suggest that the influence of chiral substituents might be significant in other types of polymerization and related studies could be useful in understanding details of the chain propagation processes.

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References and Notes

(1) P. Pino and U. V. Suter, *Polymer*, **17**, 977 (1976).
(2) C. E. H. Bawn and A. Ledwith, *Q. Rev., Chem. Soc.*, **16**, 361 (1962).
(3) P. Pino, *Adv. Polym. Sci.*, **4**, 393 (1965).
(4) F. Ciardelli, E. Chiellini, and C. Carlini, "Charged and Reactive Polymers", Vol. III, E. Selegny, Ed., D. Reidel Publishers, Dordrecht-Holland, in press; P. L. Luisi and F. Ciardelli in "Reactivity, Mechanism and Structure in Polymer Chemistry", A. D. Jenkins and A. Ledwith, Eds., Wiley, London, 1974, p 471.
(5) A. D. Ketley, "The Stereochemistry of Macromolecules", Vol. 2, A. D. Ketley, Ed., Marcel Dekker, New York, 1967, p 37.
(6) C. E. Schildknecht, S. T. Gross, and A. O. Zoss, *Ind. Eng. Chem.*, **41**, 1998 (1949).
(7) G. P. Lorenzi, E. Benedetti, and E. Chiellini, *Chim. Ind. (Milan)*, **46**, 1474 (1964); P. Pino, G. P. Lorenzi, and E. Chiellini, *Ric. Sci.*, **34**, 193 (1964).
(8) D. L. Christman and E. J. Vandenberg, U.S. Patent 3025282 (March 13, 1962).
(9) E. J. Vandenberg, *J. Polym. Sci., Part C*, **1**, 207 (1963).
(10) J. Lal and J. E. McGrath, *J. Polym. Sci., Part A*, **2**, 3369 (1964).
(11) S. Okamura, T. Higashimura, and T. Watanabe, *Makromol. Chem.*, **50**, 137 (1961).
(12) A. M. Liquori and B. Pispisa, *Chim. Ind. (Milan)*, 48, 1045 (1966).
(13) P. Pino, G. P. Lorenzi, and E. Chiellini, *J. Polym. Sci., Part C*, **16**, 3279 (1969).
(14) P. Pino, G. P. Lorenzi, E. Chiellini, and P. Salvadori, *Atti Accad. Naz. Lincei, Cl. Sci. Lis., Mat. Nat., Rend.*, **29**, 196 (1965).
(15) P. Pino, F. Ciardelli, and M. Zandomeneghi, *Annu. Rev. Phys. Chem.*, **21**, 561 (1970).
(16) P. Pino, P. Salvadori, G. P. Lorenzi, E. Chiellini, L. Lardicci, G. Consiglio, O. Bonsignori, and L. Lepri, *Chim. Ind. (Milan)*, **55**, 182 (1973).
(17) A. Ledwith, *Makromol. Chem.*, **175**, 1117 (1974).
(18) C. E. H. Bawn, C. Fitzsimmons, A. Ledwith, J. Penfold, D. C. Sherrington, and J. A. Weightman, *Polymer*, **12**, 119 (1971).
(19) T. Kunitake, Y. Magsuguma, and C. Aso, *Polym. J.*, **2**, 345 (1971); T. Kunitake, K. Takarabe, and S. Tsugawa, *ibid.*, **8**, 363 (1976).
(20) A. Ledwith and D. C. Sherrington, *Adv. Polym. Sci.*, **19**, 2 (1975).
(21) E. Chiellini, *Macromolecules*, **3**, 527 (1970).
(22) E. Chiellini, *Gazz. Chim. Ital.*, **102**, 833 (1972).
(23) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).
(24) H. Yuki, K. Ohta, and N. Yajima, *Polym. J.*, **1**, 164 (1970).
(25) R. Solaro and E. Chiellini, *Gazz. Chim. Ital.*, **106**, 1037 (1976).
(26) S. Okamura, T. Kodama, and T. Higashimura, *Makromol. Chem.*, **53**, 180 (1962); T. Higashimura, K. Suzuoki, and S. Okamura, **86**, 259 (1965); I. W. Bassi, C. Dall'Asta, U. Campigli, and E. Strepparola, *ibid.*, **60**, 202 (1963).
(27) S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *J. Polym. Sci., Part B*, **4**, 59, 65 (1966); M. Sumi, S. Nozakura, and S. Murahashi, *J. Polym. Sci., Part B*, **3**, 245 (1965); *Kobunshi Kagaku*, **24**, 424 (1967).
(28) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959).
(29) T. Kunitake and Chuji Aso, *J. Polym. Sci., Part A-1*, **8**, 665 (1970); T. Kunitake and S. Tsugawa, *Macromolecules*, **8**, 709 (1975).
(30) J. Niezette and V. Desreux, *Makromol. Chem.*, **149**, 177 (1971).
(31) In studies of the optical rotatory power of polymers prepared from chiral monomers it is usually found that unfractionated samples give a low indication of the degree of main-chain stereoregularity. The present results must, therefore, be taken as only a crude measure of the chiral influence of the (*S*)-1-methylpropyl group. Again it must be admitted that syndiotactic placements could give rise to enhancement of optical activity but as far as we are aware there is no evidence for this.

