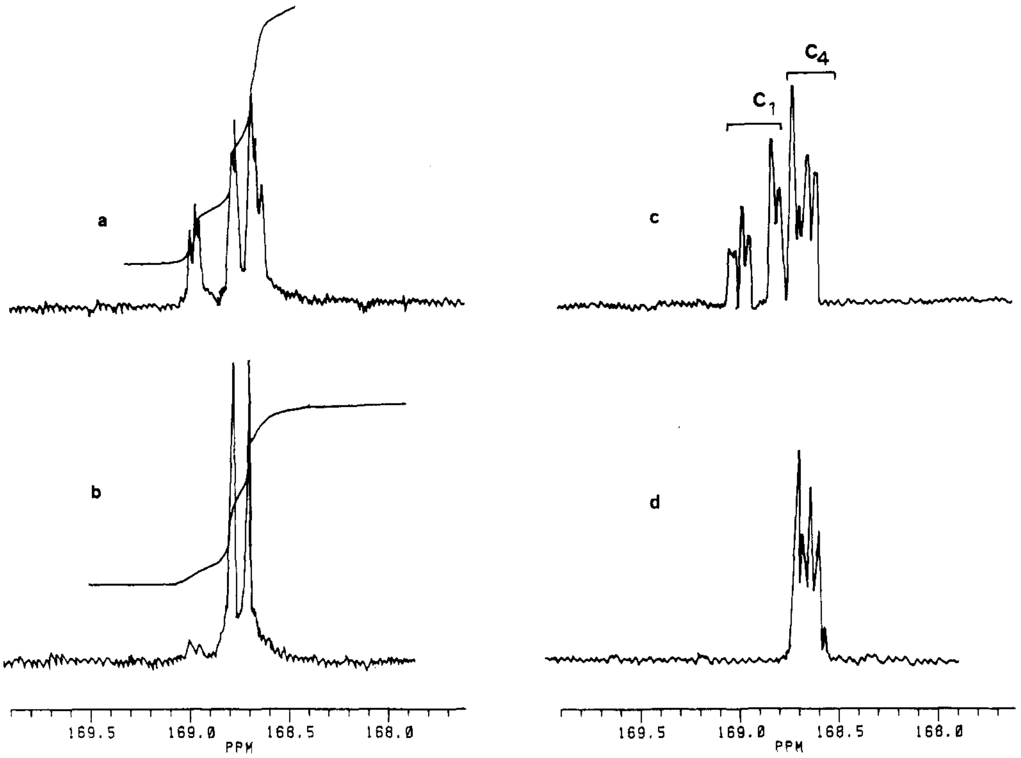
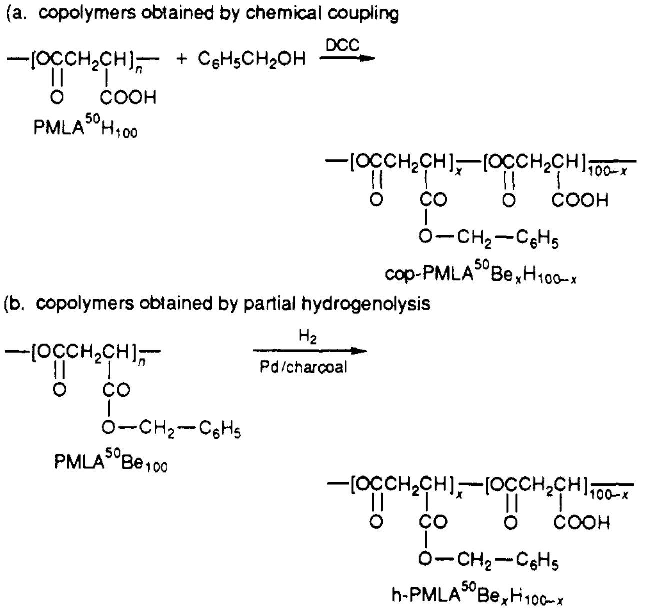
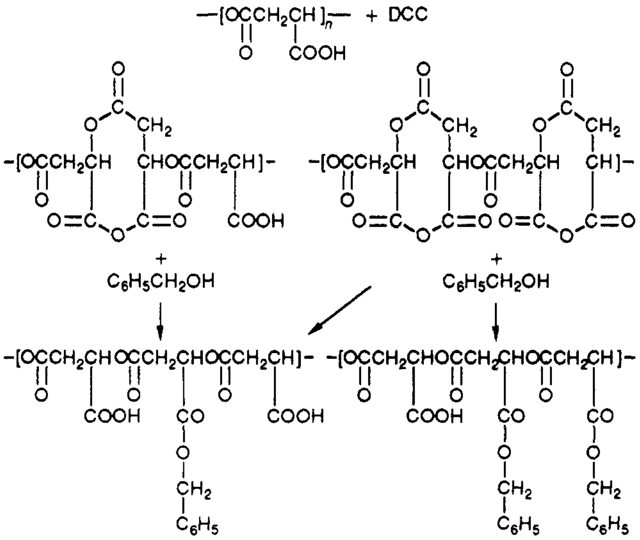


