

Figure 2. ^{13}C abundances in metabolites isolated from cultures of *Methanobacterium thermoautotrophicum* grown in the presence of $[1-^{13}\text{C}]$ acetate. Numbers indicate relative ^{13}C abundances. Carbon atoms without designations have ^{13}C abundances of 0.9–1.2.

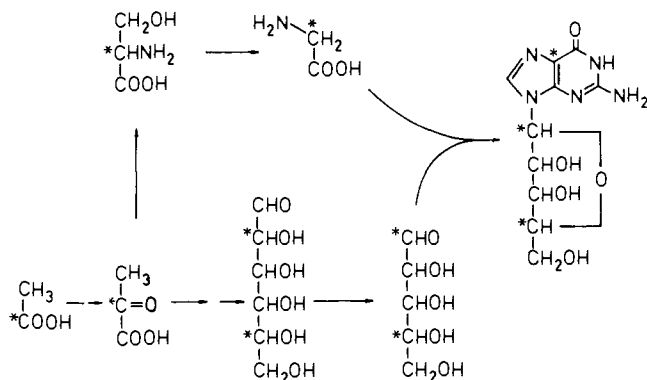


Figure 3. Carbohydrate metabolism in *Methanobacterium thermoautotrophicum*. Asterisks signify ^{13}C -labeled positions.

medium by adsorption to a column of Dowex 1. The compound was purified by chromatography on QUAE Sephadex followed by reversed-phase HPLC.⁶

The bacterial cells were treated with 0.1 M NaOH, and the nucleotides resulting from the hydrolysis of RNA were isolated by anion exchange chromatography.¹³ Treatment of 2',3'-GMP with phosphatase afforded guanosine. Tyrosine was obtained from cellular protein after acid hydrolysis by a sequence of anion exchange chromatography and HPLC.

Proton-decoupled ^{13}C NMR spectra of all isolated compounds were measured at 7.1 T on a Bruker WM-300 NMR spectrometer. Isotope enrichments were calculated from integrals by comparison with the spectra of natural-abundance material. Signal assignments for 8-hydroxy-7,8-didemethyl-5-deazariboflavin were based on chemical shift considerations, NMR titration studies, analysis of long-range ^1H - ^{13}C couplings, and low-power single-frequency ^1H -decoupling experiments.

^{13}C abundances of labeled carbon atoms are shown in Figure 2. It is immediately apparent that no substantial randomization of the isotope has occurred in agreement with observations on amino acid biosynthesis in *Methanospirillum hungatei*.¹⁴ The labeling pattern of the ribose moiety of guanosine is in line with accepted knowledge on carbohydrate metabolism pathways operating in methanogenic bacteria (Figure 3).¹⁵ The labeling pattern of tyrosine is easily explained by the shikimic acid pathway on the basis of the carbohydrate labeling pattern described above.

The labeling pattern of **4** suggests that the ribitol moiety originates by reduction of a ribose moiety and that the pyrimidine ring is derived from the pyrimidine ring of a purine precursor. The carbocyclic rings of **4** and of tyrosine show identical patterns of ^{13}C enrichment. Since tyrosine has been ruled out as precursor,¹¹ we are left with the hypothesis that the carbocyclic ring of **4** is derived from another product of the shikimate pathway. **4** shows a quasi-symmetrical distribution of isotope indicated by the dashed line in Figure 2, and, hence, the direct precursor should be a symmetrical aromatic molecule, such as 4-hydroxybenzoate.

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Chiral Complexes Polymerize Methacrylate Esters To Give Helical Polymers That Mutarotate by Uncoiling¹

