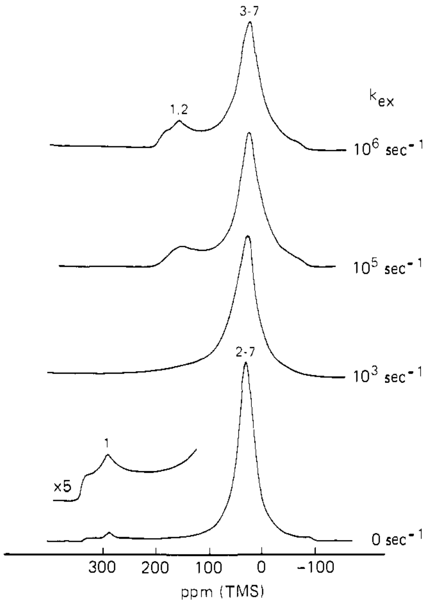
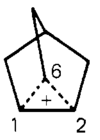
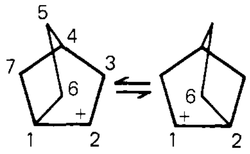


Figure 2. Simulation of two-site chemical exchange between carbons 1 and 2 of a classical 2-norbornyl cation structure (**2**). The calculation is for a nonspinning solid sample and includes the effects of a chemical shift anisotropy for carbon in a site of less-than-tetrahedral symmetry (i.e., the charged carbon). The spectrum observed at 5 K (Figure 1e) most closely resembles exchange-narrowed spectra ($k_{ex} \geq 10^5$ s^{-1}).

band is the nonspinning equivalent of the low field resonance observed in liquid-state and MAS solid-state spectra. This resonance can be interpreted in terms of the positively charged carbons of the σ-bridged (nonclassical) structure (**1**) or as the time average of rapidly equilibrating localized (classical) ions (**2**).



1



2

If one adopts the latter view, the spectrum at 5 K requires the activation energy for interconversion of localized (or partially localized) ions to be no greater than 0.2 kcal mol^{-1}.

This conclusion may be reached in the following way. The chemical shift anisotropy (CSA) patterns for C1 and C2 in **2** were calculated in the slow and fast exchange limits with the following assumptions. It was assumed that the CSA pattern for the positively charged carbon in **2** would be similar to that of the charged carbon in the isopropyl cation and that the uncharged carbon of the equilibrating pair in **2** as well as the other five carbons have isotropic environments. The CSA parameters for the charged carbon (480 ppm) were obtained from the static spectrum of the charged carbon of the isopropyl cation at 5 K, and were used to simulate the spectrum of **2** at various exchange rates (Figure 2).[6] Comparison of these calculated spectra with the observed 5 K spectrum of the norbornyl cation indicates that the observed spectrum could be explained by equilibration of localized ions (**2**) with an exchange frequency of 10^5 s^{-1} or greater. If classical rate theory applies, this indicates that the activation energy for interconversion is less than 0.2 kcal mol^{-1}.[7]

The results reported here could be taken as the most direct evidence yet obtained for the σ-bridged ion in super acid media.[8] The possible alteration of the potential surface of the norbornyl cation in the presence of solvent has been noted.[9] It will be interesting to see if solid-state NMR techniques may be useful in the investigation of the effects of solvent on the norbornyl cation potential surface.

Acknowledgment. We thank the National Science Foundation for support (CHE-8020743) and IBM Instruments, Inc., for postdoctoral support (V.M.). The skilled assistance of R. D. Kendrick is gratefully acknowledged.

Registry No. 2-Norbornyl cation, 24321-81-1.

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[6] The isopropyl cation was prepared from ^{13}C-enriched 2-chloropropane by the codeposition procedure described in ref 2. The relative insensitivity of E_a to the value of k_{ex} should be noted. A change of 10^2 in either k_{ex} or the preexponential factor will alter E_a by less than 50 cal mol^{-1}.

[7] Fong has criticized classical rate process theory and has suggested that it might be possible to account for very rapid equilibration rates of degenerate, classical norbornyl cations by a tunneling mechanism even if the intrinsic barrier is several kcal mol^{-1}. See: Fong, F. K. *J. Am. Chem. Soc.* **1974**, *96*, 7638.

