$(I_D/I_A)_0 = 18.5$, much larger than any I_C/I_A ratio observed in our study. It may then be concluded that energy transfer by the radiative mechanism made only a minor contribution to the observed effects.

The various approaches used in this study for the characterization of the texture of freeze-dried samples gave consistent results. The conclusion that the extent of chain interpenetration depends on the solution concentration before freeze-drying is also supported by the appearance of the samples, i.e., fluffy powders obtained from highly dilute solutions as against coherent elastic samples obtained from more concentrated solutions. The notion that isolated chain molecules will collapse to compact spherical particles on sublimation of the frozen solvent is also borne out by electron microscopic studies of glassy polymers when droplets of their highly dilute solutions are evaporated.[20-22]

In recent years the transition from dilute polymer solutions to semidilute solutions, in which chain interpenetration becomes important, has been a subject of much theoretical and experimental study. This transition is generally characterized by a concentration c^*, which may be estimated by a variety of methods.[23-25] Many years ago it was pointed out that c^* should be proportional to $1/[\eta]$[26] and Ferry has recently suggested[27] that experimental data are consistent with $c^* \sim 3/[\eta]$. We have indicated this estimate of c^* for comparison with the I_C/I_A data on Figure 2.

As would be expected, the degree of chain interpenetration increases gradually with increasing solution concentration. An attempt was made some years ago[28] to characterize the interpenetration by a change in the extinction coefficient of the polymer due to a change in the polarity of its microenvironment. In this study a sharp break was reported in a plot of the optical density against polymer concentration and this was taken as characterizing c^*. However, it was never clear why such a break should be seen and recent work[29] has shown that the effect is an instrumental artifact. It is, therefore, particularly welcome to see that the technique we describe in this paper offers a spectroscopic approach to the characterization of the interpenetration of flexible chains as a function of solution concentration.

References and Notes

(1) On leave from the Technical University of Łódź, Łódź, Poland.
(2) Amrani, F.; Hung, J.-M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649.
(3) Mikeš, F.; Morawetz, H.; Dennis, K. S. *Macromolecules* **1980**, *13*, 969.
(4) Morawetz, H. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 404.
(5) Ishihara, S.; Komatsu, A.; Hata, T. *Polym. J.* **1971**, *2*, 640.
(6) Schultz, A. R.; Young, A. L. *Macromolecules* **1980**, *13*, 663.
(7) Price, F. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 63*, 13.
(8) Berghmans, H.; Overbergh, N. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1757.
(9) Pouyet, G.; Kohler, A.; Dayantis, J. *Macromolecules* **1981**, *14*, 1126.
(10) Roots, J.; Nyström, B. *Eur. Polym. J.* **1979**, *15*, 1127.
(11) Gashgari, M.; Frank, C. W. *Macromolecules* **1981**, *14*, 1558.
(12) (a) Quian, R. *Pure Appl. Chem.*, in press. (b) It is possible that the decreased I_C/I_A is an artifact resulting from a decrease in light scattering from units in the pellets due to their compression.
(13) Hughes, L. J.; Britt, C. E. *J. Appl. Polym. Sci.* **1961**, *5*, 337.
(14) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.
(15) Kühnle, W.; Zachariasse, K. *J. Photochem.* **1976**, *5*, 165.
(16) Winnik, M. A.; Redpath, T.; Richards, D. H. *Macromolecules* **1980**, *13*, 328.
(17) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.
(18) Frank, C. W.; Gashgari, M. A. *Macromolecules* **1979**, *12*, 163.
(19) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(20) Siegal, R. M.; Johnson, D. H.; Mark, H. *J. Polym. Sci.* **1950**, *5*, 111.
(21) Richardson, M. J. *J. Polym. Sci., Part C* **1963**, *3*, 21. *Proc. R. Soc. London, Ser. A* **1964**, *279*, 50.
(22) Reimlinger, H. *Naturwissenschaften* **1976**, *63*, 574.
(23) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(24) Berry, G. C.; Nakayasu, H.; Fox, T. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1825.
(25) Nyström, B.; Porsch, B.; Sundelöf, L.-O. *Eur. Polym. J.* **1977**, *13*, 683.
(26) Weissberg, S. G.; Simha, R.; Rothman, S. *J. Res. Natl. Bur. Stand.* **1951**, *47*, 298.
(27) Ferry, J. D. *Macromolecules* **1980**, *13*, 1719.
(28) Destor, C.; Langevin, D.; Rondelez, F. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 229.
(29) Lee, C. H.; Waddell, W. W.; Casassa, E. F. *Macromolecules* **1981**, *14*, 1021.