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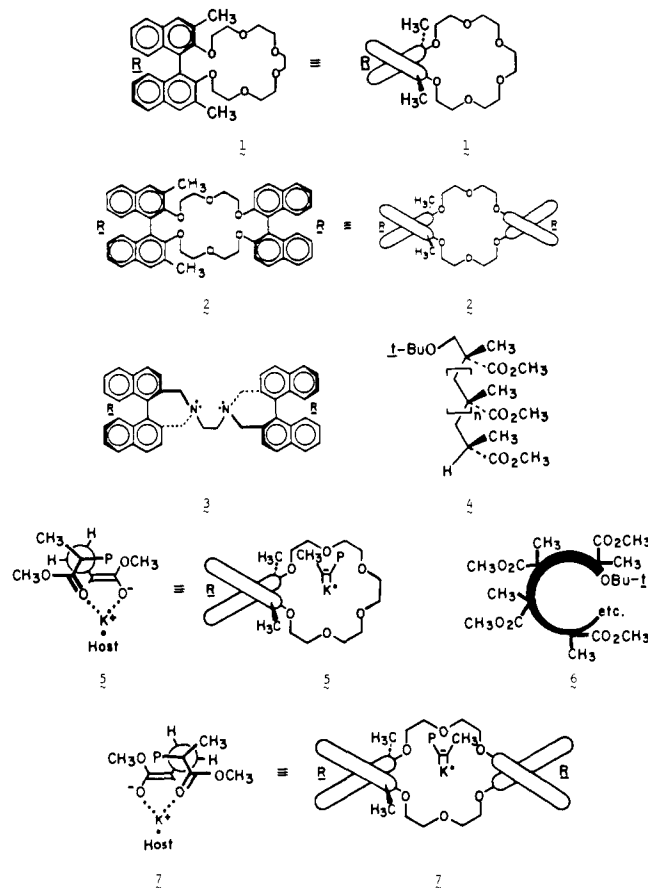
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Previous work demonstrated that potassium bases complexed to chiral hosts (*R*)-**1** and (*R,R*)-**2** catalyzed Michael additions of carbon acids to α,β -unsaturated esters and ketones with high asymmetric induction, yields, and turnover numbers.² In other work, butyllithium complexed to chiral ethylenediamine, (*R,R*)-**3**,



added to benzaldehyde to give 1-phenyl-1-pentanol with high asymmetric induction.³ The preferred configurations of the products were interpreted in terms of differences in steric interactions between catalyst and reactants in diastereomeric transition states. Since anionic polymerization of methacrylate esters is a

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Table I. Optically Active Polymers of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{R}$ Produced with Chiral Host Initiators at -78°C in 95% Toluene-5% THF, 95-100% Conversion

run no.	R of ester	catalyst	[ester]/[catalyst]	tacticity, % ^a			\bar{M}_n^b (D)	$[\alpha]^{25}_{578}$ (THF, c 2)	
				iso	syn	het		initial ^c	later, h
1	Me	(S)-1-KO- <i>t</i> -Bu	5	80	5	15	480 (1.06)	+250°	+40° (5)
2 ^d	Me	(S)-1-KO- <i>t</i> -Bu	15	78	2	20	1600 (1.2)	+248°	+20° (5)
3	Me	(S,S)-2-KO- <i>t</i> -Bu	100	88	7	5	<i>e</i>	-180°	<i>e</i>
4 ^f	Me	(S,S)-3-LiBu	10	90	2	8	1100 (1.1)	+70°	+10° (24)
5	<i>t</i> -Bu	(S)-1-KO- <i>t</i> -Bu	11	90	5	5	1600 (1.3)	+117°	+78 (18) +2° (42)
6	<i>t</i> -Bu	(R)-1-KO- <i>t</i> -Bu	30	90	7	3	<i>e</i>	-150°	<i>e</i>
7	PhCH ₂	(S)-1-KO- <i>t</i> -Bu	12	not	determ		2100 (1.5)	+350°	no change

^a Determined from ¹H NMR methyl chemical shifts in polymer backbone; isotactic, δ , 1.24; syndiotactic, 0.85; heterotactic, 1.09. The spectra were consistent with $\text{I}-[\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{R})]_n\text{-H}$ structures. ^b \bar{M}_n and \bar{M}_w determined by GPC; polydispersity, $D = \bar{M}_w/\bar{M}_n$. ^c Taken after about 5 h or less handling time at ambient temperature. ^d The procedure is illustrated. To a dry solution of 0.56 g of KO-*t*-Bu and 2.58 g of (S)-1 in 1 mL of THF stirred under Ar was added 19 mL of toluene, followed by 7.50 g of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ (dropwise, -78°C , 15 min, syringe pump). The mixture was stirred at -78°C for 3 h, 3 mL of CH_3OH was added, the solvent was evaporated under vacuum, and the product was purified by preparative GPC (Styragel-THF) and preparative HPLC (silica gel, EtOAc-BuCl, 1:1 by volume). ^e Not taken. ^f Run in pure toluene.