Active Center Determination in Ziegler–Natta Polymerization. Interference by Tritium Exchange Reactions in the Tritiated Alcohol Quench Method

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ABSTRACT: The occurrence of polymer labeling via tritium exchange reactions has been demonstrated under the conditions normally employed for tritiated alcohol quenching of Ziegler–Natta polymerization systems. The efficiency of the exchange is dependent upon the nature of the catalyst, cocatalyst, monomer, and solvent. The possible interference of such reactions in the determination of active center concentrations is discussed.

The tritiated alcohol quench method, originally developed by Feldman and Perry,[1] has been very widely used[1–10] for determining the number of active centers in Ziegler–Natta polymerization. Addition of hydroxy-tritiated alcohols to the polymerization reaction leads to destruction of the catalytically active organometallic species and simultaneous labeling of the bound polymer chain (eq 1). Determination of the number of labeled

$$\mathrm{Cat}^{+-}\mathrm{CH_2}\!\sim\!\mathrm{P} + \mathrm{ROT} \rightarrow \mathrm{Cat\text{-}OR} + \mathrm{TCH_2}\!\sim\!\mathrm{P} \qquad (1)$$

polymer molecules permits the calculation of the active center concentration. Complications arise since non-propagative metal polymer bonds are also labeled and a kinetic isotope effect is operative; however, both of these difficulties may be overcome by appropriate techniques.[7]

A serious drawback of all radiotracer methods, including the above, is a lack of precise knowledge as to the nature of the incorporated radioactivity. In the above method it is necessary to assume that tritium is only incorporated into the polymer by the quench reaction cited (eq 1) and that extraneous radioactivity may be efficiently removed. Whereas the latter may be confirmed by repetitive purification procedures, it is difficult to draw unequivocal conclusions about the former. The assumption would appear sound in the absence of any alternative reaction pathway for tritium labeling of the preformed polymer.

However, tritium exchange reactions catalyzed by Lewis acids such as $\mathrm{AlCl_3}$ are well known in the literature,[11] and while used principally for labeling aromatic compounds, exchange of aliphatic protons has been reported.[12] Since typical Ziegler–Natta catalyst formulations involve the use of Lewis acids, it seemed pertinent to investigate the possibility of such tritium exchange reactions occurring with preformed polymer, on quenching with tritiated

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Table I
Polymer Decontamination[a]

expt	[CH_3OT], mmol L^{-1}	[$AlCl_3$], mmol L^{-1}	contact time, min	temp, °C	polymer activity after repetitive purification, (cpm/g) × 10^{-4} I	II	III	IV	V
A	50	74	45	60	6.2^s	4.7^s	2.1^s	1.9^s	
B	500		90	80	0^s				
C	250	60	30	60	13.2^s	3.8^r			
D	250	49	30	60	0.34^r	0.172^r	0.137^r	0.126^r	0.140^r

[a] [Polypropylene] = 50 g/L; solvent = petroleum ether (100–120 °C); CH_3OT-specific activity = 1.9×10^{10} cpm/mol; s = soxhlet extraction with methanol for 6 h; r = reprecipitation from toluene.

alcohols. The results of such an investigation are reported in this paper and their significance discussed.

