Macromolecules 1983, 16, 608–615

High-Field ^{13}C and ^{1}H NMR Analysis of α,α-Disubstituted Poly(β-propiolactones)

Nicolas Spassky,*,† Alain Leborgne,† and William E. Hull‡

Laboratoire de Chimie Macromoléculaire, LA 24, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France, and Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten 4-FO, FRG.

Received May 17, 1982

ABSTRACT: Crystalline poly(α,α-disubstituted-β-propiolactones) prepared by anionic polymerization of racemic and enantiomerically enriched monomers were examined by 100.6-MHz ^{13}C and 500-MHz ^{1}H NMR spectroscopy. It was shown that polymers prepared from a racemic mixture of monomers have a random distribution of R and S configurational units in the chain. Thus, an equal distribution of triads for stereosensitive carbon atoms is found in the 100.6-MHz ^{13}C NMR spectra. The triad analysis performed on enantiomerically enriched poly(α-methyl-α-ethyl-β-propiolactones) fits satisfactorily to a Bernoullian distribution. Similar but more detailed results were obtained from 500-MHz ^{1}H NMR spectroscopy. Tetrad effects with some pentad splittings were observed for the methylene protons of the main chain in poly(α-methyl-α-ethyl- and α-methyl-α-n-propyl-β-propiolactones). Good agreement is again found between experimental results and the calculated tetrad contents according to Bernoullian statistics. Some irregularities in the structure, not yet identified, appear in the spectra of polymers prepared with zinc-coordinated initiators.

Introduction

Poly(α,α-disubstituted-β-propiolactones) prepared by anionic polymerization of racemic monomers show crystalline properties, the melting point being dependent on the nature of the substituents.[1,2] These findings are in contrast with results found for other heterocyclic monomers such as oxiranes or thiiranes, for which anionic, nonstereoregulating initiators lead to amorphous polymers with a random distribution of the enantiomeric units. In order to explain this behavior the hypothesis of the existence of a stereoregular structure has been advanced in the case of poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL).[3] Recently, a syndiotactic structure was proposed for PMPPL on the basis of X-ray analysis.[4]

The study of the tacticity by NMR was hindered by the minimal information obtained with conventional spectrometers. Indeed, no difference was observed at 90 MHz for ^{1}H spectra when comparing a polymer obtained by polymerization of optically active α-ethyl-α-phenyl-β-propiolactone (optical purity 80%), which must have a substantial degree of isotacticity, and a polymer obtained from the racemic monomer.[5] Similarly, no differences were observed in 25-MHz ^{13}C spectra of racemic and enantiomerically enriched PMPPL.[6]

Stereosensitivity to dyads was observed for the first time in 50-MHz ^{13}C NMR spectra of PMPPL. It was concluded that anionic-type polymers obtained from the racemic monomer have an equal distribution of syndiotactic and isotactic dyads.[6] In order to correlate the tacticity with the enantiomeric distribution of units in the chain, samples of poly(α-methyl-α-ethyl-β-propiolactones) (PMEPL) were prepared from monomers of different optical purity and examined by 62.8-MHz ^{13}C spectroscopy.[7]

Satisfactory agreement with a Bernoullian distribution of enantiomeric units along the chain was found, although this does not rule out the possibility of other distributions and/or the presence of some stereoregular structure. For this reason these polymers were reexamined at high field by 100-MHz ^{13}C NMR and 500-MHz ^{1}H NMR. The results are described in the present paper.

Experimental Section

Optically pure α-methyl-α-ethyl-β-propiolactone (MEPL) was prepared in an eight-step synthesis as described elsewhere.[7,8] Monomers of different enantiomeric composition were obtained by dilution of pure MEPL with racemic monomer. Potassium acetate/dicyclohexyl-18-crown-6 was used as anionic initiator. The properties of the polymers obtained have already been described.[8] Samples of 0, 27, 55, and 74% optical purity were used.

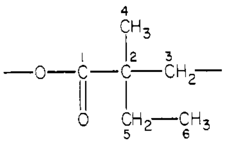
Samples obtained from racemic MPPL using a chiral initiator ("stereoelective-type polymerization")[6] were also examined.

100.6-MHz ^{13}C NMR spectra were obtained with Bruker WH- and WM-400 spectrometers, using 10-mm sample tubes (10–20% solutions in $CDCl_3$). 500-MHz ^{1}H NMR spectra were obtained with a Bruker WM-500 spectrometer, using 5-mm sample tubes (1–2% solutions in $CDCl_3$).

When so noted, resolution enhancement of the Fourier transform spectra was performed by the double-exponential Lorentz–Gaussian line shape transformation.[9] This allows a more meaningful integration of partially overlapping resonances as well as a more precise determination of tacticity splittings.

Results and Discussion

^{13}C 100.6-MHz Spectra of PMEPL. The spectra of various PMEPL samples were measured in $CDCl_3$ at 27 °C. There are six different carbon atoms in a PMEPL monomer unit, three in the backbone chain and three in the side chain. Six groups of ^{13}C signals were observed and assigned to the corresponding carbon atoms.



$$-O-\underset{\underset{O}{\|}}{\overset{1}{C}}-\overset{\overset{4}{CH_3}}{\underset{\underset{5}{CH_2}-\underset{6}{CH_3}}{\overset{2}{C}}}-\overset{3}{CH_2}-$$

Analysis of a Racemic Anionic Polymer. This polymer was obtained by polymerization of racemic MEPL using an anionic-type initiator (potassium acetate/dicyclohexyl-18-crown-6).[7,8] The ^{13}C spectrum with resolution enhancement is shown in Figure 1. The signals were assigned as follows: a low-field pattern composed of two peaks at 174.15 and 174.18 ppm (approximate ratio 1:2) was assigned to carbonyl carbon C_1. This group of signals is found at a similar position in β-substituted poly(β-propiolactones).[10] At 62.8 MHz no stereosensitivity was observed at this carbon. The pattern located around 68.6 ppm is assigned to methylene carbon C_3. It is composed of three signals located at 68.67, 68.65, and 68.57 ppm (ratio 1:1:1.8). Two well-resolved signals at 46.66 and 46.63 ppm (ratio 1:1) correspond to the quaternary carbon C_2.

Next one finds a pattern with two broad peaks at 28.55 and 28.51 ppm (ratio 1:1); these signals were assigned to methylene carbon C_5. The pattern for the methyl carbon

---

† Université Pierre et Marie Curie.

‡ Bruker Analytische Messtechnik GmbH.

