

Stereochemistry of Alternating Copolymers of Vinyl Olefins with Carbon Monoxide

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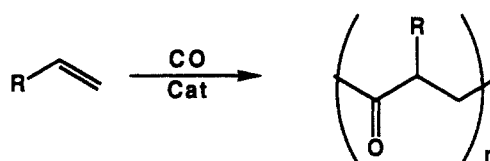
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The discovery of very efficient catalytic systems for the insertion polymerization of carbon monoxide with olefins (Scheme I) to give perfectly alternating copolymers¹ has provided a potential access to a class of interesting new materials. For a monosubstituted ethylene monomer a regioregular enchainment can lead in principle to the three well-known special stereochemical possibilities, namely, isotactic, syndiotactic, and atactic.² It has been previously reported in the patent literature that (Dppp)Pd(CF₃COO)₂ (Dppp represents 1,3-propanediylbis(diphenylphosphine)) as the catalyst precursor gives a regioregular copolymer between propylene and carbon monoxide in which no steric order can be recognized.³ The related catalytic system containing 1,3-propanediylbis(diisopropylphosphine) as the ligand allowed us to solve the problem of regioselectivity for this insertion polymerization and to realize the first synthesis of a regular poly(1-oxo-2-methyltrimethylene).⁴ The produced copolymer, which is completely soluble in chloroform, shows some stereoregularity on the basis of ¹³C-NMR; however, due to the lack of suitable models, an assignment of the bands and the determination of the prevailing stereochemical way of enchainment were not possible. The factors responsible for this partial stereoregularity are not yet known; it might be that some enantioface discrimination during the copolymerization process is determined by the chain end. The control of regioselectivity seems to be associated to electronic as well as to steric factors.⁵

We report herein on the synthesis of a regioregular poly(1-oxo-2-methyltrimethylene) which displays a rather high stereoregularity as well as a tentative assignment of the prevailing stereochemistry of the macromolecular chain through a Bernoullian statistics approach.

The copolymerization processes were carried out as previously described in the patent literature³ using a catalytic system based on palladium acetate modified with either 1,3-propanediylbis(dicyclohexylphosphine) or with the atropoisomeric chiral ligand (6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine).⁶ The obtained copolymers were recovered through filtration from the reaction mixture after dilution with methanol. The material obtained using the chiral catalyst precursor is insoluble in chloroform in contrast to that obtained with the achiral system, thus inferring a higher constitutional regularity. The ¹³C-NMR spectra of the two samples dissolved in hexafluoroisopropyl alcohol are compared in Figure 1 in the region of both the carbonyl and the methyl groups. Spectra of solutions containing both

Scheme I



samples show that the main resonances do coincide; small shifts in the reported spectra might be brought about by traces of paramagnetic impurities. The complete regioregularity for both samples is apparent from the spectrum of the carbonyl region which shows only the signal arising from a head-to-tail enchainment. Furthermore, the sample obtained with the chiral ligand shows a quite high degree of stereoregularity (Figure 1b). In fact, in the region of the spectrum corresponding to the methyl group, four main lines can be recognized in an approximate ratio of about 13:72:9:6. The sensitivity of this signal seems to be related to the four possible diastereomeric triads.

If we assume the existence of only one factor determining enantioface selection during the chain growth, the distribution of the possible stereosequences (*n*-ads) will depend only on the parameter related to the stereodiscriminating ability of the system. In Table I the triad and tetrad distributions calculated for a statistical process according to an isotactic and a syndiotactic stereochemistry are shown.⁷ For the poly(1-oxo-2-methyltrimethylene) under examination the aforementioned observed distribution of the triads is much closer to the concentrations calculated for a prevalently isotactic structure. In fact in the case of a syndiotactic situation, a system characterized by a good stereoselectivity will give a product showing essentially only three triads (one largely prevailing), the concentration of the fourth being very small. This was found to be, indeed, the case for the poly(1-oxo-2-phenyltrimethylene) obtained through copolymerization of styrene with carbon monoxide⁸⁻¹⁰ catalyzed by (1,10-phenanthroline)Pd(*p*-CH₃C₆H₄SO₃)₂ to which a syndiotactic structure was assigned on the basis of measured and calculated X-ray patterns.¹⁰ For this copolymer the ¹³C-NMR spectrum in the region of the substituted phenyl carbon atom (Figure 2b) shows essentially only three triads in a 80:10:10 molar ratio.¹⁰

