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Carbon-13 Nuclear Magnetic Resonance Structural Analysis of Atactic and Stereoregular Substituted Poly(β-propiolactones)

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ABSTRACT: Several substituted poly(β-propiolactones) prepared from racemic and optically active monomers using anionic and coordination initiators were analyzed by ^{13}C NMR spectroscopy. The experimental diad and triad contents determined from 100-MHz spectra are in good agreement with those calculated assuming Bernoullian statistics. Spectra of poly(α-methyl β-propiolactones) prepared with initiators derived from $ZnEt_2$ showed only a small enrichment in isotactic diads and triads as compared to the values expected on the basis of Bernoullian statistics.

Introduction

In general, polymers prepared from heterocyclic racemic monomers by ring-opening polymerization with nonstereospecific initiators are amorphous due to their atactic chain structure. In contrast, polymers prepared from optically active monomers, or from racemic monomers with stereospecific initiators, are semicrystalline because they have a stereoregular chain structure.[1–3]

However, substituted poly(β-propiolactones) which are prepared by ring-opening polymerization from the corresponding racemic monomers exhibit two different types of behavior: (1) atactic β-mono- and β-disubstituted poly(β-propiolactones) are amorphous[3–6] but (2) atactic α-disubstituted poly(β-propiolactones) are semicrystalline.[7–16] Isotactic substituted poly(β-propiolactones), with substituents in α- or β-positions, are semicrystalline.[5,6,11–16]

In order to complete the study of this series of polymers, we have recently prepared poly(α-methyl β-propiolactones)[17] and poly(α-phenyl β-propiolactones)[18] from racemic and optically active monomers, with anionic and some other initiators. We have then observed that, in the case of α-methyl β-propiolactone, the polymers prepared from the racemic monomer are amorphous whereas, in the case of α-phenyl β-propiolactone, they are semicrystalline.

Several hypotheses can be put forward to explain the crystallinity of a polymer prepared from a racemic monomer. It can be due to the formation of tactic sequences, during the polymerization. The hypothesis of syndiotactic sequences has been proposed on the basis of crystallographic data for poly(α-methyl α-*n*-propyl β-propiolactone).[19] However, a detailed NMR analysis of the same polymer and also of poly(α-methyl α-ethyl β-propiolactones) concluded to a random distribution of the enantiomeric units in the polymer chain.[20] In such a case, the crystalline unit cell can accommodate an irregular chain structure.[16]

In this study, ^{13}C NMR spectroscopy, at 50 and 100 MHz, in solution in $CDCl_3$ at 25 °C, has been used to study the microstructure of several substituted poly(β-propiolactones). More precisely, we have analyzed several poly(α-methyl β-propiolactones), poly(α-phenyl β-propiolactones), and poly(α-phenyl α-ethyl β-propiolactones). In addition, it has seemed interesting to look, also, at the microstructure of a β-disubstituted poly(β-propiolactone), which became recently available.[21] These polylactones were analyzed in terms of diad and triad sequences.

Table I
List of Samples

polymer	sample	monomer optical purity (%)	initiator	$\bar{M}_n{}^d$ (kg/mol)
poly(MPL)	10-E	0	CH_3COOK/ 18-C-6[a]	25.8
	15-A	51	CH_3COOK/ 18-C-6[a]	
	17-A	70	CH_3COOK/ 18-C-6[a]	
	18-A	100	CH_3COOK/ 18-C-6[a]	
	40-B	0	$ZnEt_2/H_2O$	22.1
	40-C	0	$ZnEt_2/H_2O$	18.5
	40-A	0	$ZnEt_2$/DMBD[b]	25.6
poly(PhEPL)	50-C	0	CH_3COOK/ 18-Cy-6[c]	24.5
poly(PhPL)	30-C	0	CH_3COOK/ 18-C-6[a]	31.1
	32-D	30	CH_3COOK/ 18-C-6[a]	28.6
	34-D	42	CH_3COOK/ 18-C-6[a]	32.2
poly(CF_3,Me-PL)		0	$AlCl_3$	17
		89	$AlCl_3$	
		0	$ZnEt_2/H_2O$	41
		44	$ZnEt_2/H_2O$	41
		70	$ZnEt_2/H_2O$	
		82	$ZnEt_2/H_2O$	27
		89	$ZnEt_2/H_2O$	

[a] 18-C-6: dibenzo-18-crown-6 ether. [b] DMBD: (*R*)-(−)-3,3-dimethyl-1,2-butanediol. [c] 18-Cy-6: dicyclohexyl-18-crown-6 ether. [d] Determined by membrane osmometry in dichloroethane at 25 °C.