Experimental Section

Materials. Tritiated methanol, of specific activity of about 0.07 Ci/mol, was prepared from tritiated water by a method previously described.[7] A scintillation solution of 4 g/L of PPO and 0.4 g/L of POPOP in toluene was used for the radioactive assay. Aluminum chloride, an anhydrous resublimed grade from Merck chemicals, and aluminium alkyls, from Pressure Chemical Co., were used as received. The VCl_3 catalyst has been described earlier.[7] Petroleum ether (100–120 °C fraction) was purified by standard procedures and dried over molecular sieves.[13,14] Polystyrene, polyethylene [high density], and polypropylene were commercial samples purified by reprecipitation. Poly(4-methylpentene-1) was prepared by a Ziegler–Natta catalyst described earlier.[15]

Techniques. Experimental conditions were designed so as to replicate those normally encountered during quenching of Ziegler–Natta polymerizations. Thus 1-g samples of polymer were gelled in 20 mL of dry petroleum ether by heating. The reaction vessel was flushed with nitrogen and appropriate amounts of air-sensitive catalyst added in a drybox. The flask was then capped and thermostated at the test temperature, whereupon an excess of tritiated methanol was added. After the appropriate contact time, polymer samples were isolated by pouring the mixture into a large excess of methanol. Polymer purification was effected by soxhlet extraction with methanol and/or by reprecipitation, as indicated in the text. In all cases purified polymers were vacuum dried at 50 °C overnight before assay.

Tritium Assay. Labeled polymers were assayed as gels by heating 100 mg of sample with 10 mL of scintillation solution. Sampling reproducibility of duplicate samples counted in this manner was within ±1%. The counting efficiency was found to be more than twice that of an earlier method of assay,[7] where finely powdered polymer samples were merely suspended in a gel scintillator. All radioactive measurements were made with a Beckman Model LS-100 liquid scintillation spectrometer.

Results

Polymer Decontamination. A necessary preliminary to these experiments was an investigation of the efficiency of purification procedures, in removal of extraneous tritiated impurities. The results (Table I) indicate that, whereas soxhlet extraction of the finely powdered polymer is effective in removal of excess labeled methanol (experiment B), such a procedure is not efficacious in removal of other tritiated impurities (experiments A and C). Repetitive reprecipitation of the tritiated polymer (experiment D) shows that a constant level of activity is attained after three reprecipitations.

The tabulated results clearly show that: (i) in the absence of catalyst, no detectable tritium exchange occurs between tritiated methanol and preformed polypropylene; (ii) that aluminium chloride in the presence of tritiated methanol catalyzes the tritiation of polypropylene; and (iii) that aluminium chloride also promotes the formation of low molecular weight tritiated impurities.

It is conceivable that the latter impurities could represent a low molecular weight fraction of the polymer or, alternatively, a high-boiling fraction derived from the solvent.

Table II
Efficiency of Various Catalysts in Promoting Tritium Exchange with Polypropylene[a]

catalyst	none	VCl_3	$AliBu_3$	$AliBu_2Cl$	$AliBuCl_2$	$AlCl_3$
polymer activity, (cpm/g) × 10^{-3}	n.d.	n.d.	n.d.	0.590	3.90	6.40

[a] [Polypropylene] = 50 g/L; solvent = petroleum ether (100–120 °C); CH_3OT-specific activity = 1.9×10^{10} cpm/mol; [catalyst] = 50 mmol/L; [CH_3OT] = 250 mmol/L; temperature = 60 °C; contact time = 60 min. Purification by triplicate reprecipitation. n.d. = no detectable activity.

Table III
Effect of Temperature and Contact Time on Tritium Exchange Reactions[a]

contact time, min	polymer activity, (cpm/g) × 10^{-3} 30 °C	60 °C	90 °C
5		14.0	
30	11.7	9.8	21.3
1440		31.3	

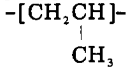
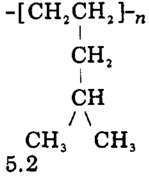
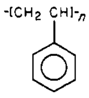
[a] [Polypropylene] = 50 g/L; solvent = petroleum ether (100–120 °C), CH_3OT-specific activity = 1.9×10^{10} cpm/mol; [CH_3OT] = 250 mmol/L; [$AliBuCl_2$] = 50 mmol/L; purification by triplicate reprecipitation.