0024-9297/83/2216-0608$01.50/0 © 1983 American Chemical Society

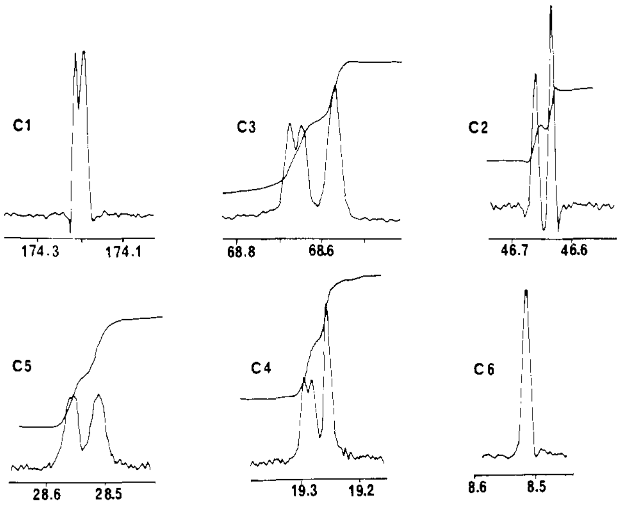


Figure 1. 100.6-MHz ^{13}C spectrum (resolution enhanced) of racemic PMEPL in $CDCl_3$ (in ppm from Me_4Si).

C_4 is composed of a partially resolved doublet, 19.295 and 19.28 ppm, and a single peak at 19.25 ppm (ratio 1:1:2). Finally, the methyl carbon C_6 of the ethyl group appears as a singlet at 8.51 ppm.

Thus, except for carbon C_6, all the carbon atoms are stereosensitive. These stereochemical effects are due to the presence of the asymmetrical carbon atom C_2 in the monomeric unit. This carbon atom may have an *R* or *S* configuration and the successive enchainment of configurational units of *R* or *S* type leads to the triads shown in Chart I. These triads are derived from two types of dyads: (1) the dyad usually called "isotactic" has the threo structure e.g., -*RR*- or -*SS*- and shall be designated i_d, avoiding the terminology m (meso) used for vinyl polymers and not applicable for this stereochemistry. (2) The "syndiotactic" dyad, i.e., -*RS*-, is designated s_d, avoiding the use of r (racemic) for the same reason.

Racemic MEPL is an equimolar mixture of two enantiomers: one having a carbon atom with an *R* configuration and one having a carbon atom with an *S* configuration. During the polymerization, ring-opening occurs exclusively between the CH_2-O bond: therefore the configuration of the asymmetric carbon remains unchanged. It is possible to establish a correlation between the enantiomeric composition of the initial monomer and the tacticity of the polymer formed, i.e., the distribution of different triads. Such a correlation was established for heterocyclic polymers in the case of a Bernoullian process.[11] If we define $p = (S)/(R)$ to be the enantiomeric ratio in the initial monomer with $(R) + (S) = 1$, one finds the following relations for the triads:

$$i = (p^3 + 1)/(p + 1)^3$$

$$s = h_s = h_i = p(p + 1)/(p + 1)^3$$

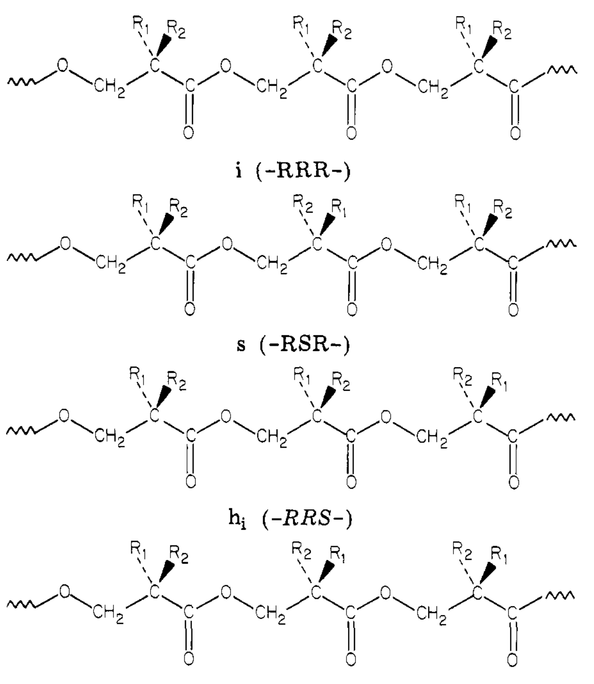
The corresponding dyad values are

$$i_d = i + h_i = (p^2 + 1)/(p + 1)^2$$

$$s_d = s + h_s = 2p/(p + 1)^2$$

For a completely random distribution in the polymer when starting from a racemic mixture ($p = 1$), one finds $i = s = h_s = h_i = 0.25$ and $i_d = s_d = 0.5$. Such distributions have already been observed for polymers prepared from racemic heterocyclic mixtures using anionic nonstereoregulating initiator systems. Examples are propylene sulfide,[11] propylene oxide,[12] and several other thiiranes and oxiranes.[13]

Chart I



i (-RRR-)

s (-RSR-)

h_i (-*RRS*-)

h_s (-*RSS*-)

In the spectrum of PMEPL one finds the following: (1) for each of the carbon atoms C_2 and C_5 there are two peaks of equal area, corresponding to dyads i_d and s_d, in a 1:1 ratio.

(2) For each of the carbon atoms C_3 and C_4 the lower field signal splits into two signals of equal area (triad effect) and the upfield dyad peak of C_3 shows a line width indicating an unresolved splitting. These peaks can be resolved by a curve-resolving instrument into four peaks of identical magnitude, which are ascribed to the four triads i, s, h_s, and h_i.

It is now necessary to assign the different peaks observed to corresponding dyads or triads. In the racemic monomer both of the stereoisomers are present in equal amounts and no differentiation is possible. The use of optically active monomers allows the preparation of polymers enriched in sequences of one type of configurational unit, for example *S*. This provides one possible way to identify unambiguously the isotactic triad -*SSS*- and to correlate the triad distribution with a propagation process, in particular the Bernouillian one.

Polymers with Different Enantiomeric Composition. Monomer mixtures with different enantiomeric compositions ((*S*)/(*R*)) were polymerized with the same anionic initiator, and the polymers were examined by ^{13}C NMR spectroscopy. Four different compositions were used:

polymer	(*S*)/(*R*)	optical purity, %
I	50/50	0
II	63.5/36.5	27
III	77.5/22.5	55
IV	87/13	74

As discussed above, all carbon atoms, except C_6, are stereosensitive, giving dyad or triad effects. The ^{13}C signal patterns for stereosensitive carbon atoms in polymers I and III are given in Figure 2. It is clear that in each pattern one of the peaks is increasing with optical purity and these peaks can be unambiguously assigned to isotactic dyads -*SS*- (or -*RR*-) or isotactic triads -*SSS*- (or -*RRR*-). These peaks are located as follows: at high field, in C_1 (174.18 ppm) and C_4 (19.29 ppm); at low field, in C_3 (68.71

Table I
Isotactic Dyad Content (i_d) for PMEPL Polymers of Different Optical Purity

polymer	optical purity, %	isotactic dyad content theor[a]	C_2	C_3	C_5	C_4
I	0	0.50	0.49	0.51	0.51	0.50
II	27	0.53	0.49	0.53	0.53	0.51
III	55	0.65	0.63	0.64	0.64	0.63
IV	74	0.77	0.72	0.76	0.76	0.76

[a] According to a Bernoullian distribution $i_d = (p^2 + 1)/(p + 1)^2$.

ppm), C_2 (46.69 ppm), and C_5 (28.59 ppm).