[8] Recent calculations of relative SCF energies of the norbornyl cation with a 4-21 G basis set augmented by d polarization functions on all carbons indicated that the nonclassical form is 0.2 kcal mol^{-1} more stable than the "classical" form. See Goddard, J. D.; Osamura, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 325.

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Experimental Evidence for the Existence of Catalytic Sites with Different Steric Structures in Supported Ziegler–Natta Catalysts

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Catalytic systems prepared from TiCl$_4$ supported on MgCl$_2$ and aluminum trialkyls polymerize α olefins to form polymers having widely different stereoregularities.[1]

It has been assumed[1,2] that, as is the case for traditional Ziegler–Natta catalysts,[3] there are sterically different catalytic centers in the supported catalysts which would produce isotactic polymers or mostly stereoirregular polymers. However, experimental evidence for this assumption is very scarce.

We present some results concerning the polymerization of racemic 4-methyl-1-hexene (4-MH) with the above catalytic systems in the presence of (*l*)-menthyl-*p*-methoxybenzoate ((–)-MA) that show that atactic and isotactic polymers are indeed produced by sterically different catalytic centers.

In a typical experiment (*R*,*S*)-4-MH (0.14 mol) was polymerized at room temperature in heptane (100 cm^3) in the presence of Al(i-C$_4$H$_9$)$_3$ (0.012 mol) and a catalyst (0.377 g), containing 3.9% Ti, prepared by grinding anhydrous MgCl$_2$ with the complex (–)MA–TiCl$_4$.[4]

Different amounts of (–)-MA were added to the mixture, the molar ratio [(–)-MA]/([Al] + [Ti]) (r) varying between 0.131 and 0.796 (Table I). Furthermore, in a series of experiments the above ratio was kept constant (r = 0.293) and the conversion of monomer to polymer was varied between 8% and 90% (Table II). The polymers obtained were fractionated by boiling solvents extraction[5] and characterized as reported in Tables II and III.

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[4] Pure (–)-MA showed $[\alpha]^{25}_{546}$ –97.9° (c 5.14, methanol).

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Table I. Stereoelective Polymerization[a] of (*R*,*S*)-4-Methyl-1-hexene with Different Ratios [(–)-MA]/([Al] + [Ti])

				recovered monomer			polymerized monomer[c] B[d]		C[e]		D[f]		E[g]	
run	r	productivity[b]	conversion, %	$[\alpha]^{25}_{365}$,[h] deg	op,[i] %	prev chir	op,[j] %	prev chir	op,[j] %	prev chir	op,[j] %	prev chir	op,[j] %	prev chir
1	0.131	159	88	nd[k]	nd	nd	0.67	*S*	0.19	*R*	0.50	*R*	0.68	*R*
2	0.408	67	15	–0.033	0.3	*S*	0.25	*S*	1.67	*R*	1.34	*R*	3.33	*R*
3	0.501	24	40	–0.104	1.1	*S*	0.55	*S*	1.71	*R*	0.61	*R*	1.48	*R*
4	0.538	53	66	–0.239	2.2	*S*	1.39	*S*	1.05	*R*	0.54	*R*	1.62	*R*
5	0.796	4	43	–0.293	2.7	*S*	0.63	*S*	3.55	*R*	2.03	*R*	1.67	*R*

[a] Polymerization conditions: catalytic system $TiCl_4$–(–)-MA/$MgCl_2$/Al(i-C_4H_9)$_3$/(–)MA; g of Ti/g of $MgCl_2$ = 0.039; temperature 25 °C. [b] Productivity = (g of polymer)/[(g of Ti) × *h* × (mol of olefin) × l^{-1}]. [c] In all experiments, a low molecular weight, acetone soluble, fraction A (4–10% of the total polymer) was obtained. [d] Acetone-insoluble, ethyl acetate soluble fraction. [e] Ethyl acetate insoluble, diethyl ether soluble fraction. [f] Diethyl ether insoluble, diisopropyl ether soluble fraction. [g] Diisopropyl ether insoluble, methylcyclohexane-soluble fraction. [h] Neat. [i] A sample of (*S*)-4-MH, having $[\alpha]^{25}_{589}$ – 2.70° (neat) [optical purity 89% (Pino, P.; Lardicci, L.; Centoni, L. *Gazz. Chim. Ital.* 1961, *91*, 428–440)] showed $[\alpha]^{25}_{365}$ – 9.63° (neat). [j] Optical purity of a monomer giving rise to a polymer fraction having the same rotatory power and solubility (data calculated on the basis of values reported in the following: Pino, P.; Ciardelli, F.; Montagnoli, G.; Pieroni, O. *Chim. Ind.* (*Milan*) 1966, *48*, 635–636). [k] Not determined.