Effect of Catalyst Type. The effectiveness of a series of catalysts in promoting tritium exchange reactions was investigated under standardized conditions (Table II). The results show that the catalysts may be placed in the following decreasing order of catalytic activity: $AlCl_3 > AliBuCl_2 > AliBu_2Cl > AliBu_3$. In the case of triisobutylaluminium and vanadium trichloride no detectable exchange occurred. Direct comparison of the relative reactivity of aluminium chloride with the other aluminium compounds is hampered since aluminium chloride is not appreciably soluble in petroleum ether, and consequently the measured activity probably reflects the catalytic effect of only a small fraction of surface exposed species.

Nevertheless, it is clear that the catalytic activity of the aluminium compounds increases with the number of chlorine atoms. The order of reactivity thus increases with the Lewis acidity of these compounds.[16]

Effect of Temperature and Contact Time. The reproducibility of the catalyzed exchange reactions is rather poor, and variations in polymer activity of a factor of 2, in the case of $AliBuCl_2$, have been observed under apparently identical conditions. This is almost certainly due to the inhomogeneity of the reaction system, since the polypropylene is present as a gel/suspension, the actual composition of which probably varies considerably from sample to sample. Consequently, the results presented in Table III with regard to the effect of temperature and contact time on the exchange reaction are of somewhat

Table IV
Polymer Reactivity toward Tritium Exchange Reaction[a]

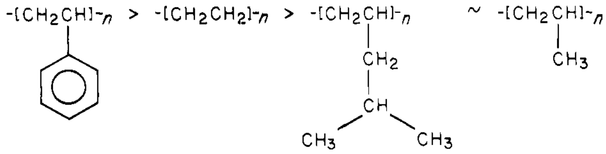
polymer	polyethylene	polypropylene	poly(4-methylpentene-1)	polystyrene
repeating unit	$-[CH_2CH_2]-_n$	 $-[CH_2CH(CH_3)]-_n$	 $-[CH_2CH(CH_2CH(CH_3)_2)]-_n$	
polymer activity, (cpm/g) × 10^{-4}	66.1	0.98	5.2	241

[a] [Polymer] = 50 g/L; solvent = petroleum ether (100-120 °C); CH_3OT-specific activity = 1.9 × 10^{10} cpm/mol; [$AliBuCl_2$] = 50 mmol L^{-1}; [CH_3OT] = 250 mmol L^{-1}; purification by triplicate reprecipitation; contact time = 30 min; reaction temperature = 60 °C.

limited significance. Nevertheless, it would appear that the rate of the exchange reaction is not markedly temperature dependent and that the exchange reaction is very rapid being essentially complete within the first 5 min.

Since only a small fraction, ca. 0.02%,[17] of the total added tritium is found in the polymer even after an extended reaction time, it would appear that the active exchange catalyst is rapidly deactivated after addition of excess methanol. Consequently, the apparent independence of the rate of exchange with respect to temperature may reflect the competition between catalyst deactivation and exchange reactions.

Polymer Reactivity Toward Tritium Exchange Reactions. Since the structure of the polymeric repeating unit would be expected to influence the tritium exchange reaction, experiments were conducted with four different polymers frequently studied in Ziegler-Natta polymerization systems. A quantitative comparison of the reactivity of the different polymers toward tritium exchange is hampered by differences in polymer solubility/gel formation during the exchange reaction, and by small variations in the counting efficiencies of the labeled polymers. Notwithstanding the above, it is clear from an examination of the results (Table IV) that the polymers may be placed in the following decreasing order of reactivity toward exchange:



Not surprisingly, polystyrene is the most reactive toward tritium exchange reactions. This is in accord with earlier work[11] on the synthesis of tritium labeled compounds wherein it was shown that aromatic compounds, in particular alkyl-substituted aromatics, were much more reactive than alkanes toward exchange catalyzed by Lewis acids.