In carbon atoms C_3 and C_4 triad effects are observed but the four peaks are not always well separated. However, the curve-resolving analysis could be done with sufficient accuracy.

For carbon atoms C_2 and C_5 only dyads are seen, which are combinations, as described before, of triads $i_d = i + h_i$ and $s_d = s + h_s$. For the carbonyl carbon C_1 four peaks corresponding to triad effects were identified in some polymers but were not resolved in the spectra of others.

First, we have examined the dyad effects for all carbons, as all the patterns can be easily separated into two sets of peaks. The experimental data concerning the isotactic peaks are reported in Table I. The results found for different carbons agree satisfactorily and the values found are very close to those calculated for a Bernoullian distribution. This confirms the conclusions of a previous dyad analysis obtained on the methylene carbon C_3 at 62.8 MHz.[7]

Next we examined the triads at carbon atoms C_3 and C_4. As mentioned before and shown in Figure 1, the two peaks at low field appear generally well separated, while the two high-field peaks show increased line width or a visible shoulder. Nevertheless, the resolution of four peaks could be done more or less easily in each case and the results are given in Table II. From these data the following conclusions can be made: (1) For the racemic polymers one finds essentially an equal distribution (0.25) for the different triads. (2) For enantiomerically enriched polymers three of the triad peaks have almost the same magnitude. These are heterotactic peaks h_i, h_s, and s. (3) The experimental values found for the isotactic peak i and the heterotactic peaks fit satisfactorily with theoretical values calculated in each case for a Bernoullian distribution.

Polymers Obtained with $ZnEt_2$–MeOH Initiator. Tsuruta has shown that the $ZnEt_2$–MeOH initiator system is stereospecific for the polymerization of oxiranes, giving polymers containing amounts of purely isotactic fractions.[14] Racemic MEPL was polymerized with this initiator. No insoluble part could be isolated and the NMR spectrum was run on the whole polymer sample ($\bar{M}_n$ = 7000 by osmometry). The same type of stereosensitivity as in anionic polymers was observed (polymer V in Figure 2); i.e., C_1, C_2, and C_5 are resolved as dyads, C_3 and C_4 are resolved as triads, and C_6 shows no stereosensitivity. The analysis performed on all carbons shows no predominance of isotacticity (~50% in dyads). This means that this initiator is not stereospecific in the case of β-propiolactones. Moreover, for each carbon signal pattern several small additional peaks appeared at lower and higher fields. They may be due to some irregular structures that were not identified.

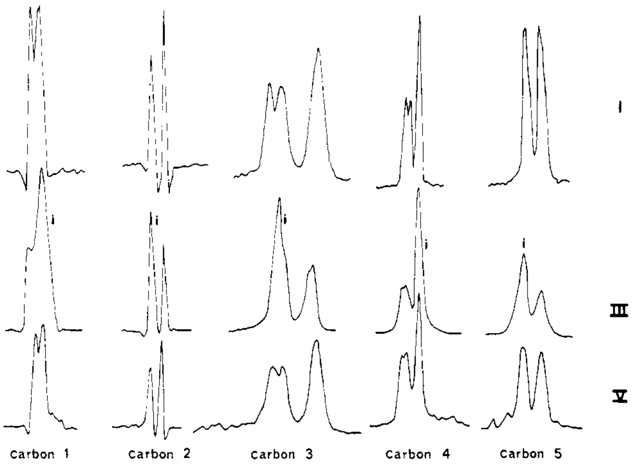
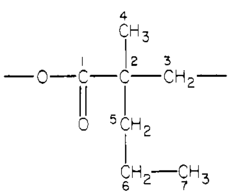


Figure 2. 100.6-MHz ^{13}C spectra (resolution enhanced) of various PMEPL's in $CDCl_3$ (in ppm from Me_4Si): I, prepared from racemic monomer with an anionic-type initiator; III, prepared from monomer of 55% optical purity with an anionic-type initiator; V, prepared from a racemic monomer with a 1:2 $ZnEt_2$–MeOH initiator system.

100.6-MHz ^{13}C Spectra of PMPPL. Poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL) is the polymer most studied for its structural properties[3] and also for the kinetics of anionic polymerization.[15] Stereoelective polymerization was also first tried with success on MPPL.[6] It was therefore interesting to determine the stereoregularity of the polymers, which are crystalline with a melting point close to 90 °C. A first analysis at 50.3 MHz allowed the observation of dyad effects at the methylene carbons. It was proposed that the structure of the anionic polymer may be random.[6] A triad analysis at higher field is therefore of interest to test this hypothesis. Spectra of PMPPL were taken in $CDCl_3$ at 32 °C (Figure 3). The chemical shifts for the various carbons are discussed below and the assignments were substantiated by ^1H decoupling experiments.



$$-O-\overset{1}{C}(=O)-\overset{2}{C}(\overset{4}{C}H_3)(\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3)-\overset{3}{C}H_2-$$

Carbonyl carbon C_1 is found as an unresolved pattern with a main peak at 174.31 ppm. The quaternary carbon C_2 of the chain appears as a well-resolved doublet at 46.42

Table II
Triad Contents in PMEPL Polymers of Different Optical Purity

polymer	theory i[a]	theory h[b]	C_3 i	C_3 h_i	C_3 s	C_3 h_s	C_4[c] h_s	C_4[c] s	C_4[c] h_i	C_4[c] i
I	0.25	0.25	0.25	0.25	0.25	0.25	0.24	0.24	0.24	0.27
II	0.31	0.23	0.30	0.23	0.23[c]	0.23[c]				
III	0.48	0.17	0.45	0.19	0.17	0.19	0.17	0.17	0.17	0.48
IV	0.66	0.11	0.64	0.12	0.12[c]	0.12[c]	0.12	0.12	0.12	0.63

[a] Obtained from the Bernoullian relation $i = p^3 + 1/(p + 1)^3$. [b] Obtained from the Bernoullian relation $h_i = h_s = s = p(p + 1)/(p + 1)^3$. [c] Recalculated from the corresponding dyad effect assuming $s = h_s = h_i$.