Experimental Section

Poly(α-methyl β-propiolactones) (poly(MPL)), poly(α-phenyl β-propiolactones) (poly(PhPL)), poly(α-phenyl α-ethyl β-propiolactones) (poly(PhEPL)), and poly(β-methyl β-trifluoromethyl β-propiolactones) were prepared from racemic and optically active monomers by anionic, cationic, and coordination polymerization, as described in previous publications.[17,18,21] The anionic initiator used was usually potassium acetate complexed with 1 equiv of dibenzo-18-crown-6 ether (18-C-6) and the coordination initiator diethylzinc/water (1/1 ratio). One sample of poly(MPL) was also prepared with diethylzinc/3,3-dimethyl-1,2-butanediol (DMDB), an initiator which shows, in the polymerization of some β-propiolactones,[22,23] a stereoselective character. The main characteristics of the polylactones used in this paper are given in Table I.

NMR spectra were taken with Varian XL-200 and Bruker WH-400 apparatus. The polymers were dissolved in $CDCl_3$ at a concentration of about 10% and the spectra taken at 25 °C using tetramethylsilane as a reference. A pulse width of 1.9 μs and a pulse delay of 679 ms were used. The number of scans was close to 2000. Spin–lattice relaxation times were not measured since

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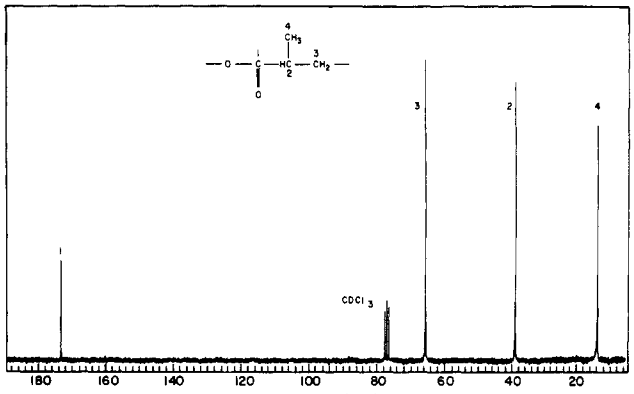


Figure 1. ^{13}C NMR spectrum of poly(α-methyl β-propiolactone).

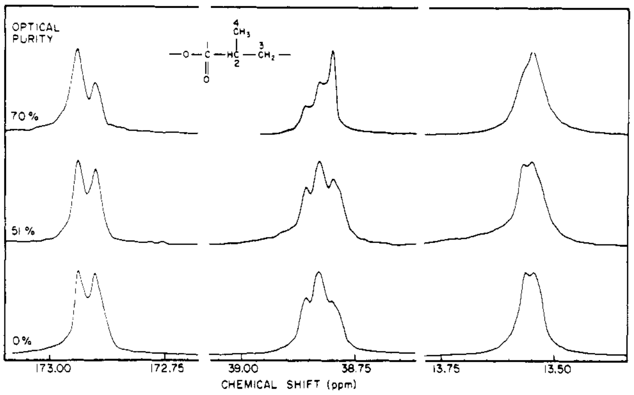


Figure 2. Expansion of the ^{13}C NMR spectra of poly(α-methyl β-propiolactones) with optical purities of 0, 51, and 70% in the C-1, C-2, and C-4 areas, respectively.

the analysis done does not involve any comparison between different carbon atoms but only the analysis of the surface areas of peaks found under a given carbon atom. Curve deconvolution was carried out assuming a 100% Lorentzian shape[24] and keeping the width at half-height of each peak constant.

Results

Analysis of Poly(α-methyl β-propiolactones). Figure 1 shows the ^{13}C NMR spectrum of atactic poly(MPL) taken at 50.3 MHz. The following chemical shifts are then observed (on a magnified spectrum): C-1, 172.9 ppm (doublet); C-2, 38.8 ppm; C-3, 65.4 ppm; C-4, 13.6 ppm. At 50.3 MHz, only the C-1 carbon is stereosensitive with a doublet (diad effect) not very well resolved.

However, at 100.6 MHz, the C-2 and C-4 signals also become stereosensitive. Figure 2 shows an expansion of the corresponding peaks of three poly(MPL)'s with optical purities of 0, 51, and 70%. A variation of the relative intensity of these peaks is clearly seen with optical purity. The two peaks of the C-1 carbon atom of the atactic polymer have the same intensity; however, the peak at low field (172.94 ppm) increases its intensity relative to the one at high fields (172.90 ppm) with the optical purity. Therefore, the low-field peak can be assigned to the isotactic diad and the high-field peak to the syndiotactic diad. Similarly, a doublet is observed for the C-4 carbon atom. This time, the high-field peak (13.55 ppm) increases in intensity with optical purity relatively to the second one (13.57 ppm) and is assigned to the isotactic diad.