Isotactic Polymerization of Propene: Stereoregularity of the Insertion of the First Monomer Unit as a Fingerprint of the Catalytic Active Site

Adolfo Zambelli,*,† Paolo Locatelli,‡ Maria Carmela Sacchi,‡ and Incoronata Tritto‡

Istituto Chimico, Università di Napoli, 80134 Napoli, Italy, and Istituto di Chimica delle Macromolecole del CNR, 20133 Milano, Italy.

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ABSTRACT: The results of the ^{13}C NMR analysis of the end groups of polypropylene samples prepared in the presence of different catalytic systems are evaluated and compared with the "enantiomorphic site" statistical model. The stereoregulating capability of the active sites for different Al alkyl cocatalysts is discussed, as well as the role of a Lewis base as a modifier of a $MgCl_2$-supported catalytic system.

1. Introduction

Isotactic polymerization of propene involves stereospecific insertion of the prochiral monomer on reactive metal–carbon bonds (active sites)[1]

$$\mathrm{Mt{-}P} + C_3H_6 \rightarrow \mathrm{Mt{-}}C_3H_6\mathrm{P}$$

where Mt is the metal atom of the active site and P represents the growing polymer chain.

The chain propagation approaches the "enantiomorphic site" statistic model.[2,3] Accordingly, the ideal isotactic catalyst is a racemic mixture of enantiomorphic active sites (D-preferring sites and L-preferring sites). The stereo-

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† Istituto Chimico, Università di Napoli.
‡ Istituto di Chimica delle Macromolecole del CNR.

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Table I
Polymerizations[a]

sample	Ti catalyst[b]	Al alkyl[c]	Zn alkyl[d]	*t*, °C	time, h	yield, g
a	δ-$TiCl_3$	$Al(^{13}CH_3)_2Cl$		20	20	0.4
b	δ-$TiCl_3$	$Al(^{13}CH_3)_3$	$Zn(^{13}CH_3)_2$	20	22	9.5
c	δ-$TiCl_3$	$Al(^{13}CH_3)_2I$		75	2	7.5
d	δ-$TiCl_3$	$Al(^{13}CH_2CH_3)_3$	$Zn(^{13}CH_2CH_3)_2$	20	48	8.5
e	$TiCl_4$-$MgCl_2$ ethyl benzoate	$Al(^{13}CH_2CH_3)_3$	$Zn(^{13}CH_2CH_3)_2$	20	2	22.5

[a] The polymerization runs were performed under the following conditions: 100 mL of heptane (samples a, b, d, and e), 250 mL of toluene (sample c); 1 g of C_3H_6 (sample a), C_3H_6 at atmospheric pressure (samples b, d, and e), C_3H_6 at 2.5 atm (sample c). [b] 2 g (sample a); 1 g (sample b, c, and d); 0.3 g (sample e). [c] 8.5 mmol (sample a); 2.85 mmol (samples b and d); 9.2 mmol (sample c); 2 mmol (sample e). [d] Al/Zn = 1.5.

specific propagation parameters are $P_{DD} = P_{LL}$ and $P_{DL} = P_{LD} = 1 - P_{DD}$, where P_{DD} is the probability of D insertion on the D-preferring sites, P_{LL} is the probability of L insertion on the L-preferring sites, P_{DL} is the probability of L insertion on the D-preferring sites, and P_{LD} is the probability of D insertion on the L-preferring sites.