Table III
Dyad and Triad Contents Determined by 100.6-MHz ^{13}C NMR for Racemic and Optically Active PMPPL

	C_3		C_2		C_4			
polymer	i_d	s_d	i_d	s_d	h_s	s	i	h_i
VI[a]	0.50	0.50	0.47	0.53	0.24	0.26	0.24	0.27
VII[b]	0.55	0.45	0.54	0.46	0.22	0.24	0.27	0.28

[a] Racemic polymer prepared by anionic initiation. [b] Optically active polymer prepared by the stereoelective method; 10–12% signal integral due to irregularities in the polymer structure.

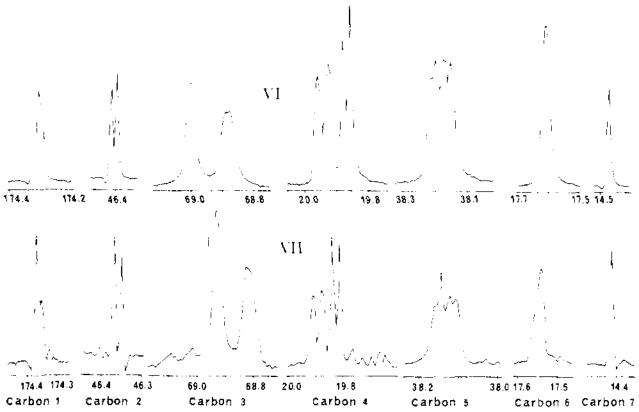


Figure 3. 100.6-MHz ^{13}C spectra (resolution enhanced) of PMPPL's in $CDCl_3$ (in ppm from Me_4Si): VI, prepared from a racemic monomer with an anionic-type initiator; VII, optically active polymer prepared from a racemic monomer with a stereo elective-type initiator.

and 46.40 ppm. The methylene carbon of the chain, C_3, is composed of two peaks, located at 69.00 and 68.88 ppm, with the upfield signal showing a poorly resolved splitting. The methylene carbon C_5 is seen as a pattern of four peaks, not completely resolved, located at 38.21, 38.195, 38.17, and 38.15 ppm. The most interesting finding comes from the methyl carbon C_4, which now appears as two well-resolved doublets at 19.96, 19.93, 19.88, and 19.86 ppm. Carbons C_6 and C_7 are not stereosensitive (the line width of C_6 suggests unresolved tacticity effects) and they appear as singlets at 17.60 and 14.48 ppm, respectively. From the analysis of the spectra of VI in Figure 3 one may conclude that, as in the case of PMEPL, similar dyad and triad effects are observed for analogous carbons.

The stereosensitivity for PMPPL appears to be somewhat less than for PMEPL for the C_2 and C_3 carbons of the chain. In contrast, the substituent carbons C_4 and C_5 close to the chain are more stereosensitive in PMPPL and show well-separated triads. According to signal integration, we are dealing again with a random distribution with equal populations for dyads or for triads (Table III).

In order to assign the different peaks to the corresponding triads and particularly to the isotactic triad, one must use enantiomerically enriched polymers. We have examined for this purpose not a polymer obtained by anionic polymerization of an enantiomerically enriched monomer as for MEPL but a polymer prepared by stereoelective polymerization. In this type of process a racemic monomeric mixture is polymerized in the presence of a chiral initiator. The latter chooses preferentially one of the enantiomers and, therefore, polymers enriched in one type of configurational unit are obtained. The polymer that we have examined was prepared from racemic MPPL using a 1:1 $ZnEt_2$/(−)-3,3-dimethyl-1,2-butanediol initiator system and has a rotatory power $[\alpha_p]^{25}{}_D$ −1.7 ($CHCl_3$).[6] The spectrum of stereoelective polymer VII in Figure 3 was taken under the same conditions as the anionic polymer and it gives the following information concerning the stereoregularity:

(1) In the signal patterns showing tacticity effects, one signal shows increased intensity compared to the random polymer VI and can be assigned to the isotactic dyad or triad. For C_1 the triplet pattern is still not well resolved, but apparently one of the central peaks is increased. For C_2 and C_3 the lowest field signal is assigned to isotactic units. For C_5 the isotactic signal appears to be the second peak from the low-field side. For C_4 the isotactic unit is the third signal from the low-field side.

(2) The dyad tacticity calculated on different carbons gives similar results (Table III) and is close to 53–55%.

(3) Triad tacticity was estimated for C_4 and C_5.

(4) The following triad assignments (from low to high field) are suggested:

C_5	h_i h_i	i i	h_s s	s h_s
C_4	s h_s	h_s s	i i	h_i h_i

These assignments are also consistent with the results for PMEPL, where the i and h_i triads are not completely resolved (compare Figure 2).

(5) In comparison with the anionic polymerization several secondary peaks are found in each pattern (up to 10–12% of the overall amount). This is similar to the findings in PMEPL prepared with $ZnEt_2$–MeOH initiator and indicates the production of some, not yet identified structural irregularities when using zinc alkoxide initiators. It is possible that some ring-opening of the acyl bond occurs, together with the ether cleavage as suggested before for zinc catalysis in β-propiolactone cleavage.[16]

500-MHz ^1H NMR of PMEPL. For structural analysis of polymers ^{13}C NMR is usually simpler and gives more information. The use of ^1H NMR requires in the case of polyheterocyclic polymers deuterated compounds and high-field apparatus. For example, triads could be observed and identified in the case of deuterated poly(propylene sulfide) at 300 MHz.[11] In the case of substituted poly(β-propiolactones) no stereosensitivity was observed in 100-MHz ^1H spectra. Dyad effects were identified for poly(α-methyl-α-n-propyl-β-propiolactones) at 250 MHz in o-dichlorobenzene at 110 °C,[6] but only qualitative analysis was performed.

We report that at 500 MHz it is possible to identify triad and tetrad effects in PMEPL and to analyze them quantitatively. The results were correlated with those found by 100-MHz ^{13}C analysis and good agreement was observed. To assist the analysis of the ^1H NMR spectra a Bernoullian statistics calculation for tetrad populations was carried out. There are four pairs of triads and eight pairs of tetrads, whose populations are summarized in Chart II as a function of $p = (S)/(R)$. When Bernoullian statistics is obeyed, $p = 1$ results in equal populations for all n-ads. It is important to note that at the triad level $p > 1$ allows the isotactic triad to be distinguished, while the other three triads have equal populations.