Concerning the C-2 carbon atom, a triad effect is observed (Figure 2): three peaks are seen with the one at high fields (38.80 ppm) increasing in intensity relative to the one at low fields (38.86 ppm) with the optical purity. The former was assigned to the isotactic triad, the latter to the syndiotactic triad, and the intermediate one (38.83 ppm) to the hetero triads.

Chart I

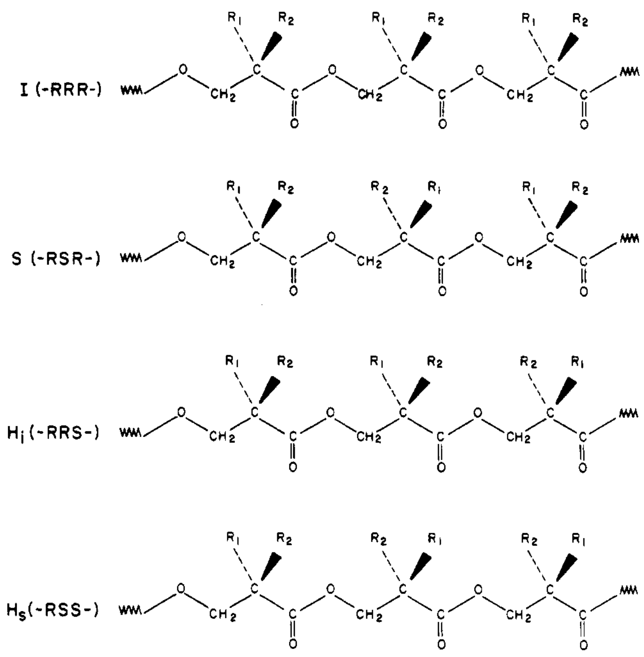


Table II
Tacticity of Poly(α-methyl β-propiolactones) Prepared with Anionic Initiators

monomer optical purity (%)	isotacticity (%)		
	exptl		
	C-1	C-4	calcd[a]
0	50	50	50
51	64	67	63
70	78	74	74

[a] Bernoullian distribution.

It is possible to correlate the diad and triad contents of the chain with the enantiomeric distribution ($p = R/S$) or with optical purity ($\alpha/\alpha_0 = |R - S|/R + S$) assuming a Bernoullian statistics. For the diads, the isotactic (i_d) and syndiotactic (s_d) fractions are given by the following formula:[20,25]

$$i_d = (p^2 + 1)/(p + 1)^2 = (1 + (\alpha/\alpha_0)^2)/2 \qquad (1)$$

$$s_d = 2p/(p + 1)^2 = (1 - (\alpha/\alpha_0)^2)/2 \qquad (2)$$

For the triads, the isotactic (I), syndiotactic (S), heteroisotactic (H_i), and heterosyndiotactic (H_s) fractions are given by[20,25]

$$I = (p^3 + 1)/(p + 1)^3 = (1 + 3(\alpha/\alpha_0)^2)/4 \qquad (3)$$

$$S = p(p + 1)/(p + 1)^3 = H_i = H_s = (1 - (\alpha/\alpha_0)^2)/4 \qquad (4)$$

For a completely random distribution in the polymer, when starting from a racemic mixture with $p = R/S = 1$ ($\alpha/\alpha_0 = 0$), one finds $i_d = s_d = 0.5$ and $I = S = H_i = H_s = 0.25$. Such distributions have already been observed for polymers prepared from racemic mixtures of heterocyclic monomers.[20,25]

It is worthy to recall that, in the case of polymers obtained by ring-opening polymerization of heterocycles bearing an asymmetric carbon atom, four types of different triads can be defined. An illustration of these triads in the case of poly(α-substituted β-propiolactones) is given in Chart I.

The C-1 and C-4 peaks of Figure 2 (diad analysis) were then deconvoluted and relative peak areas calculated. The values obtained are given in Table II. A good agreement

Table III
Triad Analysis of Poly(α-methyl β-propiolactones) Prepared with Anionic Initiators

monomer optical purity (%)	tacticity (%) C-2 triad exptl I	$H_i + H_s$	S	calcd I	$S = H_s = H_i$
0	27	45	28	25	25
51	41	42	17	44.5	18.5
70	64	25	11	61.7	12.7

Table IV
Diad and Triad Analysis of Poly(α-methyl β-propiolactones) Prepared with Different Kinds of Initiators

sample	initiator	tacticity diad i_d C-1	C-4	C-2 triad S	$H_s + H_i$	I
10-E	CH_3COOK/18-C-6[a]	50	50	27	45	28
40-A	$ZnEt_2$/DMBD[b]	56	56	26	43	32
40-B	$ZnEt_2/H_2O$	58	57	25	43	33
40-C	$ZnEt_2/H_2O$	60	58	25	45	30
eq 1-4		50	50	25	50	25

[a] Dibenzo-18-crown-6 ether. [b] (R)-(−)-3,3-Dimethyl-1,2-butanediol.