The rather similar reactivities of polypropylene and poly(4-methylpentene-1) may be attributed to the identical distribution of primary, secondary, and tertiary carbon centers in these polymers, since the reactivity of hydrogen toward exchange should be dependent upon the nature of the carbon center to which it is attached.

Intuitively, if the exchange reaction involves carbonium ion or pseudo-carbonium ion intermediates, the position of polyethylene in the series would appear to be anomalous.[18] The enhanced reactivity could be caused by decreased steric effects due to the absence of pendant groups or conceivably to a reaction pathway involving pseudo-carbanion intermediates.

Table V
Effect of Prior Quenching on Exchange Reaction[a]

system	polymer activity, cpm/g × 10^{-4} control	polymer activity, cpm/g × 10^{-4} prequenched with inactive methanol[b]
polyethylene/ petroleum ether/ $AliBuCl_2$	66.1	0.33

[a] [Polymer] = 50 g/L; solvent = petroleum ether (100-120 °C); CH_3OT-specific activity = 1.0 × 10^{10} cpm/mol; [$AliBuCl_2$] = 50 mmol/L; [CH_3OT] = 250 mmol/L; *a* – [CH_3OH] = 250 mmol/L; contact time = 30 min; reaction temperature = 60 °C.

Table VI
Effect of Solvent Type on Exchange Reaction[a]

system	polymer activity, cpm/g × 10^{-4} petroleum ether (100-120 °C)	polymer activity, cpm/g × 10^{-4} toluene
polyethylene/ solvent/$AliBuCl_2$	66.1	0.15

[a] [Polymer] = 50 g/L; CH_3OT-specific activity = 1.0 × 10^{10} cpm/mol; [CH_3OT] = 250 mmol/L; [$AliBuCl_2$] = 50 mmol/L; contact time = 30 min; reaction temperature = 60 °C.

Effect of Prior Quenching with Inactive Methanol. The effect of contact time on the exchange reaction was probed further by prequenching the reaction mixture with inactive methanol for 5 min before the addition of tritiated methanol. It may be clearly seen (Table V) that the effect of prior quenching is to grossly inhibit the exchange reaction. This confirms the earlier tentative conclusions that the exchange reaction is rapid, being essentially complete within the first 5 min.

Effect of Solvent. The results (Table VI) clearly indicate that the nature of the solvent affects the incorporation of tritium into the polymer. It would appear that, because of the rapid deactivation of the exchange catalyst, the tritium distribution between solvent and polymer is determined by kinetic rather than thermodynamic parameters. Thus the tritium distribution is the consequence of the relative rates of the competing reactions:

$$\text{solvent-H} + CH_3OT \xrightarrow[\text{cat.}]{k_s} \text{solvent-T} + CH_3OH$$

$$\text{polymer-H} + CH_3OT \xrightarrow[\text{cat.}]{k_p} \text{polymer-T} + CH_3OH$$

Clearly in the case of toluene, which undergoes facile exchange, the ratio k_s/k_p is greater than for petroleum ether and consequently the polymer activity is markedly decreased.

Discussion

Relevence of Exchange Reactions to Active Center Determination. The foregoing results clearly indicate

Table VII
Comparison of the Magnitude of C_0 and $[\mathrm{MPB}]_{\mathrm{exch}}$ Terms

cocatalyst	$[\mathrm{MPB}]_{\mathrm{exch}}$,[a] mol/L × 10^6	catalyst[b] system	C_0,[b] mol/L × 10^6
	Polypropylene		
$\mathrm{Al(iBu)_2Cl}$	1.6	$\mathrm{TiCl_3(AA)/AlEt_2Cl}$	40
$\mathrm{AliBuCl_2}$	10		
$\mathrm{AlCl_3}$	17		
	Polyethylene		
$\mathrm{AliBuCl_2}$	1700	$\mathrm{TiCl_3(AA)/AlEt_2Cl}$	51

[a] Calculated for $K = 1$, $G = 50$ g/L. [b] Data from ref 6.

that tritium exchange reactions can occur under the quench conditions normally employed in Ziegler–Natta polymerization studies. The extent of the exchange reaction is markedly dependent upon the nature of the co-catalyst, solvent, and the preformed polymer but is relatively independent of temperature. Whether or not the exchange phenomenon will have a significant effect on the determination of active centers by the tritiated alcohol quench method will thus be largely dependent on the nature of the system under study.