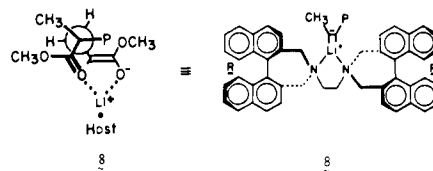
special example of the Michael addition reaction, we anticipated that 1-3 complexed with metal bases would act as chiral catalysts to "stamp out" asymmetric units to give optically active isotactic polymers. The carbanion ion paired to the host-bound cation is present at the growing end of the chain. Thus, any configurational "mistake" would tend to be corrected rather than perpetuated in the successive generation of asymmetric centers.⁴ After we had observed high rotations for our methyl methacrylate polymer, Yuki et al. reported that (-)-sparteine-BuLi-initiated polymerization of trityl methacrylate gave optically stable isotactic polymer whose high optical rotation was attributed to helicity.⁵ The only other known synthetic polymers that are helically chiral are the poly-(alkyl isocyanides), which show high configurational stability.⁶

Table I illustrates our results. Runs not recorded here established that for each of the three catalysts, inverting the configurations of the catalysts inverted the signs of rotation of the polymer produced, as is illustrated in runs 5 and 6. When the *tert*-butyl polyester from run 5 ($[\alpha]^{25}_{578} +117^\circ$) was cleaved in methanolic HCl under mild conditions, and the polyacid produced was treated with CH_2N_2 , the methyl polyester obtained gave $[\alpha]^{25}_{578} +2^\circ$. The chromatographic and ¹H NMR properties of the polymers showed the absence of byproducts that often accompany anionic polymerization.⁷

The results indicate that all three catalysts with methyl, *tert*-butyl, or benzyl methacrylate gave highly isotactic polymers with high optical rotations whose sign depended on the configuration of the catalyst and was independent of the nature of the R group of the ester monomer. More interestingly, the polymers with methyl and *tert*-butyl ester groups mutarotated at ambient temperature over a period of hours to give rotations close to zero, whereas the polymer with the benzyl ester group was optically stable over similar time spans. We conclude that the high rotations are due to helicity of the polymers induced by the chiral cavities of the catalyst in which each unit is added to the growing chain. The helices of at least the methyl and *tert*-butyl ester polymers appear to be thermodynamically unstable kinetic products of the polymerization, whose conformations randomize over a period of hours to give a small residual optical rotation associated with the mesolike interior and different end groups of isotactic polymer (i.e., 4 produced in run 1). We do not understand why the benzyl ester helix is more stable than the *tert*-butyl ester helix. As expected, the polyacid derived from the optically active *tert*-butyl ester polymer randomized before it could be reesterified.

The patterns of relationships between the configurations of the catalysts employed and the signs of rotations of the helical

polymers produced are coherent with the patterns observed for the simple Michael reactions. Thus, (S)-1-KOBu-*t* always gave (+) polymer and (S,S)-2-KOBu-*t* gave (-) polymer. These two catalysts provided opposite chiral biases in the Michael additions as well.² Similar stereoelectronic factors probably operate in both the Michael additions and polymerizations. Structures 5, 7, and 8 are suggested models for the dominant transition states for the



carbon-carbon bond-forming steps of the propagation reactions. These models account for the facts, predict the configurations of the asymmetric centers of the polymers, and predict the helical configurations as well. Thus, 5 and 8 predict helical polymer 6 with a counterclockwise helix, while 6 predicts an enantiomeric polymer with a clockwise configuration. The mechanism of the conformational randomization of helical isotactic poly(methyl methacrylate) presents an interesting problem potentially amenable to a computational modeling.

Electronic Conductivity of Poly[tris(5,5'-bis[(3-acrylyl-1-propoxy)carbonyl]-2,2'-bipyridine)ruthenium(0)]

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We have previously reported electrochemical and spectral studies of electrodes modified with polymer films (poly-1) prepared from the monomeric complex RuL_3^{+2} (1) where L = 5,5'-bis-[(3-acrylyl-1-propoxy)carbonyl]-2,2'-bipyridine.^{1,2} These films are electroactive having seven stable oxidation states (2+ to 4-).² Here we report that, under certain solution and potential conditions, poly-1 in its zero formal oxidation state is an electronic conductor having specific conductivities approaching those reported for doped polyquinoline.³ By employing a soluble cationic polymer as the supporting electrolyte, negative formal oxidation states of poly-1 are prevented from forming by the selective steric exclusion of cations. By thus locking poly-1 into a single oxidation state it is possible to measure its electronic conductivity without the

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