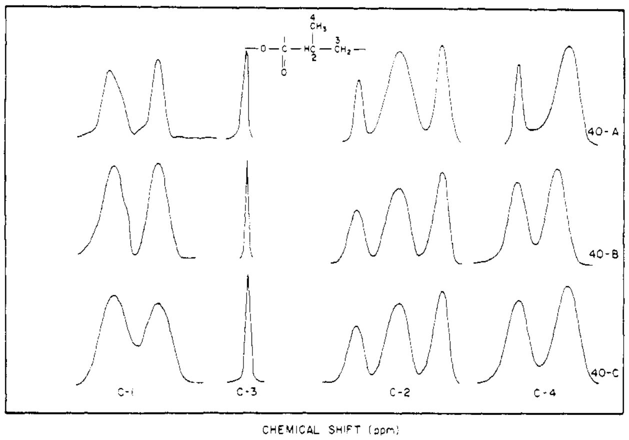


Figure 3. Expansion of the ^{13}C NMR spectrum of poly(α-methyl β-propiolactones) prepared with three different initiators in the C-1, C-2, C-3, and C-4 areas.

between experimental and calculated values according to a Bernoullian statistics is observed.

A similar analysis was carried out for the C-2 peaks of Figure 2 (triad analysis), and the result of this analysis is reported in Table III, along with the values calculated with eq 3 and 4. Again, the agreement with the calculated values is satisfactory in view of the relative difficulty met with the deconvolution.

Three other poly(MPL) samples, two of them prepared with $ZnEt_2/H_2O$ and the other with $ZnEt_2$/DMBD, have been analyzed by ^{13}C NMR spectroscopy at 100.62 MHz. An expansion of the different signals areas is given in Figure 3.

The surface areas of these peaks were calculated by deconvolution, as done before, the C-1 and C-4 carbons exhibiting a diad effect and the C-2 carbon a triad effect. The areas thus calculated are given in Table IV. There is, first of all, a good agreement between tacticity values calculated from the C-1 and C-4 peak areas. Second, the values obtained with $ZnEt_2/H_2O$ and $ZnEt_2$/DMBD are similar, but they show slightly larger isotactic contents than the sample prepared with CH_3COOK/18-C-6. These findings indicate that the former initiators produce, from a racemic monomer, a polymer with only a slight degree of stereoregularity. These initiators have thus only a slight stereospecific activity in the case of substituted β-propiolactones. This behavior is also substantiated by the low stereoselectivity observed in the polymerization of racemic α-methyl β-propiolactone with chiral $ZnEt_2$/(R)-(−)-DMBD initiator. For example, at a conversion of 66%, the unreacted monomer has a very low optical activity, $[\alpha]_D^{25}$ = +0.25 (neat, dm).

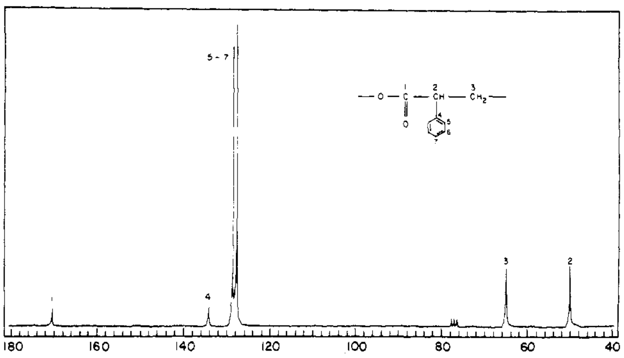


Figure 4. ^{13}C NMR spectrum of poly(α-phenyl β-propiolactone).