For tetrad effects $p > 1$ gives the isotactic tetrad the largest population. The four tetrads with numerator (see Chart II) $p^2(p + 1)$ will have higher populations than the

Chart II

tetrads

$$
\begin{aligned}
(\text{-}RRRR\text{-}) + (\text{-}SSSS\text{-}) &= \frac{p^4 + 1}{(p + 1)^4} \\
(\text{-}RRRS\text{-}) + (\text{-}SSSR\text{-}) &= \frac{p^2(p + 1)}{(p + 1)^4} \\
(\text{-}RRSR\text{-}) + (\text{-}SSRS\text{-}) &= \frac{p^2(p + 1)}{(p + 1)^4} \\
(\text{-}RRSS\text{-}) + (\text{-}SSRR\text{-}) &= \frac{2p^2}{(p + 1)^4} \\
(\text{-}RSRR\text{-}) + (\text{-}SRSS\text{-}) &= \frac{p^2(p + 1)}{(p + 1)^4} \\
(\text{-}RSRS\text{-}) + (\text{-}SRSR\text{-}) &= \frac{2p^2}{(p + 1)^4} \\
(\text{-}RSSR\text{-}) + (\text{-}SRRS\text{-}) &= \frac{2p^2}{(p + 1)^4} \\
(\text{-}RSSS\text{-}) + (\text{-}SRRR\text{-}) &= \frac{p^2(p + 1)}{(p + 1)^4}
\end{aligned}
$$

triads

$$
\begin{aligned}
i = (\text{-}RRR\text{-}) + (\text{-}SSS\text{-}) &= \frac{p^3 + 1}{(p + 1)^3} \\
h_i = (\text{-}RRS\text{-}) + (\text{-}SSR\text{-}) &= \frac{p(p + 1)}{(p + 1)^3} \\
s = (\text{-}RSR\text{-}) + (\text{-}SRS\text{-}) &= \frac{p(p + 1)}{(p + 1)^3} \\
h_s = (\text{-}RSS\text{-}) + (\text{-}SSR\text{-}) &= \frac{p(p + 1)}{(p + 1)^3}
\end{aligned}
$$

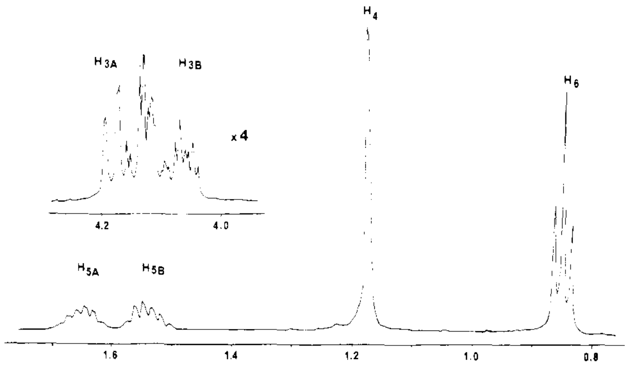


Figure 4. 500-MHz ^{1}H spectrum of racemic PMEPL (I) in $CDCl_3$ (in ppm from Me_4Si).

remaining three with numerator $2p^2$.

^{1}H NMR spectra of PMEPL were run in $CDCl_3$ at 27 °C. A typical spectrum is given in Figure 4 without resolution enhancement. One observes a triplet (1:2:1) centered at 0.846 ppm due to methyl protons. Between 1.5 and 1.7 ppm one finds two complex patterns (composed of at least eight peaks each) centered around 1.55 and 1.65 ppm. These patterns can be attributed to nonequivalent methylene protons H_{5A} and H_{5B} of the ethyl group. Finally, at the lowest field, one finds between 4.00 and 4.20 ppm a complex pattern with two groups of peaks: eight peaks between 4.20 and 4.13 ppm and generally more than eight peaks for the second group located between 4.13 and 4.03 ppm. These patterns are due to the nonequivalent protons H_{3A} and H_{3B} of the methylene group of the main chain.

Using resolution-enhanced spectra, it is possible to perform calculations of triad distributions for methylene protons from the main chain and from the side chain for polymers with different enantiomeric composition. We have performed such an analysis for protons H_{3A} at ca. 4.16 ppm. Eight resonances can be resolved for H_{3A} corresponding to parts of four AB ($^2J = -13$ Hz) spin systems (i.e., the four possible triads). Figure 5 compares the ^{1}H signals for H_{3A} in PMEPL polymers of different optical purity. The two signals (7 and 8) for the H_{3A} to lowest field increase with increasing enantiomeric enrichment and, thus, correspond to the isotactic triad. The other H_{3A}

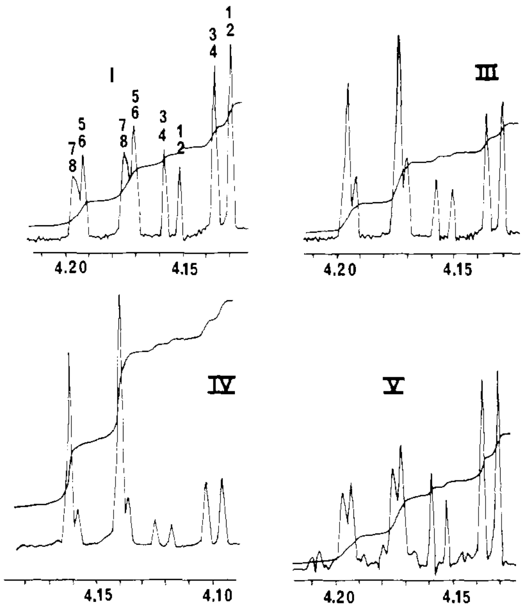


Figure 5. 500-MHz ^{1}H NMR spectra (resolution enhanced) of the H_{3A} region for PMEPL's of different enantiomeric compositions in $CDCl_3$ (in ppm from Me_4Si): I, prepared from a racemic monomer ((S)/(R) = 50/50) with an anionic-type initiator; III, prepared from a monomer ((S)/(R) = 77.5/22.5) with an anionic-type initiator; IV, prepared from a monomer ((S)/(R) = 87/13) with an anionic type initiator; V, prepared from a racemic monomer with a 1:2 $ZnEt_2$-MeOH initiator system.

Table IV
Triad Contents Determined from the H_{3A} Proton Signals (500 MHz) for PMEPL Polymers with Different Optical Purity

	theory		H_{3A} signals			
polymer	i^a	h^b	7,8	6,5	3,4	1,2
I	0.25	0.25	0.25	0.24	0.26	0.25
III	0.48	0.17	0.48	0.16	0.18	0.18
IV	0.66	0.11	0.66	0.10	0.13	0.12
$V^{c,d}$			0.25	0.26	0.26	0.24

[a] Calculated from the Bernoullian distribution $i = p^3 + 1/(p + 1)^3$. [b] Calculated from the Bernoullian distribution $s = h_s = h_i = p(p + 1)/(p + 1)^3$. [c] 1:2 $ZnEt_2$-MeOH initiator system. [d] Impurity peaks: 10% of the overall amount.