**Figure 4.** $^{13}C$ NMR spectra of PMLA$^{x}$Be$_{100}$ (carbonyl carbon atom region) in deuterated $CD_2Cl_2$: (a) PMLA$^{50}$H$_{100}$ under normal conditions; (b) PMLA$^{98}$Be$_{100}$ under normal conditions; (c) PMLA$^{50}$Be$_{100}$ under normal conditions with field-scale magnification; (d) PMLA$^{50}$Be$_{100}$ after Selective INEPT sequence.



5a shows the rather complex NMR spectrum given by the polymer mixture in the carbonyl carbon atom region. This spectrum was used as a standard for the typical NMR resonances of ester and acid repeat units when they are surrounded by similar units only, as is the case in a block copolymer. Six resonance peaks are observed, three corresponding to PMLA$^{50}$H$_{100}$ (169.99 (C4), 169.27, 169.00 (C1) ppm) and three corresponding to PMLA$^{50}$Be$_{100}$ (169.06, 168.86 (C1), 168.77 (C4), ppm), the two latter giving two lines due to the stereosensitivity of C1 and C4 carbons to tacticity in deuterated acetone. Normal NMR spectra given by cop-PMLA$^{50}$Be$_{22}$H$_{78}$ and h-PMLA$^{50}$Be$_{22}$H$_{78}$ copolymers (Figures 5a and 5b) appeared very much different. The significant shifts and peak broadenings which are easily detected by comparison with Figure 5a, showed that none of the two compounds is a mixture of homopolymers. In the spectrum of cop-PMLA$^{50}$Be$_{22}$H$_{78}$ (Figure 5b), no signal was detected at 168.77 ppm, where the peak of the C4 of benzyl ester units surrounded by two similar units normally appears. This finding suggests that no such triad exists in the cop-PMLA$^{50}$Be$_{22}$H$_{78}$ chain. The absence of benzyl–benzyl–benzyl triads is consistent with the fact that the coupling of benzyl alcohol to poly($\beta$-malic acid) in the presence of DCC actually proceeds via anhydrization of the polymer according to the following ways:[9]



Indeed, the reaction of an 8-membered anhydride ring, as the one proposed, with benzyl alcohol can lead to isolated benzyl ester repeating units or to dyads but not to triads. Furthermore, cop-PMLA$^{50}$Be$_{22}$H$_{78}$ and h-PMLA$^{50}$Be$_{22}$H$_{78}$ copolymers have different repeat unit distributions since