The propagation parameters are related to the stereochemical sequence of the configurations of the monomer units; e.g.

$$[mm] = P_I^D P_{DD} P_{DD} P_{DD} + P_I^D P_{DL} P_{DL} P_{DL} + P_I^L P_{LL} P_{LL} P_{LL} + P_I^L P_{LD} P_{LD} P_{LD} \quad (1)$$

where P_I^D is the probability that a catalyst site will show a "D" preference, P_I^L is the probability that a catalyst site will show an "L" preference, and $P_I^D + P_I^L = 1$. By assuming $P_{DD} = P_{LL}$ and $P_{DL} = P_{LD}$, eq 1 becomes

$$[mm] = (P_I^D + P_I^L)(P_{DD})^3 + (P_I^D + P_I^L)(1 - P_{DD})^3 = (P_{DD})^3 + (1 - P_{DD})^3 \quad (2)$$

and

$$[mr + rm] = 2P_{DD}^2(1 - P_{DD}) + 2P_{DD}(1 - P_{DD})^2 \quad (3)$$

$$[rr] = P_{DD}^2(1 - P_{DD}) + P_{DD}(1 - P_{DD})^2 \quad (4)$$

where [mm], [mr + rm], and [rr] are the molar fraction of isotactic, heterotactic, and syndiotactic stereochemical triads.[4,5]

Such a propagation model implies that the steric control ultimately comes from the asymmetric environment of the active sites. As a consequence, the stereochemical sequence of the configuration of the monomer units, or any related parameter (e.g., P_{DD}), is a sort of fingerprint of the structure of the active site.

In principle, by determining, for example, the value of P_{DD} for polymers obtained in the presence of different catalyst systems, one should be able to compare the structure of the relative isotactic specific site. In practice, the real catalytic systems do not contain only isotactic specific sites, and the polymers consist of very stereoregular isotactic macromolecules together with less (or none at all) isotactic macromolecules deviating from the enantiomorphic site model.

As a consequence it often happens that P_{DD} cannot be determined with adequate accuracy by means of the available methods of investigating the polymer structure (e.g., ^{13}C NMR).

The initiation of the polymerization process occurs on Mt–R active sites. R can be H, CH_3, C_2H_5, or another alkyl group, depending on the catalytic system, and, at least in some cases, it can be identified on the end groups.[6] By extending the enantiomorphic site model to stereospecific initiation, one can define four stereospecific initiation parameters: $I_{DD} = I_{LL}$ and $I_{DL} = I_{LD} = 1 - I_{DD}$. They are related to the stereochemical structure of the polymer by the relationships

$$[e] = I_{DD}P_{DD} + (1 - I_{DD})(1 - P_{DD}) \quad (5)$$

$$[t] = I_{DD}(1 - P_{DD}) + P_{DD}(1 - I_{DD}) \quad (6)$$

where [e] is the molar fraction of monomer units bonded to R flanked by a first neighboring unit having the same configuration and [t] is the molar fraction of monomer units bonded to R flanked by a first neighboring unit having the opposite configuration (see Figure 1).

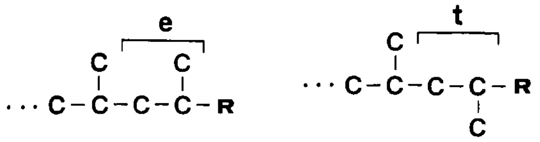

Figure 1. Fisher projection of e and t monomer units.

Of course, it is assumed that P_{DD} is the stereospecific insertion parameter for all the monomer molecules but the first inserted one.

We have recently observed that when R = CH_3 or C_2H_5, the isotactic initiation process is less stereospecific than the isotactic chain propagation.[7] Therefore I_{DD} is a more sensitive fingerprint than P_{DD} of the structure of the active sites.