Table II. Stereoelective Polymerization of (*R*,*S*)-4-Methyl-1-hexene at Different Conversions[a]

		recovered monomer			polymerized monomer[c] B[d]			C[e]			D[f]			E[g]		
run	conversion, %	$[\alpha]^{25}_{365}$,[h] deg	op,[i] %	prev chirality	yield, %	op,[j] %	prev chirality	yield, %	op,[j] %	prev chirality	yield, %	op,[j] %	prev chirality	yield, %	op,[j] %	prev chirality
6	8	*k*	*l*	*S*	14.6	0.23	*S*	31.6	1.08	*R*	5.5	0.90	*R*	37.3	1.72	*R*
7	33	–0.041	0.4	*S*	14.1	0.53	*S*	31.8	1.29	*R*	8.9	0.84	*R*	34.7	1.43	*R*
8	71	–0.138	1.3	*S*	12.0	1.09	*S*	38.6	1.04	*R*	10.7	0.47	*R*	31.3	*l*	*R*
9	90	–0.241	2.2	*S*	12.5	1.50	*S*	32.9	0.95	*R*	19.6	0.21	*R*	29.6	1.25	*R*

[a] r = 0.293. [c–j] See the corresponding footnotes of Table I. [k] Negative value <0.004. [l] Not determined.

Table III. Fractionation[a,b] and Characterization of the Polymers Obtained in the Stereoelective Polymerization of (*R*,*S*)-4-Methyl-1-hexene

	polymer fractions B[d,h]			C[e,h]			D[f,i]			E[g,l]		
run	yield, %	$[\eta]$,[n] dL/g	$[\alpha]^{25}_{D}$,[m] deg	yield, %	$[\eta]$,[n] dL/g	$[\alpha]^{25}_{D}$,[m] deg	yield, %	$[\eta]$,[n] dL/g	$[\alpha]^{25}_{D}$,[m] deg	yield, %	$[\eta]$,[n] dL/g	$[\alpha]^{25}_{D}$,[m] deg
1	14.7	0.24	+2.67	25.6	1.34	–0.87	10.9	1.87	–2.59	44.7	3.33	–4.25
2[c]	6.6	0.22	+1.0	23.7	1.63	–7.7	8.2	2.2	–6.9	39.8	5.54	–20.7
3	9.9	0.28	+2.2	28.5	nd	–7.9	5.5	2.66	–3.1	48.1	nd	–8.2
4	4.5	0.25	+5.5	27.9	1.40	–4.8	5.01	1.57	–2.76	52.8	4.8	–10.1
5	6.9	0.3	+2.5	22.4	2.58	–16.4	4.7	2.31	–10.4	57.6	5.19	–10.4
6	14.6	0.36	+0.94	31.6	1.78	–4.9	5.5	1.79	–4.7	37.3	0.96	–16.6
7	14.1	0.28	+1.98	31.8	1.95	–5.8	8.9	2.33	–5.9	34.7	1.04	–8.8
8	12	0.27	+4.23	38.6	2.08	–4.7	10.7	2.75	–4.6	31.3	2.77	nd
9	12	0.26	+5.51	32.9	1.81	–4.3	19.6	2.57	–4.2	29.6	1.16	–7.8

[a] By extraction with boiling solvents. [b] In all experiments an oily fraction (4–10%) soluble in boiling acetone was obtained. [c] The boiling-acetone-soluble fraction was 21%. [d] Acetone-insoluble/methyl acetate soluble fraction. [e] Ethyl acetate insoluble/diethyl ether soluble fraction. [f] Diethyl ether insoluble, diisopropyl ether soluble fraction. [g] Diisopropyl ether insoluble/methylcyclohexane-soluble fraction. [h] The fractions are amorphous at X-ray examination and show by ^{13}C NMR examination a large amount of stereoirregularities. [i] The fractions were crystalline; mp, determined by DTA, between 201 and 210 °C. [l] The fractions are highly stereoregular (^{13}C NMR) and had a melting point, determined by DTA, between 213 and 217 °C. [m] c = 10–20 mg/cm^3 in methylcyclohexane. [n] In methylcyclohexane at 60 °C.