Table V
Tetrad Contents Determined from the H_{3B} Proton Signals (500 MHz) for PMEPL with Different Optical Purity[a]

polymer		tetrad 1′	2′	3′	4′	5′	6′	7′	8′
I	exptl	13.2	12.4	12.0	12.7	12.4	11.6[b]	12.3	13.2
	calcd	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
III	exptl	7.2	10.2	11.2	7.1	11.0	7.2[c]	33.6	12.3
	calcd	6.1	11.4	11.4	6.1	11.4	6.1	36.3	11.4

[a] Tabulated experimental values for 6′ and 7′ are corrected, assuming the signal labeled 6′ in Figure 6 is one of two equally populated pentads. [b] Measured values for signals 6′ and 7′ are 5.8 and 18.1, respectively. [c] Measured values for signals 6′ and 7′ are 3.6 and 37.2, respectively.

Chart III
Assignment Scheme for Tetrad Tacticity

-SR- s *-SS-* i

-SRS- s *-SRR-* h_s *-SSR-* h_s *-SSS-* i

-RSRS- 1 *-SSRS-* 2 *-RSRR-* 3 *-SSRR-* 4 *-SSSR-* 5 *-RSSR-* 6 *-SSSS-* 7 *-RSSS-* 8

signals show equal populations at various values of p and correspond to the other three triads as previously discussed for deuterated poly(propylene sulfide).[11]

From integration of the peaks one obtains the populations for the corresponding triads, which are given in Table IV, and these data suggest the following: (1) experimental i values are in good agreement with the theoretical values calculated for a Bernoullian process; (2) the heterotactic triads have almost equal populations ($h_i = h_s = s$), which again agree with the Bernoullian calculation; (3) polymer V prepared with the $ZnEt_2$–MeOH initiator shows a random distribution of n-ads as seen for polymer I; and (4) all determined values are in good agreement with the corresponding findings in the ^{13}C NMR spectra.

^1H 500-MHz calculations for H_{3A} protons are more accurate than for ^{13}C spectra since much better signal separation is obtained (compare Figures 1 and 5). The dyad tacticity effect in ^{13}C NMR for C_3 is ca. 0.1 ppm and in ^1H NMR for H_{3A} ca. 0.04 ppm. For C_3 only the triad splitting between h_i and i could be resolved but both triad effects are seen for H_{3A}. The direction of the dyad effect is the same for ^1H and ^{13}C.

A more detailed examination of the H_3 region in the ^1H NMR spectrum shows that the eight possible tetrads can be resolved for H_{3B} and can be partially resolved for the i triad of H_{3A} (Figure 6). The H_{3B} signal pairs have been numbered 1′–8′ from low to high field. The corresponding H_{3A} signals are numbered 1–8 from high to low field, whereby only the tetrad splitting between 7 and 8 is at all observable. The chemical shift difference between H_{3A} and H_{3B} increases in going from tetrad 1 to tetrad 8. It is noteworthy that for H_{3B} tetrads 3′, 4′, 6′, and 8′ show a hint a pentad splittings, and for 6′ one pentad lies under the tetrad 7′. This has been taken into account in the quantitative analysis.

In Figure 6 polymer I has no optical activity ($p = 1$) while polymer III has $p = 77.5/22.5$. For the latter polymer it is readily apparent that the isotactic tetrad gives the signals 7 and 7′. Furthermore, increases in the populations for tetrads 2′, 3′, 5′, and 8′ relative to 1′, 4′, and 6′ are observed, as summarized in Table V. Considering those data at the triad level (i.e., 1′ + 2′, 3′ + 4′, etc.), reasonable agreement with Bernoullian statistics is obtained, as was the case for H_{3A}.

At the tetrad level certain discrepancies between experimental and theoretical values are observed but cannot be judged as significant due to the increased uncertainty in the integrals for the tetrads.

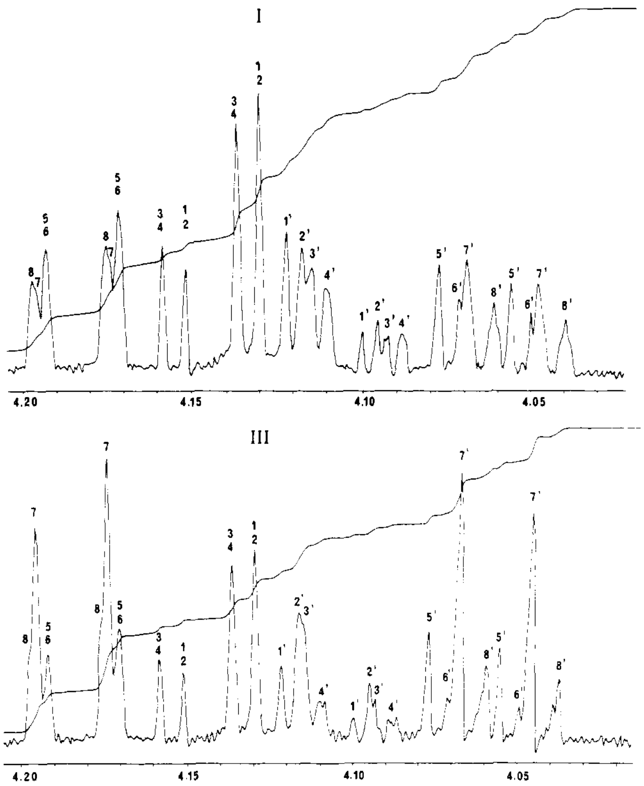


Figure 6. 500-MHz ^1H NMR spectra (resolution enhanced) of the H_3 region for PMEPL's of different enantiomeric composition in $CDCl_3$ (in ppm from Me_4Si): I, prepared from a racemic monomer ((S)/(R) = 50/50) with an anionic-type initiator; III, prepared from a monomer ((S)/(R) = 77.5/22.5) with an anionic-type initiator.

The tetrad population data provide important information that allows a tentative assignment of all tetrads for H_{3B}. In the assignment scheme outlined in Chart III it is assumed that tacticity splittings decrease in going to higher n-ads and that the higher order tacticity effects have opposite sign for *-SS-* compared to *-SR-* dyads.