In this paper we report the P_{DD} and I_{DD} values of some polymers prepared in the presence of different catalytic systems, together with some inferences concerning the structure of the active sites. The function of ethyl benzoate in modifying the stereospecificity of a $MgCl_2$-supported catalytic system will be discussed.

2. Experimental Part

2.1. Reagents. ^{13}C-enriched (30–50%) aluminum and zinc alkyls were prepared and purified as described previously.[7]

δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene. The $TiCl_4$-$MgCl_2$-ethyl benzoate supported catalyst system was prepared as described in the patent literature.[8] The Ti content was 1.5% by weight.

2.2. Polymerization. Polymerization runs were performed in a glass reactor or in an autoclave.

The experimental conditions and the yields are reported in Table I. Run c was carried out at higher temperature (75 °C) in order to obtain lower molecular weights. When we take into account that the stereoregularity usually drops when temperature increases, the conclusions concerning the catalytic system c appear even more reliable (see later).

2.3. Polymer Fractionation. The fractionation of polymer samples with boiling hydrocarbons was carried out by conventional methods.[9] The heptane-insoluble fractions of samples d and e were subjected to a further extraction with octane at a controlled temperature (110 °C). Table III shows the fractionation results of samples d and e (for the explanation see text).

2.4. ^{13}C NMR Analysis. ^{13}C NMR analyses of the polymers dissolved in 1,2,4-trichlorobenzene containing 1% $C_2D_2Cl_4$ as an internal standard were carried out at 140 °C in the PFT mode

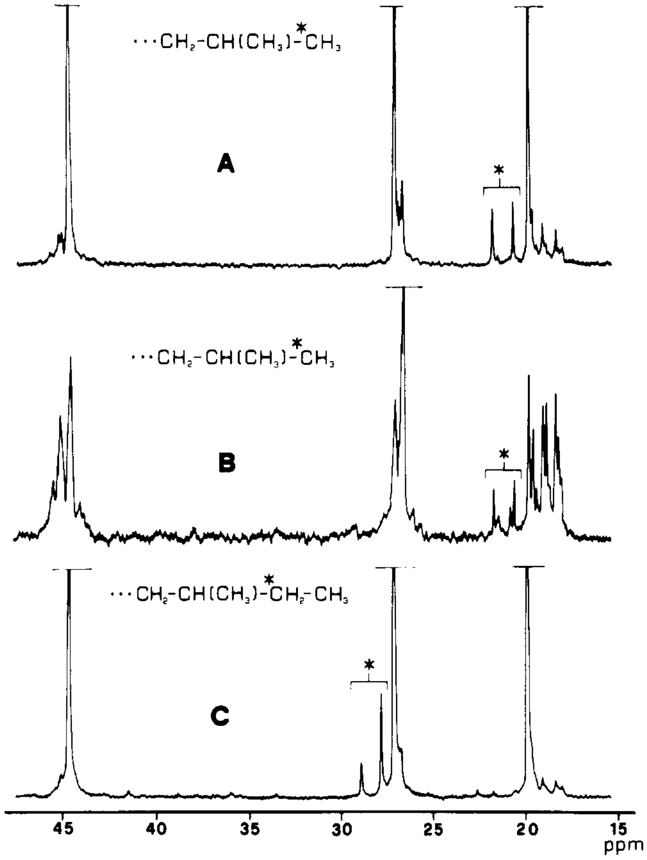

Figure 2. ^{13}C NMR spectra of the heptane-soluble (A) and pentane-soluble (B) fractions of sample b and of the heptane-soluble fraction (C) of sample d.

on a Bruker MX-90 spectrometer operating at 22.63 MHz. The chemical shifts are relative to HMDS. The steric triad composition of each fraction reported was determined from the methyl carbon triad intensities according to the literature.[10]

Spectra A and B of Figure 2 are, respectively, the spectra of the heptane- and pentane-soluble fractions of sample b. The resonances of the methyl carbons of the isobutyl end groups are detectable (marked by a star) in the methyl region of the spectra. The chemical shifts and the stereochemical assignment[4] are reported in footnote 11. Note that in the spectrum of the more regular fraction (Figure 2A), the resonances at 20.8_7 and 21.5_4 ppm, calling for second-inserted monomer units irregularly arranged, are practically absent. This means that the insertion of monomer units on primary alkyl groups equal to or larger than isobutyl undergoes practically the same degree of steric control.