The nonpolymerized monomer was recovered, and after thorough purification, its optical purity was determined.

As predicted on the basis of earlier data[2], productivity[6] rapidly decreases when (r) is increased.

Also the diastereomeric composition of the polymer changes with r: the ratio between the amount of the diisopropyl ether insoluble crystalline fraction and that of the acetone-insoluble, ethyl acetate soluble amorphous fraction is higher in the experiments with higher r (Table III). This ratio does not change significantly with the conversion (Table II).

For $r > 0.1$, the optical activity of the recovered monomer is negative and increases, in the experiments with similar conversions, with increasing r (Table I); at constant r the optical purity of the recovered 4-MH increases with increasing conversion (Table II). This shows that the overall polymerization process is stereoelective, overall stereoelectivity being much larger than that previously reported for the polymn. of the same olefin with other stereoelective catalytic systems.[7]

Surprisingly, the prevailing chirality of the monomeric units forming the macromolecules of the amorphous fraction is the same as that prevailing in the recovered monomer. The optical purity estimated for the polymerized monomer in this fraction is lower than that of the recovered monomer for conversions of 50% or larger, and it increases with the increasing optical purity of the not yet polymerized monomer.

On the other hand, as expected,[7] the prevailing chirality of the monomeric units included in the most isotactic[8] fraction is opposite

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(6) See Table I, footnote a; "productivity" has been used instead of "activity" to indicate the amount of polymer produced per unit weight of catalyst per hour for a given monomer concentration, as this quantity depends not only on the "activity" of the catalytic centers but also on the number of centers present per unit weight of catalyst.

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to that of the recovered monomer, the enantiomeric excess decreasing by increasing conversion (experiments 6–9).

The above experiments clearly show the existence, in the catalytic system used, of at least two classes of catalytic centers. The first one is made of highly stereospecific, catalytic centers (C_l and C_d)[8] which are stereoelective and prevailingly polymerize the (*R*)-antipode of the monomer producing the highly isotactic diisopropyl ether insoluble polymer. The second class that synthesizes the amorphous ethyl acetate soluble polymer (C), is made of substantially nonstereospecific catalytic centers that have a very low stereoelectivity, if any. For this last type of centers not only the productivity but also the relative activity and/or concentration in the catalyst decreases by increasing *r*.

The stereoregulating and antipode discriminating capacity of the optically active Lewis base can satisfactorily be explained by assuming the following: (i) (–)-MA, as Lewis base (B*), substantially decreases the number and/or the activity of the nonstereospecific catalytic centers, C, which evidently possess a Lewis acidity larger than AlR_3 (eq 1); (ii) stereoelective, highly

$$C_{solid} + AlR_3B^* \overset{K_1}{\rightleftharpoons} CB^*_{solid} + AlR_3 \qquad (1)$$

$$C^*_{d(solid)} + AlR_3B^* \overset{K_2}{\rightleftharpoons} C^*_dB^*_{solid} + AlR_3 \qquad (2)$$

$$C^*_{l(solid)} + AlR_3B^* \overset{K_3}{\rightleftharpoons} C^*_lB^*_{solid} + AlR_3 \qquad (3)$$

stereospecific, chiral centers (C^*_d; C^*_l) are, probably for steric reasons, weaker Lewis acids than the less stereospecific centers C [$K_1 > K_2$ and $K_1 > K_3$ (eq 1–3)]; (iii) the observed stereoelectivity in the synthesis of the most stereoregular fraction is due to the different tendencies of the chiral catalytic centers (C^*_d; C^*_l) to form complexes (and then to lose or decrease their catalytic activities) with the chiral base B*, the equilibrium constants K_2 and K_3 being different, in keeping with the formation of the diastereomeric complexes $C^*_dB^*$ and $C^*_lB^*$, respectively.