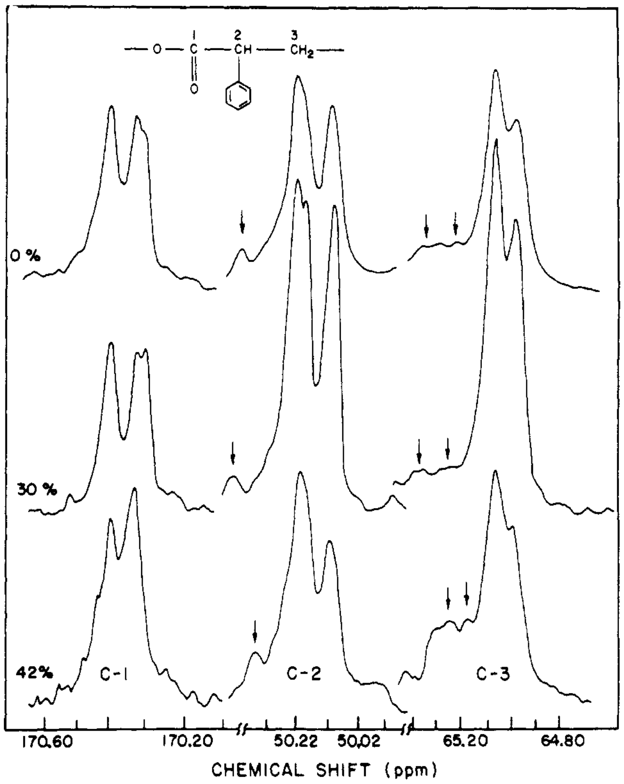


Figure 5. Expansion of the ^{13}C NMR spectra of poly(α-phenyl β-propiolactones) with optical purities of 0, 30, and 42% in the C-1, C-2, and C-3 areas, respectively (peaks assigned in the text to "chain irregularities" are shown with arrows).

Analysis of Poly(α-phenyl β-propiolactones). Figure 4 shows the ^{13}C NMR spectrum of atactic poly(PhPL) taken at 50.3 MHz. The following chemical shifts are then observed (on an expanded spectrum): C-1, 170.4 ppm (doublet); C-2, 50.1 ppm (doublet); C-3, 65.1 ppm; C-4, 134.2 ppm; C-5–7, between 128.8 and 127.2 ppm. In this case, carbon atoms C-1, C-2, and C-4–7 are stereosensitive but with a poor resolution of the peaks.

In order to obtain a better resolution of the peaks, the samples were run at 100.6 MHz. At this field, all carbon atoms are stereosensitive (Figure 5). Carbon C-3, which showed a single peak at lower field, now exhibits a doublet

Table V
Diad Analysis of Poly(α-phenyl β-propiolactones) of Different Optical Purities

optical purity (%)	tacticity (%) (i_d) exptl	tacticity (%) (i_d) calcd
0	51	50
30	53	54.5
42	57	58.8

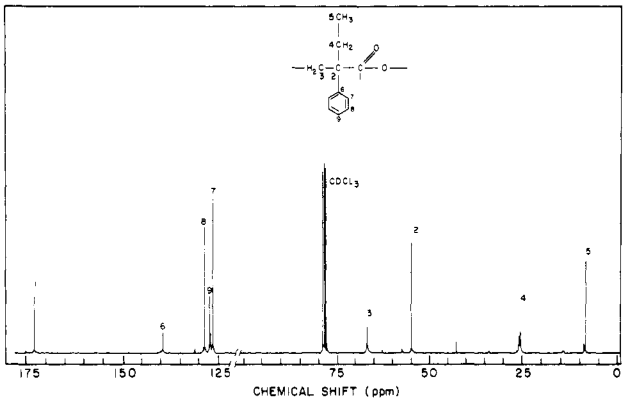


Figure 6. ^{13}C NMR spectrum of poly(α-ethyl α-phenyl β-propiolactone).

at 65.00 and 65.10 ppm. Additional peaks are also distinguishable in the C-2 and C-3 peak patterns; they can be due to chain irregularities, although their origin is not clear at the present time.

Figure 5 shows an expansion of the corresponding signals for three poly(PhPL)'s with optical purities of 0, 30, and 42% for the C-1, C-2, and C-3 peaks, respectively. The intensity of the peaks varies clearly with the optical purity, but a quantitative analysis was only carried out on the C-1 carbon which is better resolved.

The C-1 peak can be divided into a doublet, corresponding to a diad effect. The peak at high field at 170.30 ppm increases in intensity with optical purity and has been assigned to the isotactic diad whereas the other one, at 170.40 ppm, has been assigned to the syndiotactic one. After deconvolution of these peaks, the isotactic content of each polymer was determined and is reported in Table V. These values are in good agreement with those calculated from eq 1.

Analysis of Poly(α-phenyl α-ethyl β-propiolactones). A poly(PhEPL) sample, prepared from the racemic monomer with an anionic initiator, was also analyzed at 100.62 MHz. The corresponding ^{13}C NMR spectrum is given in Figure 6. The observed chemical shifts are the following: C-1, 172.4 ppm (doublet); C-2, 54.0 ppm; C-3, 65.6 ppm; C-4, 25.4 ppm (doublet). C-5, 8.3 ppm (triplet); C-6, 139.1 ppm (doublet); C-7, 126.2 ppm (triplet); C-8, 128.3 ppm (doublet); C-9, 127.0 ppm.