This statistical approach is further corroborated from a closer examination of the ¹³C-NMR spectrum of the region of the carbonyl group (Figure 1). The higher complexity of the signal pattern must be related to *n*-ads of order higher than 3. For poly(1-oxo-2-methyltrimethylene) on the basis of the isotactic prevalence evaluated from the methyl region one would expect (Table I) for the possible tetrads the observed feature (Figure 1b) of a large signal accompanied by four weaker ones. Consistently, for the largely stereoregular syndiotactic structure of the aforementioned poly(1-oxo-2-phenyltrimethylene)¹⁰ only three small signals and a large one are observed in the same region (Figure 2b). In this figure also the spectrum (a) of a completely atactic material is shown for comparison.^{10,11}

In conclusion, the Bernoullian statistics approach seems to be substantially valid for both the copolymers of carbon monoxide with propylene and styrene. In the latter case the prevailing syndiotactic structure is confirmed. For the former copolymer the extrapolated prevailing structure is in keeping with the intuitive consideration that an isotactic structure is more likely associated to an enantio-morphic site control than to a chain end control.¹² In fact, the nature of the catalytic system used and the type

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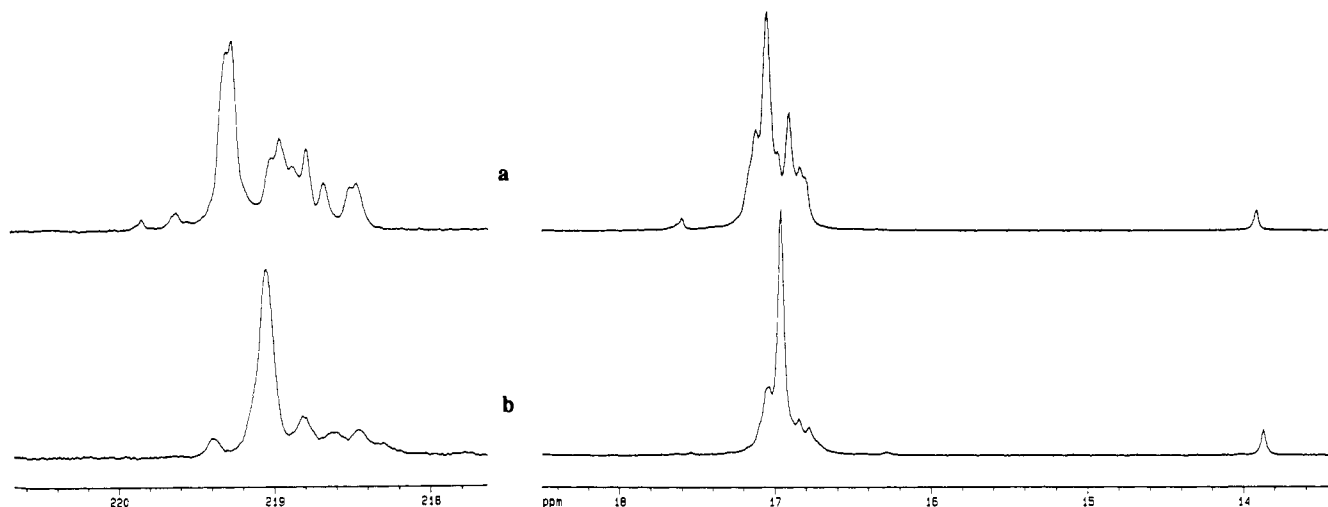


Figure 1. ^{13}C -NMR spectra (125.8 MHz, $(\text{CF}_3)_2\text{CHOH}$) of the carbonyl region and of the methyl group region of the propylene-carbon monoxide copolymers obtained with palladium catalysts modified by the ligands 1,3-propanediylbis(dicyclohexylphosphine) (a) or with (6,6'-dimethylbiphenyl-2,2'-diyl)bis(dicyclohexylphosphine) (b).