It is perhaps of some use to outline that as previously reported,[12] the methyl carbons of the isobutyl end groups are diastereotopic with respect to the methyls of the inner monomer units.

Therefore, depending on the fact that, not the monomer, but the Al alkyl cocatalyst is ^{13}C enriched, the stereoregularity of the insertion of the first monomer unit is related to the intensity of the resonance at 20.6_9 ppm (^{13}C-enriched methyl carbons of the end group in threo, i.e., syndiotactic, steric placement) while the stereoirregularity of the insertion of the same monomer unit is related to the intensity of the resonance at 21.7_6 ppm (^{13}C-enriched methyl carbons of the isobutyl end group in erythro, i.e., isotactic, steric placement).

Figure 2C shows the spectrum of the highly regular heptane-soluble fraction of sample d.

Of course, in this case, depending on the Al alkyl used, the resonances at 27.7_2 and 28.8_2 ppm (previously identified[7] and marked by a star) of the ^{13}C-enriched methylene carbon of the 2-methylbutyl end groups are detectable in the methylene region of the spectrum.

The same stereochemical relationship with respect to the stereoregularity of the insertion of the first monomer unit, pointed out for the spectra considered above, is effective for the methylenic resonances.

Table II[a]
Stereochemical Composition and Propagation Parameters of the Examined Polymers

	triad composition					
sample	[mm]	[mr + rm]	[rr]	[e][d]	P_{DD}[d]	I_{DD}[d]
a[b]	0.76	0.12	0.12	0.50	0.92	0.50
b[b]	0.79	0.11	0.10	0.52	0.93	0.52
c[b]	0.82	0.10	0.08	0.75	0.94	0.78
d[c]	0.91	0.05	0.04	0.79	0.97	0.80
e[c]	0.89	0.06	0.05	0.80	0.96	0.83

[a] All fractions reported have enough isotactic stereoregularity to permit a correct determination of the P_{DD} and I_{DD} parameters and a relatively low molecular weight so that a good evaluation of the stereoregularity of the end group ([e] value) is possible. [b] Fraction soluble in boiling heptane. [c] Fraction soluble in octane at 110 °C. [d] Defined in section 1.

All the results concerning the steric triad composition and the first monomer unit configuration are summarized in Table II.

3. Results and Discussion

3.1. Structure of the Isotactic Sites. Five samples of polypropylene have been prepared in the presence of the following catalytic systems: (a) $TiCl_3$–$Al(^{13}CH_3)_2Cl$, (b) $TiCl_3$–$Al(^{13}CH_3)_3$–$Zn(^{13}CH_3)_2$, (c) $TiCl_3$–$Al(^{13}CH_3)_2I$, (d) $TiCl_3$–$Al(^{13}CH_2CH_3)_3$–$Zn(^{13}CH_2CH_3)_2$, (e) $TiCl_4$–$MgCl_2$–ethyl benzoate–$Al(^{13}CH_2CH_3)_3$–$Zn(^{13}CH_2CH_3)_2$.

By ^{13}C NMR, ^{13}C-enriched methyl end groups have been detected in polymers a, b, and c and ^{13}C-enriched methylene end groups in polymers d and e. The polymers have been fractionated with boiling solvents and the different fractions have been analyzed by ^{13}C NMR for determining the stereochemical triad composition and the stereoregularity of the end groups (i.e., [e]) (see section 2).