An expansion of the different peak areas shows that most carbon atoms are stereosensitive; however, the C-7 carbon area is better resolved than the other ones. An expansion of this peak area is shown in Figure 7. A triad effect is clearly observed. After deconvolution, one finds relative areas of 26% (126.13 ppm), 49% (126.18 ppm), and 25% (126.20 ppm). One then finds a good agreement with the values calculated with eq 3 and 4. It is, therefore, concluded that there is a random distribution of the *R* and *S* units on the poly(PhEPL) chain since it shows a Bernoullian behavior.

Analysis of Poly(β-methyl β-trifluoromethyl β-propiolactones). β-Disubstituted β-propiolactones of different optical purities have been polymerized with a coordination ($ZnEt_2/H_2O$) initiator.[21] Poly(β-methyl β-trifluoromethyl β-propiolactones) were particularly studied, and it appeared that the racemic polymer is not crystalline. Crystallization and fusion appear only for polymers with enantiomer excesses larger than 70%. It was interesting to examine these polymers by ^{13}C NMR spectroscopy in order to know the enantiomeric distribution in the polymer chain. The spectrum at 50.3 MHz of the racemic polymer in $CDCl_3$ solution is given in Figure 8. The following chemical shifts are observed: C-1, 165.6 ppm; C-2, 37.7 and 37.1 ppm; C-3, 80.1 ppm (quadruplet); C-4, 18.0 ppm; C-5, 123.9 ppm (quadruplet).

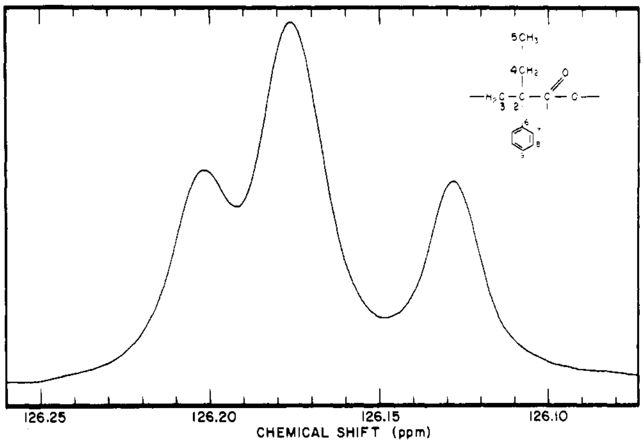


Figure 7. Expansion of the ^{13}C NMR spectrum of poly(α-ethyl α-phenyl β-propiolactone) in the aromatic (C-7) area.

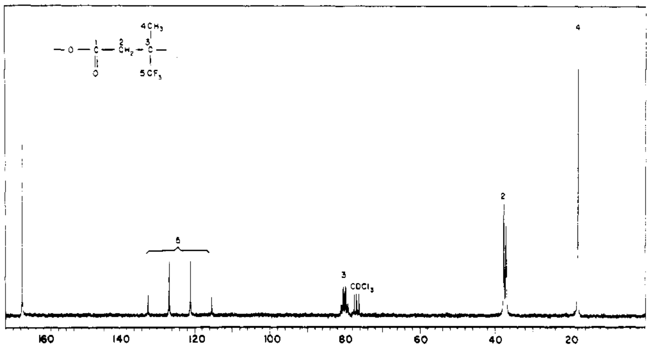


Figure 8. ^{13}C NMR spectrum of poly(β-methyl β-trifluoromethyl β-propiolactone).

Quadruplets observed with the C-3 and C-5 carbon atoms correspond to a coupling with the fluorine atoms of the CF_3 substituent. The methylenic C-2 carbon atom is stereosensitive and can be examined as a function of the enantiomeric excess variation. Expanded signals are given in Figure 9. The pattern is composed of two signals: a single peak at 37.7 ppm which increases with optical purity and is, therefore, assigned to isotactic enchainments and another signal centered at 37.1 ppm and analyzed as a doublet which corresponds to the syndiotactic placement.

Both peaks in the latter signal have an identical magnitude. It is not possible to resolve the isotactic peaks into two components. The triad analysis consists to assign the low-field signal at 37.7 ppm to the $I + H_i$ triads, while the two other peaks are assigned to H_s and S, respectively. Deconvolution of corresponding areas are given in Table VI. It appears again that there is a good agreement between experimental data and calculated values on the basis of Bernoullian statistics. Two other polymers prepared with $AlCl_3$, a non-stereospecific cationic initiator, from a racemic monomer and a monomer with the highest possible optical purity, were also examined (Table VI and Figure 9). Their spectra and their tacticity analysis are almost identical with those of the corresponding polymers pre-