The tetrads in Chart III are numbered corresponding to the signal assignments of Figure 6. The order of tetrads in Chart III from left to right represents H_{3B} chemical shifts from low to high field and the reverse sense for H_{3A}. The scheme makes the following predictions, which are confirmed by the data of Tables IV and V and Figure 6: (a) tetrad 7 is isotactic; (b) tetrads 2, 3, 5, and 8 should increase with increasing $p = (S)/(R)$; (c) the i triad has the

Table VI
Tetrad Contents Determined from the H_{3B} Proton Signals (500 MHz) for Two MPPL Polymers

polymer		tetrads 1′	2′	3′	4′	5′	6′	7′	8′
VI	exptl (±0.5)	12.1	12.5	11.8	13.1	13.1	13.1	11.8	12.5
	calcd	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
VII	exptl (±0.7)	11.2	11.2	13.5	11.2	12.4	29.7		10.3

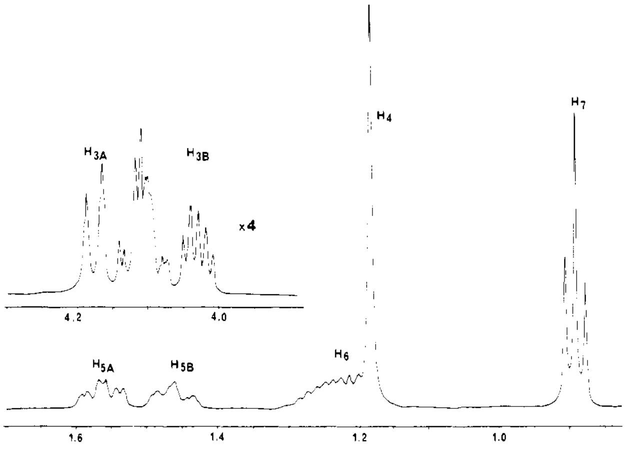


Figure 7. 500-MHz ^1H NMR spectrum of racemic PMPPL (VI) in $CDCl_3$ (in ppm from Me_4Si).

largest shift difference for H_{3A} and H_{3B}.

The assignments for tetrads derived from *-SS-* are unequivocally confirmed by the data. An ambiguity still exists for the *-SR-* branch. A reversal of the ordering for s and h_s triads and also for the tetrad effects to give *-SSRR-*, *-RSRR-*, *-SSRS-*, and *-RSRS-* for tetrads 1-4 is also consistent with the data. An assignment of *-RSRS-* is necessary to distinguish between the two possibilities.

For PMEPL the H_5 protons show tacticity effects as well, but the complexity of the ABX_3 spin system prohibits detailed analysis. The isotactic signals could be identified and the chemical shifts are 1.537 and 1.650 ppm for H_{5A} and H_{5B}, respectively. Finally, the methyl protons H_4 show only a very small dyad splitting (ca. 0.004 ppm) compared to triad effects seen in ^{13}C NMR.

500-MHz ^1H NMR of PMPPL. Spectra were taken with conditions as for PMEPL and an overview spectrum is shown in Figure 7. Again the H_3 region provides the most tacticity information, and with resolution enhancement it is possible to observe 6 of the 8 possible tetrads for H_{3A} and 12 of the possible 16 pentads for H_{3B} (Figure 8). Comparing Figure 6 and Figure 8, one finds that the distribution of chemical shifts is remarkably similar, with the *n*-propyl side chain of PMPPL serving to simply amplify the tacticity effects already discussed for PMEPL. For example, for H_{3A} the dyad and triad effects in PMEPL are 0.04 ppm and not greater than 0.006 ppm, respectively. For PMPPL the corresponding values are 0.05 ppm and not greater than 0.008 ppm. The pentad effects hinted at in Figure 6 are clearly resolved in Figure 8 (ca. 0.002 ppm).

The numbering scheme introduced in Figure 6 has been incorporated for PMPPL as well, whereby the tetrads 3′, 4′, 6′, 7′, and 8′ are now split into pentads. Analysis of H_{3A} for triads gives the following populations for the anionic racemic polymer VI: (1 + 2) = 24.1; (3 + 4) = 26.2; (5 + 6, 7 + 8) = 22.8 -26.9. Thus, no significant departure from Bernoullian statistics is found at the triad level.

Analysis of H_{3A} for tetrads is not possible due to the equivalences of 1,2 and 6,7. A nonuniform population at the tetrad level is suggested by the relative intensities of signals 8,5 and 4,3. This is, however, not borne out by a tetrad integral analysis of H_{3B} given in Table VI. Considering the error limits of the measurements, no systematic departure from Bernoullian statistics is observed for PMPPL.

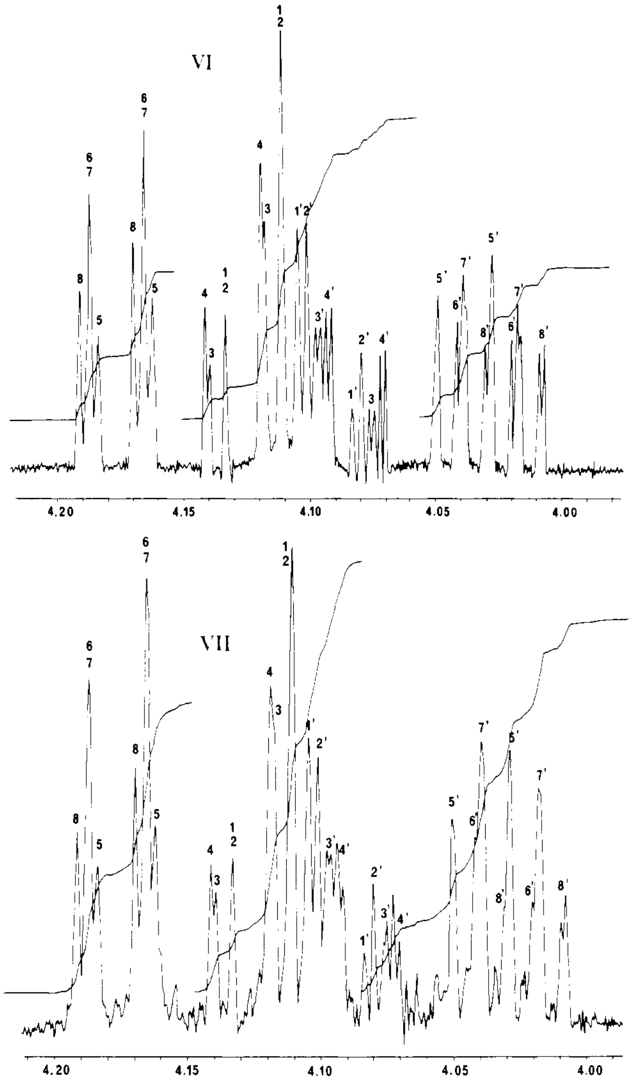


Figure 8. 500-MHz ^1H NMR spectra (resolution enhanced) of the methylene H_3 region for different PMPPL in $CDCl_3$ (in ppm from Me_4Si): VI, prepared from a racemic monomer with an anionic-type initiator; VII, prepared from a racemic monomer with a stereoelective-type initiator.