In Table II are reported the stereochemical triad composition, [e], P_{DD}, and I_{DD} for the more stereoregular fractions of all polymer samples. The structure of these fractions is characteristic of the more isotactic specific sites. It can be observed that the stereochemical triad composition is nearly the same for all the fractions. The values of P_{DD} are also very close to each other.

On the contrary, [e] and I_{DD} have generally different values: $I_{DD} \simeq [e] \simeq 0.5$ for a and b, $I_{DD} \simeq [e] \simeq 0.8$ for c, and $I_{DD} \simeq [e] \simeq 0.8$ for d and e.

With the assumption that the isotactic sites are monometallic,[13] a comparison of the values of I_{DD} suggests the following: (1) the structures of the isotactic sites are the same for a and b as well as for d and e; (2) the size of R affects the steric control since a and b have a different I_{DD} in comparison with d; (3) iodine is present in the environment of the active sites of c as a result of halide exchange with the organometallic cocatalyst[14] and enhances the steric control (cf. a and b); (4) zinc does not affect stereospecificity (cf. a and b); and (5) unless I is present, R must be bulkier than CH_3 for the occurrence of stereospecific initiation.

3.2. $MgCl_2$-Supported Catalyst. $TiCl_4$ supported on $MgCl_2$ in the presence of an organometallic cocatalyst such as $Al(C_2H_5)_3$ is a very active catalyst for propene polymerization.[15] However, the amount of highly isotactic polymer (i.e., insoluble in boiling heptane) produced in the presence of this catalyst does not exceed 50%. This fact is due to the presence of a large number of nonisotactic specific active sites together with the isotactic specific ones. The stereoregulation capability of such a catalytic system is successfully increased by means of suitable modifiers, e.g., ethyl benzoate.[8] In principle, ethyl benzoate could modify the behavior of the catalytic system either by se-

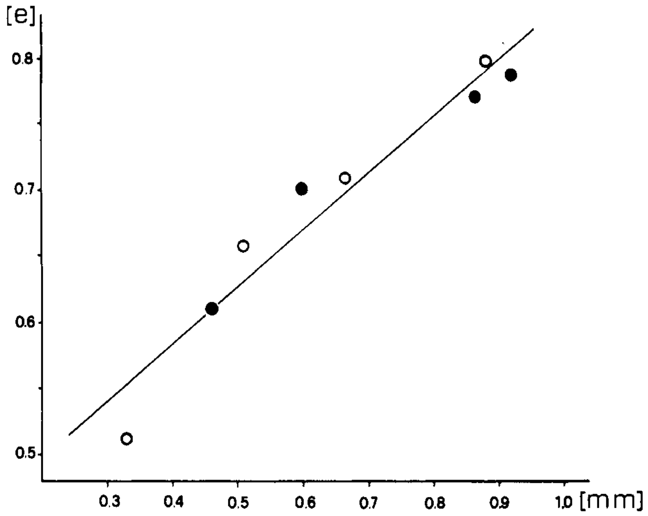

Figure 3. Stereoregularity of the insertion of the first monomer unit ([e]) vs. molar fraction of isotactic triads ([mm]) for different fractions of samples d (●) and e (○) (see Table III).

Table III

sample	polymer fractions no.[a]	polymer fractions in wt %	[mm]	[e]
d	S.5	5.3	0.46	0.61
	I.5-S.6	1.3	0.60	0.70
	I.6-S.7	7.0	0.86	0.77
	I.7-S.110	8.4	0.92	0.79
e	S.5	3.1	0.33	0.51
	I.5-S.6	2.1	0.51	0.66
	I.6-S.7	5.7	0.67	0.71
	I.7-S.110	6.5	0.89	0.80

[a] S.5: fraction soluble in boiling pentane; I.5-S.6: fraction insoluble in boiling pentane and soluble in boiling hexane; I.6-S.7: fraction insoluble in boiling hexane and soluble in boiling heptane; I.7-S.110: fraction insoluble in boiling heptane and soluble at 110 °C.