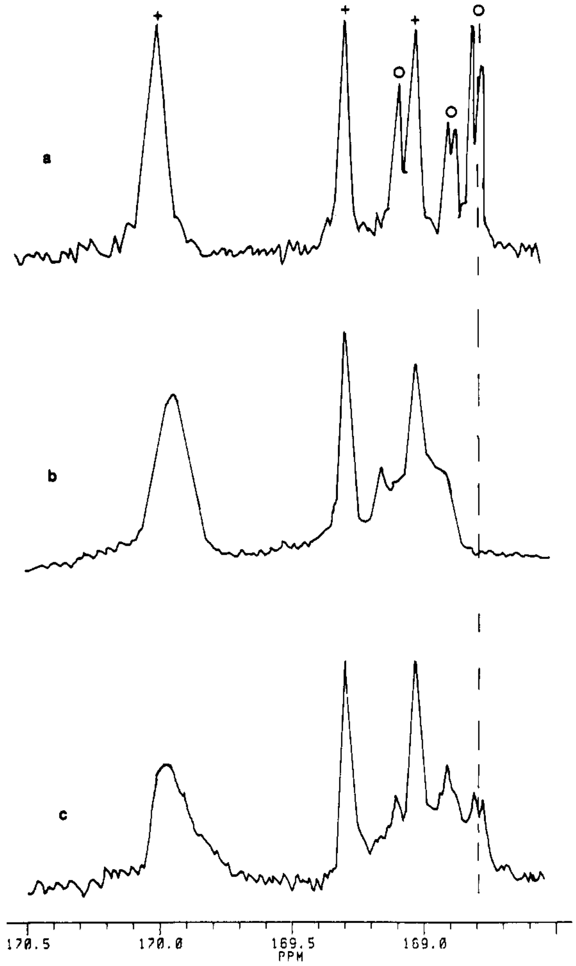


**Figure 5.** $^{13}$C NMR spectra (carbonyl carbon atom region) in deuterated acetone under normal conditions: (a) 2 to 1 mixture of PMLA$^{50}$H$_{100}$ (+) and PMLA$^{50}$Be$_{100}$ (O); (b) cop-PMLA$^{50}$-Be$_{22}$H$_{78}$; (c) h-PMLA$^{50}$Be$_{22}$H$_{78}$.

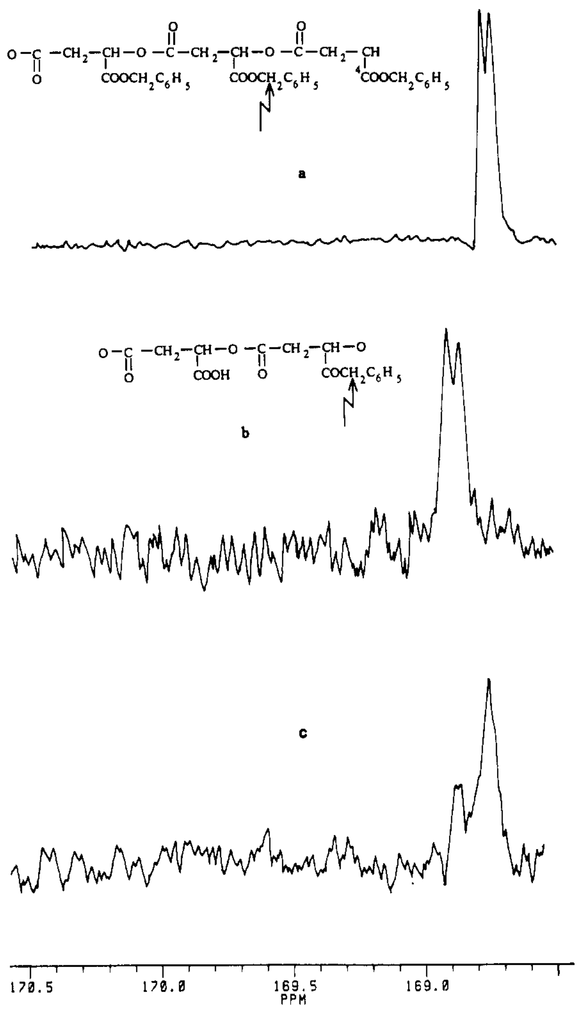


**Figure 6.** $^{13}$C NMR spectra (carbonyl carbon atom regions) in deuterated acetone after selective INEPT sequence: (a) PMLA$^{50}$-Be$_{100}$; (b) cop-PMLA$^{50}$Be$_{22}$H$_{78}$; (c) n-PMLA$^{50}$Be$_{22}$H$_{78}$.

the corresponding spectra are dramatically different (Figure 5b and 5c). In particular, the spectrum of h-PMLA$^{50}$Be$_{22}$H$_{78}$ exhibits a peak at 168.77, which is typical of benzyl ester triads.