Polymer VII has a small enantiomeric enrichment and the isotactic tetrad is number 7, as for PMEPL. In this case the increase in population for i is only about 7%. In Figure 8 it appears that the relative amounts of tetrads 3, 5, and 8 for H_{3A} increase from polymer VI to polymer VII, analogous to the results found for PMEPL and in agreement with the proposed assignments. Considering the resolved pentad effects in Figure 8, it appears that the upfield pentad of 7′ and 8′ and the downfield pentad of 4′ increase with increasing $p > 1$. The logical extension of the tetrad assignment scheme proposed for PMEPL and a population analysis for pentads does indeed predict that

Macromolecules **1983**, *16*, 615–623

the pentads -*SSSSS*- and -*RSSSS*- should be upfield with increased populations for 7′ and 8′, respectively. The observations in the 3′,4′ region for polymer VII are not dependable due to the irregularities present. Thus, our assignment scheme for the -*SR*- dyad region can only be properly tested with purer polymer of higher optical activity.

Finally, it should be mentioned that the H_4 methyl protons show triad effects with three signals, 1:2:1 being observed for polymer VI at 0.9 ppm.

Conclusion

The study of α,α-disubstituted poly(β-propiolactones) with high-field NMR has allowed us to obtain detailed information on the microstructure of the polymer chain.

Polymers prepared by anionic initiation starting from a racemic mixture of monomer have a random distribution of configurational units *R* and *S* in the chain. This was substantiated by a 100.6-MHz ^{13}C NMR analysis, for which an equal distribution of triads for stereosensitive carbon atoms was found. This rules out a stereoregular structure of the type of -*RRSS*-, which would be consistent with a 0.50:0.50 dyad distribution but not with the results of triad analysis.

The triad analysis performed on enantiomerically enriched polymers fits satisfactorily to Bernoullian distribution.

The most stereosensitive carbons are the methylene carbon C_3 in the main chain and the side-chain methyl carbon C_4.

Very similar and even more detailed results were obtained with 500-MHz ^1H NMR spectroscopy. For the α-methyl-α-*n*-propyl-substituted polymer tetrad effects with some pentad splittings were observed on methylene protons H_{3A} and H_{3B}, the latter being more stereosensitive than the former. Tetrad contents were calculated for polymers of various enantiomeric compositions according to Bernoullian statistics and good agreement with experimental results was found.

An assignment scheme for H_{3A} and H_{3B} tacticity effects on ^1H chemical shifts has been proposed. The ^1H NMR data for *n*-ad populations (Bernoullian) as a function of the enantiomeric enrichment parameter $p = (S)/(R)$ allow confirmation of the scheme out to the pentad level in the -*SS*- dyad. For the -*SR*- dyad two possible assignments schemes are consistent with the data at the tetrad level. Unequivocal assignment of the -*RSRS*- tetrad is necessary to remove this ambiguity.

Polymers prepared with zinc-coordinated initiators show up to 10% irregularities in structure due to side reactions (not yet characterized). For PMEPL using achiral initiator 1:2 $ZnEt_2$–MeOH almost no stereoselection occurred. For PMPPL using chiral initiator 1:1 $ZnEt_2$–DMBD a slight enrichment of the isotactic tetrad (ca. 7%) was observed.

References and Notes

(1) Thiebault, R.; Fischer, N.; Etienne, Y.; Coste, J. *Ind. Plast. Mod.* **1962**, *14*, 1.
(2) Lenz, R. W. *Glasn. Hem. Drus. Beograd* **1974**, *39*, 395.
(3) Cornibert, J.; Marchessault, R. H.; Allegrezza, A. E.; Lenz, R. W. *Macromolecules* **1973**, *6*, 676.
(4) Marchessault, R. H.; Saint-Pierre, J.; Duval, M.; Perez, S. *Macromolecules* **1978**, *11*, 1281.
(5) D'Hondt, C.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 261.
(6) Leborgne, A.; Spassky, N.; Sigwalt, P. *Polym. Bull.* **1979**, *1*, 825.
(7) Leborgne, A.; Grenier, D.; Prud'homme, R. E.; Spassky, N. *Eur. Polym. J.* **1981**, *17*, 1103.
(8) Grenier, D.; Leborgne, A.; Spassky, N.; Prud'homme, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1781.
(9) Ferrige, A. G.; Lindon, J. C. *J. Magn. Reson.* **1978**, *31*, 337.
(10) Iida, M.; Hayase, S.; Araki, T. *Macromolecules* **1978**, *11*, 490.
(11) Sepulchre, M.; Spassky, N.; van Ooteghem, D.; Goethals, E. J. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1683.
(12) Coulon, C.; Spassky, N.; Sigwalt, P. *Polymer* **1976**, *17*, 821.
(13) Spassky, N.; Dumas, P.; Sepulchre, M.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 52*, 327.
(14) Tsuruta, T. *J. Polym. Sci., Part D* **1972**, *6*, 179.
(15) Bigdeli, E.; Lenz, R. W. *Macromolecules* **1978**, *11*, 493.
(16) Noltes, J. G.; Verbeek, F.; Overmars, H. G. J.; Boersma, J. *J. Organomet. Chem.* **1970**, *24*, 257.

Secondary Structure of Peptides. 3. ^{13}C NMR Cross Polarization/Magic Angle Spinning Spectroscopic Characterization of Solid Polypeptides

Hans R. Kricheldorf*

Institut für Anorganische und Angewandte Chemie der Universität,
Martin-Luther-King-Platz 6, D-2000 Hamburg 13, West Germany

Detlef Müller

Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten,
West Germany.

Received March 31, 1982

ABSTRACT: Natural-abundance 75.5-MHz ^{13}C NMR spectra of various solid polypeptides were measured by using the CP/MAS technique. The polypeptides were prepared by polymerizations of amino acid *N*-carboxyanhydrides under various conditions. The 75.5-MHz ^{13}C NMR CP/MAS spectra allow one to determine qualitatively and quantitatively α-helices in the presence of the antiparallel pleated sheet structure (or vice versa), to determine the poly(glycine II) structure (3_1 helix) in the presence of the poly(glycine I) structure (pleated sheet), and to distinguish the poly(proline I) structure (10_3 helix) from that of poly(proline II) (3_1 helix). A spectroscopic rule of general validity was found stating that in the case of CO and α-carbons the pleated sheet structure absorbs upfield of the α-helices, while it absorbs downfield in the case of β-carbons. The signals of γ-, δ-, and ϵ-carbons are not sensitive to a change of the secondary structure, except in the case of polyproline. A comparison of various polypeptides having identical secondary structures revealed that the chemical shifts of individual carbons obey the same substituent effects as in solution.

Introduction

In the past 5 years, ^{13}C NMR CP/MAS spectra have proved to be useful for the characterization of glassy[1–4] or partially crystalline polymers.[5–7] Crystalline and glassy areas of the same polymer may exhibit signals of different chemical shift and different line shape. Furthermore,

0024-9297/83/2216-0615$01.50/0 © 1983 American Chemical Society