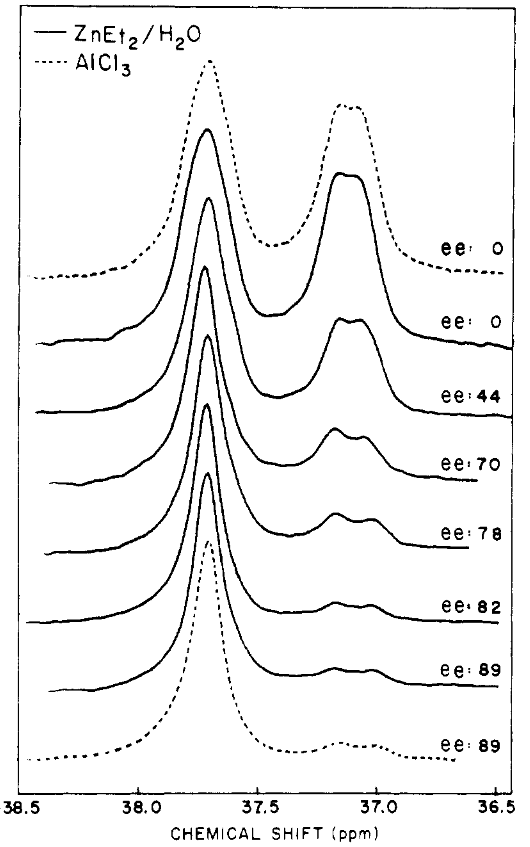


Figure 9. Expansion of the C-2 area of the ^{13}C NMR spectra of poly(β-methyl β-trifluoromethyl β-propiolactones) with different enantiomeric excess (ee).

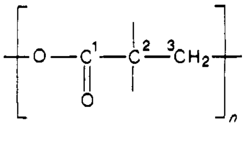
Table VI
Triad Analysis of Poly(β-methyl β-trifluoromethyl β-propiolactones)

		$I + H_i$		H_s		S	
initiator	ee, %	exptl	calcd	exptl	calcd	exptl	calcd
$AlCl_3$	0	51	50	25	25	23	25
	89	90	90	5	5	5	5
$ZnEt_2/H_2O$	0	51	50	25	25	24	25
	44	63	60	19	20	19	20
	70	75	75	14	13	11	13
	78	80	80	11	10	9	10
	82	89	84	6	8	5	8
	89	88	90	6	5	6	5

pared with the $ZnEt_2/H_2O$ system. It was, therefore, concluded from those results that $ZnEt_2/H_2O$ is not a stereospecific initiator for these β-disubstituted β-lactones and produces polymers in which the distribution of enantiomeric units obeys to a Bernoullian statistics. The presence of a sequence composed of an average of about 7 successive units of the same configuration (optical purity ≥ 70%) is necessary in order to obtain the crystallization. Thus the behavior of β-disubstituted poly(β-propiolactones) is significantly different from that of the corresponding α-disubstituted polylactones in which the racemic atactic polymers are already crystalline.

Discussion and Conclusions

Several substituted poly(β-propiolactones) have been analyzed by high-resolution ^{13}C NMR spectroscopy. At 100 MHz, most of the carbon atoms are stereosensitive:



$$\left[-O-\underset{\underset{O}{\Vert}}{C^{1}}-\underset{|}{\overset{|}{C^{2}}}-{}^{3}CH_2-\right]_n$$

In the case of α-monosubstituted poly(β-propiolactones) such as the methyl- and phenyl-substituted polymers studied in this paper, it appears that the carbonyl (C-1) and methine (C-2) carbon atoms have almost the same stereosensitivity in both cases; the methylene carbon atom (C-3) is not stereosensitive at all in the case of poly(MPL), while a diad effect appears in the case of poly(PhPL). The stereosensitivity of C-3 is preserved with poly(PhEPL). In the case of α,α-disubstituted poly(β-propiolactones), the methylenic C-3 carbon atom is much more stereosensitive than the C-2 one.[20,22] With poly(β-methyl β-propiolactone), C-3 is stereosensitive while C-2 is not at 50.3 MHz,[23] which is opposite to the case of the α-substituted products. The same behavior was observed with poly(β-ethyl β-propiolactone) studied at 25.16 MHz.[4]

The diad and triad analyses reported above show that the polymerization with anionic initiators of β-lactones obeys a Bernoullian statistics, namely, that the distribution of the *R* and *S* units along the chain occurs is random, in agreement with eq 1–4. In other words, the configuration of the chain end does not influence the choice of the monomer molecule which is of *R* and *S* configuration.

A similar result was obtained with poly(α-methyl α-ethyl β-propiolactone) and poly(α-methyl α-n-propyl β-propiolactone). High-field NMR spectroscopy has shown that the *R* and *S* units of these two polymers, at different optical purities, are distributed randomly in the chain.[20] A diad effect was observed at 62.8 MHz (^{13}C) and 250 MHz (^{1}H), while a triad effect was seen at 100.6 MHz (^{13}C) and 360 MHz (^{1}H).