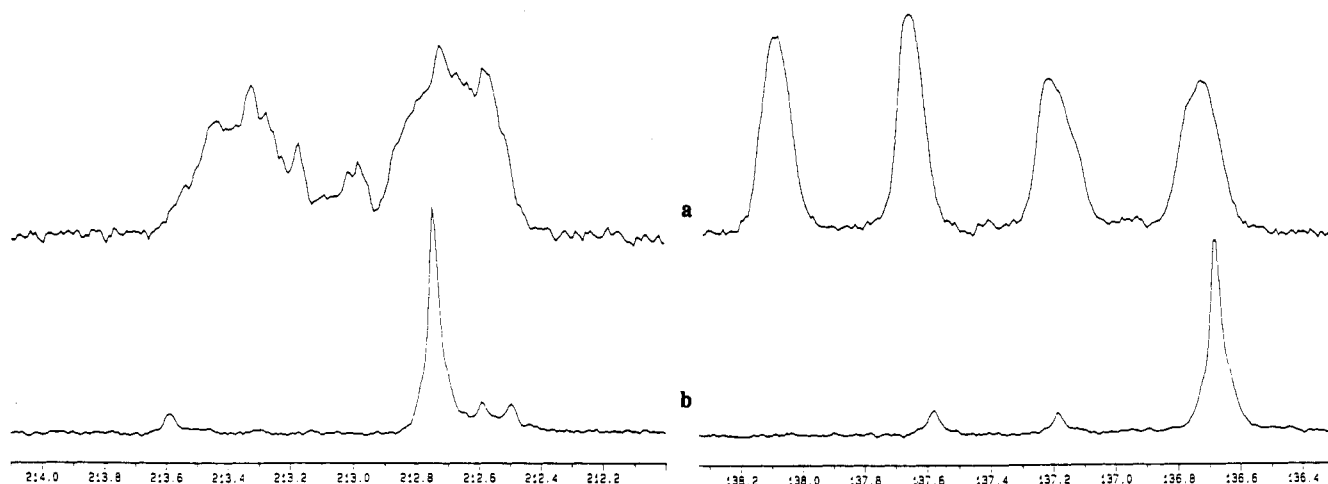


Figure 2. ^{13}C -NMR spectra (125.8 MHz, $(\text{CF}_3)_2\text{CHOH}$) of the carbonyl region and of the ipso carbon atom region for an atactic (a) and a syndiotactic (b) styrene-carbon monoxide copolymer.

Table I
Distribution of the Triads and Tetrads for Bernoullian Statistics According to Different Stereochemistry

<i>n</i> -ads	frequencies of the possible stereosequences				
	<i>lk</i> -enantiomeric selection ^a	<i>p</i> = 0.04 ^b	<i>ul</i> -enantiomeric selection ^c	<i>q</i> = 0.07 ^d	<i>p</i> or <i>q</i> = 0.5 ^e
mm	$1 - 3p + 3p^2$	0.88	q^2	~0	0.25
mr	$p - p^2$	0.04	$q - q^2$	0.07	0.25
rr	$p - p^2$	0.04	$1 - 2q + q^2$	0.86	0.25
rm	$p - p^2$	0.04	$q - q^2$	0.07	0.25
mmm	$1 - 4p + 6p^2 - 4p^3 + 2p^4$	0.85 ₀	q^3	~0	0.125
mmr	$p - 3p^2 + 4p^3 - 2p^4$	0.03 ₆	$q^2 - q^3$	~0	0.125
mrr	$p - 3p^2 + 4p^3 - 2p^4$	0.03 ₆	$q - 2q^2 + q^3$	0.06 ₀	0.125
rrm	$p - 3p^2 + 4p^3 - 2p^4$	0.03 ₆	$q - 2q^2 + q^3$	0.06 ₀	0.125
rmm	$p - 3p^2 + 4p^3 - 2p^4$	0.03 ₆	$q^2 - q^3$	~0	0.125
mrmm	$2p^2 - 4p^3 + 2p^4$	~0	$q^2 - q^3$	~0	0.125
rmr	$2p^2 - 4p^3 + 2p^4$	~0	$q - 2q^2 + q^3$	0.06 ₀	0.125
rrr	$2p^2 - 4p^3 + 2p^4$	~0	$1 - 3q + 3q^2 - q^3$	0.80 ₄	0.125

^a In a situation where the monomer is attached to the growing end always on the same enantioface, *p* is the probability of an *ul*-enantiomeric selection. ^b Evaluated from the ^{13}C -NMR spectrum of the poly(1-oxo-2-methyltrimethylene) in the region of the methyl groups (Figure 1b); small *p* leads to an isotactic structure. ^c In a situation where the monomers are attached to the growing end alternatingly by one and the other enantioface, *q* is the probability of a sequence of two *lk*-enantiomeric faces, i.e., the probability of having an *m* diad. ^d Evaluated from the ^{13}C -NMR spectrum of the poly(1-oxo-2-phenyltrimethylene) in the region of the ring ipso carbon atom (Figure 2b); small *q* leads to a syndiotactic structure. ^e *p* or *q* values for an evenly and fully epimerized sample.

of triad distribution strongly suggest the former type of stereocontrol.

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Registry No. (CH₃CH₂CO₂)₂Pd, 3375-31-3; H₂C=CHCH₃/CO (copolymer), 122741-16-6; 1,3-propanediylbis(dicyclohexylphosphine), 103099-52-1; 6,6'-dimethylbiphenyl-2,2'-diylbis(dicyclohexylphosphine), 141397-77-5.