lectively poisoning the nonisotactic sites or by modifying their structure to additional isotactic ones. A possible mechanism for selective poisoning or modifying the active sites is selective complexation on the less sterically hindered (nonstereospecific) sites.[16] The results reported in section 3.1 suggest that the structure of the most stereospecific sites is the same (i.e., without benzoate in the environment) as for the $TiCl_3$-$Al(C_2H_5)_3$ system. In fact, the presence of different ligands on the environment of the catalytic Mt should change I_{DD} (cf. a and c, d and a).

As pointed out in section 1, the evaluation of P_{DD} and I_{DD} is difficult for the less isotactic polymer fractions since their structure deviates from the enantiomorphic site model. However, it is still possible to compare the stereochemical sequence of the configurations and the stereospecificity of the initiation.

All the fractions obtained from samples d and e have been analyzed by ^{13}C NMR (see Table III). In Figure 3 the molar fraction of mm triads is plotted against the fraction of erythro placement at the end groups considered for all the fractions.

It may be observed that both [mm] and [e] change from one fraction to another but all the experimental points lie on the same slope. In other words, the fraction having the same [mm] also has the same [e]. This fact suggests not only that the highly isotactic sites have the same structure and the same ligand environment for the catalytic systems d and e but that this is also true for the other sites.

Of course, since in catalytic system d there is no benzoate, all the active sites of e should be also free from benzoate. The enhancement of the stereoregulating capability of e should only arise from selective poisoning of most of the nonisotactic specific sites.

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References and Notes

(1) Natta, G. *J. Inorg. Nucl. Chem.* **1958**, *8*, 589. Cossee, P. *Tetrahedron Lett.* **1960**, 12. Boor, J., Jr. *Macromolecules* **1967**, *2*, 115.
(2) Shelden, R. A.; Fueno, T.; Tsunetsugu, T.; Furukawa, J. *J. Polym. Sci., Part A* **1965**, *3*, 23.
(3) Zambelli, A.; Gatti, G.; Sacchi, M. C.; Crain, W. O., Jr.; Roberts, J. D. *Macromolecules* **1971**, *4*, 475. Zambelli, A.; Locatelli, P.; Zannoni, G.; Bovey, F. A. *Ibid.* **1978**, *11*, 923. Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.
(4) Zambelli, A. *NMR Basic Princ. Prog.* **1971**, *4*, 101.
(5) Frisch, H. L.; Mallows, C. L.; Bovey, F. A. *J. Chem. Phys.* **1966**, *45*, 1565.
(6) Zambelli, A.; Locatelli, P.; Rigamonti, E. *Macromolecules* **1979**, *12*, 156.
(7) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 211.
(8) Luciani, L., et al. German Patent 26 431 436, 1977.
(9) Natta, G.; Morandi, M.; Crespi, G.; Moraglio, G. *Chim. Ind. (Milan)* **1957**, *39*, 275.
(10) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687.
(11) The chemical shift and the configurational relationship with respect to the methyl carbon of the inner monomer units up to six or less bonds distant are as follows: 20.6_9 ppm, $\delta_t\zeta_t$; 20.8_7 ppm, $\delta_t\zeta_e$; 21.5_4 ppm, $\delta_e\zeta_t$; 21.7_6 ppm, $\delta_e\zeta_e$.[4]
(12) Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Rigamonti, E. *Macromolecules* **1980**, *13*, 798.
(13) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerization"; Academic Press: New York, 1979; Chapter 13.
(14) Doi, Y.; Kohara, T.; Koiwa, H.; Keii, Y. *Makromol. Chem.* **1975**, *176*, 2159.
(15) See, for instance: Duck, E. W.; Grant, D.; Krongli, E. *Eur. Polym. J.* **1979**, *15*, 625.
(16) Pino, P.; Mülhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857.