Therefore, these poly(β-lactones) prepared from racemic monomers with anionic initiators are atactic, and the crystallinity observed in the case of poly(PhPL) and poly(PhEPL) is not due to the presence of some stereoregularity of the chain. We must then retain the explanation put forward previously with poly(α-methyl β-propiolactone):[15] the crystalline unit cell of the polylactone is large enough to accommodate the substituents of the atactic chain.

However, when the polymerization is carried out with $ZnEt_2/H_2O$ and $ZnEt_2$/(R)-(−)-3,3-dimethyl-2,2-butanediol as initiator, then the isotactic diad and triad contents of the polylactone chain are somewhat larger than those expected from eq 1–4. This means that these initiators are slightly stereoselective with these α-substituted monomers, although their selective and elective efficiency is much lower than in the case of the polymerization of certain thiiranes and oxiranes.[26] In contrast, the $ZnEt_2/H_2O$ initiator seems not to be stereospecific at all in the case of β-disubstituted poly(β-lactones) leading to polymers obeying a Bernoullian distribution of enantiomeric units.

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Registry No. MPL (homopolymer), 38566-36-8; MPL (SRU), 26099-72-9; PhPL (homopolymer), 116102-85-3; PhPL (SRU), 116102-87-5; PhEPL (homopolymer), 64946-23-2; PhEPL (SRU), 65014-66-6; CF_3PL (homopolymer), 116102-86-4; CF_3,Me-PL (SRU), 116102-88-6; DMBD, 31612-63-2; 18-C-6, 14187-32-7; 18-Cy-6, 16069-36-6; CH_3CO_2K, 127-08-2; $ZnEt_2$, 557-20-0; H_2O, 7732-18-5; $AlCl_3$, 7446-70-0.

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Effects of Chain Stiffness on NMR Properties. Wiener-Integral Description

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ABSTRACT: This work deals with the description of stiffness effects upon the magnetization relaxation of nuclei attached to polymer chains, in a melt or in a gel. A Wiener-integral approach is used to calculate the residual energy of tensorial spin–spin interactions, taking chain stiffness effects into consideration. It is shown how the effect of chain length competes with that of stiffness. The distribution function of the residual energy existing along a chain segment is calculated in the case where a force is applied to chain ends. It is shown that the usual description of stiffness leads to a residual energy equivalent to that associated with an ideal chain. A local interaction is introduced to modify the residual energy. The case where a chain has fixed end points is considered to illustrate properties of gel systems.

I. Introduction

It is now well established that the magnetic relaxation of nuclei attached to polymer chains can reflect topological constraints resulting either from the presence of entanglements in a melt or from that of cross-links in a covalent gel.[1-3] These constraints induce a diffusional asymmetry of motions of monomeric units which gives rise to a residual energy of tensorial interactions of nuclear spins. The relaxation of the transverse nuclear magnetization is usually found to exhibit a pseudosolid behavior governed by the residual energy of spin–spin interactions. Nonisotropic diffusion processes of segments hence manifest through this specific behavior and the residual energy Δ_e averaged over a whole sample can be considered as pertinent parameters measuring the state of constraints in a polymer whether it is a melt or a covalent gel. The parameter Δ_e has proved a convenient quantity to characterize stretching effects of chain segments resulting either from the isotropic swelling of a gel[4] or from the uniaxial elongation of such a system.[5] These investigations stress the need to quantitatively relate Δ_e not only to collective topological constraints exerted on polymers by one another but also to specific properties of individual chains. More precisely, it is necessary to discriminate the contribution to Δ_e induced by the stiffness of a chain from the contribution due to surrounding obstacles.

The purpose of this work is to propose a continuous chain approach to the description of stiffness effects on NMR properties. The stiffness is actually expected to enhance the steric hindrance affecting skeletal motions of any chain segment with end points fixed in space. According to continuous chain descriptions previously proposed by Edwards[6] and Freed,[7] the polymer will be pictured as the trajectory of a fictitious particle in a three-dimensional space. Furthermore, it will be shown that the residual energy of spin–spin interactions can be given an expression similar to that of the velocity of the fictitious particle. Consequently, the Wiener-type functional integral method will prove well appropriate to the description of NMR properties.

II. Real Chain Description

Eliminating excluded-volume effects throughout this work, the configurational statistics of a single chain will be considered by taking only short-range interactions into consideration. The description of a flexible polymer starts from a simple Gaussian chain model as usual; the nonideal behavior is then introduced through potential functions acting on the configurations. It is now well-known that the statistical description of macromolecules can rely upon

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