Figure 6 shows the selective INEPT spectra of (a) PMLA$^{50}$Be$_{100}$, (b) cop-PMLA$^{50}$Be$_{22}$H$_{78}$, and (c) h-PMLA$^{50}$-Be$_{22}$H$_{78}$ after application of the specific pulse sequence to the benzylic C$H_2$ protons. Selective INEPT NMR spectra appeared simplified as already observed for homopolymers.

The spectrum of cop-PMLA$^{50}$Be$_{22}$H$_{78}$ is reduced to a peak with two lines located at 168.85 ppm (Figure 6a). According to previous homopolymer peak assignments, this peak can be attributed to the C4 carbonyl carbon atoms of the benzyl repeat units. It is noteworthy that this peak is located at a chemical shift typical of C1 in the PMLA$^{50}$Be$_{100}$ homopolymer. This discrepancy must be regarded as typical of closest neighbor effects in agreement with the fact that benzyl triads do not exist in this copolymer. This conclusion was further supported by the fact that the spectrum of cop-PMLA$^{50}$Be$_{35}$H$_{65}$ exhibited only one double peak located also at 168.85 ppm.

The selective INEPT spectrum of the h-PMLA$^{50}$Be$_{22}$H$_{78}$ copolymer (Figure 6c) appeared also simplified and displayed two peaks of different intensities. One peak is located at 168.77 ppm, i.e., at the chemical shift characteristic of benzylic C4 carbonyl carbon atoms as they are in the PMLA$^{50}$Be$_{100}$ homopolymer (Figure 6a). Despite the rather low resolution of the spectrum, a small peak assignable to an NMR resonance is detected at 168.85 ppm, i.e., at the location of C4 atoms as they were observed in random copolymers (Figure 6b). This feature is considered as being in good agreement with the presence of a small proportion of C4 atoms in benzylic units surrounded by carboxylic ones as is the case in random copolymers. The large predominance of C4 atoms engaged in benzyl–benzyl–benzyl triads, as they are in the PMLABe$_{100}$ homopolymer (Figure 6a), is consistent with the presence of rather long blocks of adjacent benzyl units already suspected from the ability of hydrogenolyzed copolymers with large content in acidic repeating units to aggregate in water.[10,11] Similar findings were observed for the h-PMLA$^{50}$Be$_{25}$H$_{75}$ copolymer.

In conclusion, it has been shown that the use of polarization transfer for simplifying $^{13}$C NMR spectra of complex copolymers and thus for making easier the identification of overlapping or multiple resonances is feasible. Resonances typical of the carbonyl atoms C1 of the main-chain aliphatic ester groups and C4 of side-chain ester groups of poly($\beta$-malic acid) benzyl and methyl ester copolymers have been distinguished and assigned in the case of the racemic main chain. It has also been shown that the selective INEPT method can be used to correlate peak splittings and iso, syndio, and heterosyndio stereosequences in poly($\beta$-malic acid) benzyl ester stereocopolymers. It is likely that the method can be applied to other derivatives. Finally, selective INEPT has also been used to show that rather long blocks of benzyl units exist in copolymers obtained by hydrogenolysis on Pd/charcoal, even when benzyl units are a minority with respect to acid units. This conclusion and the facts that long blocks of benzyl units have been found previously by selective degradation and that h-PMLA$^{50}$Be$_x$H$_{100-x}$ with $x < 10$ form micellar aggregates of malic acid sequences allow us to conclude that the chemical modification appear in good agreement and allow us to conclude that cleavage of benzyl protecting groups by heterogeneous Pd/charcoal-catalyzed hydrogenolysis does lead to the formation of block copolymer. This conclusion can be extended to the other benzyl-protected polycarboxylic acids which can be liberated by Pd/charcoal-catalyzed hydrogenolysis.

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**Registry No.** Cop-PMLA, 137257-54-6.