We take the decrease of catalyst productivity by increasing *r* as an indication that the surface complexes CB*, C_dB^*, and C_lB^* are not catalytically active. However, the present data do not exclude the existence of different stereoregulating and antipode discriminating mechanisms connected with the existence of other types of centers (C′B*) that might be still catalytically active and, because of the presence of the chiral base B*, might be able to distinguish between the two antipodes of the monomer.[9]

Registry No. (±)-4-MH, 13643-03-3; (*l*)-MA, 4951-49-9; isotactic poly((±)-4-methyl-1-hexene), 33409-74-4; poly((±)-4-methyl-1-hexene), 30775-40-7; $TiCl_4$, 7550-45-0; $MgCl_2$, 7786-30-3; $Al(i\text{-}C_4H_9)_3$, 100-99-2.

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(9) Pino, P.; Mülhaupt, R., to be submitted for publication.

Circular Dichroism Spectrum of C_3-Cyclotriguaiacylene after Ionization of the Phenolic Groups. Experimental Approach to the "Magic Angle" Region in C_3-Cyclotriveratrylene Derivatives

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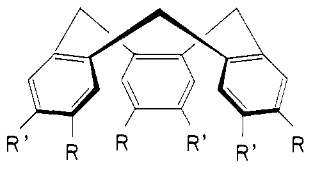
In previous papers,[1,4] we reported the circular dichroism (CD) spectra of some C_3-chiral derivatives of cyclotriveratrylene (CTV) and their interpretation in terms of exciton coupling between the transition moments of the three aryl chromophores. The presence of substituents having spectroscopic moments of different magnitudes ($R \neq R'$) was considered to cause a rotation of the electric transition moments of each individual aryl chromophore from the symmetrical positions ($\theta = 0$ or 90°); in this way, collinear components of the magnetic and electric moments are generated in the "trimer" (Figure 1). In the exciton approximation, the symmetric *A* coupling depicted in Figure 1 generates a high-energy negative CD component for the B_{2u} transition and a low-energy positive component for the B_{1u}. In the CD spectrum of (*M*)-(+)-C_3-cyclotriguaiacylene[2] **1** in methanol (Figure 2), these components correspond to the bands observed at ca. 277 and 250 nm; the bands at ca. 299 and 236 nm correspond instead to the degenerate *E* components of the two transitions.[1]



M-(+) 1 R = OCH_3
R' = OH

This picture is true as long as the value of θ is less than ~45°, which represents in the point-dipole approximation the "magic angle" θ_m at which the potential *V* is zero:[11]

$$V = (D_{mon}/d^3)(\cos^2\theta\cos^2\Phi + \tfrac{7}{4}\cos^2\theta\sin^2\Phi - \tfrac{5}{4}\sin^2\theta) \qquad (1)$$

When 45° < θ < 90°, the symmetric *A* coupling of the B_{2u} transitions still corresponds to a negative CD, but this time at lower energy; similarly, for $180° - 45° < \theta + 90° < 180°$, the *A* coupling of the B_{1u} transitions always gives positive CD, but now at higher energy; in other words, the sequence of bands should be inverted with the overall effect of generating a mirror image spectrum.[13]

The value of θ in all C_3-CTV derivatives studied so far is usually small, and in order to reach the region of the "magic angle", substituents R and R′ should have spectroscopic moments of very different magnitude. We expected that such a situation could be obtained in (*M*)-(+)-**1**, *after ionization* of the phenolic groups. As our previous work has shown,[1] when the phenolic groups are undissociated (in neutral or acidic methanol), their spectroscopic moment is slightly higher than the methoxy one, and the value of θ was calculated to be of the order of 3–4°. Ionization of **1** (in 0.2 N sodium methoxide/methanol solution) determines, as expected,[3] a ca. 2-fold increase of the band areas of both the B_{2u} and B_{1u} transitions in the isotropic absorption spectrum, and a shift to longer wavelengths of all observed bands (Figure 2). Guaiacol, which represents the "active monomer" of trimer **1**, shows a ca. 3-fold increase in the band area of the B_{2u} transition on passing from acid methanol to a 0.2 N solution of sodium methoxide in methanol. The band areas of both B_{2u} and B_{1u} transitions of **1** are about 40% larger than 3 times the values observed for guaiacol, indicating nonadditive contributions to the total isotropic intensity which are probably due to homoconjugation effects. After subtraction of these contributions, the increase in the absorption band areas of **1** after ionization becomes comparable to that of guaiacol.

In the case of strongly conjugative substituents such as OCH_3 and particularly O^-,[5] it is not possible to predict quantitatively

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