Normally, the active center concentration (C_0) is most satisfactorily evaluated by extrapolation of the total metal–polymer bond concentration [MPB] to zero conversion,[7,10] on the basis of equations such as:

$$[\mathrm{MPB}] = C_0 + \frac{k_\mathrm{a}[\mathrm{A}]G}{k_\mathrm{p}[\mathrm{M}]} \qquad (2)$$

where k_a and k_p are the rate constants for chain transfer with metal alkyl and propagation, respectively, [M] and [A] are the monomer and metal-alkyl concentrations, and G is the polymer yield. The metal–polymer bond concentration is in turn calculated from the relationship:

$$[\mathrm{MPB}] = KAG/a \qquad (3)$$

where K is the correction factor for the isotope effect and A and a are the specific activities of the polymer and quench alcohol, respectively.

The net effect of the exchange reaction is to increase the apparent metal–polymer bond concentration, and thus eq 2 becomes:

$$[\mathrm{MPB}] = C_0 + \frac{k_\mathrm{a}[\mathrm{A}]G}{k_\mathrm{p}[\mathrm{M}]} + [\mathrm{MPB}]_{\mathrm{exch}} \qquad (4)$$

where $[\mathrm{MPB}]_{\mathrm{exch}}$ is the metal–polymer bond equivalent of the exchanged tritium.

A comparison of the relative magnitudes of the two terms C_0 and $[\mathrm{MPB}]_{\mathrm{exch}}$ for polyethylene and polypropylene (Table VII) shows that the exchange term is potentially highly significant, particularly for polyethylene. The actual effect of this additional term on the extrapolated value of C_0 will depend on the kinetics of the exchange reaction and, in particular, on the distribution of exchanged tritium between polymer and solvent.

If the term $[\mathrm{MPB}]_{\mathrm{exch}}$ is directly proportional to the polymer yield, then the interference will be restricted to an apparent increase in the rate of metal–polymer bond formation, and the intercept value (C_0) will not be markedly affected (Figure 1, curve B). On the other hand, if the extent of exchange with polymer is controlled primarily by the cocatalyst concentration, or becomes less efficient during the course of polymerization due to precipitation of the polymer, then an apparent increase in C_0 will be observed (Figure 1, curve C) (clearly, the plot may also be nonlinear).

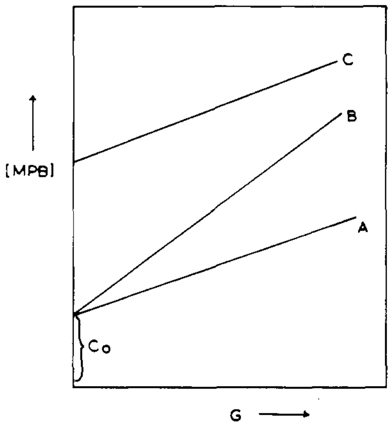


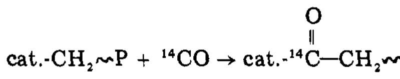
Figure 1. Possible effects of tritium-exchange interference on C_0 evaluation: A, no exchange reactions; B, exchange, $[\mathrm{MPB}]_{\mathrm{exch}} \propto G$; C, exchange, $[\mathrm{MPB}]_{\mathrm{exch}}$ independent of G.

Table VIII
Comparison of Some Results[a] Obtained for ^{14}CO and ^{3}H-Alcohol Methods

		active center concn (C_0) × 10^3 mol/mol Ti		
cocatalyst	monomer	^{3}H quench	^{14}CO method	$C_0(^3\mathrm{H})/C_0(^{14}\mathrm{CO})$
$\mathrm{AlEt_3}$	$\mathrm{C_2H_4}$	2.0[b]	0.16[b]	13
	$\mathrm{C_3H_6}$	2.1[b]	0.94[b]	2.2
$\mathrm{AlEt_2Cl}$	$\mathrm{C_2H_4}$	7.0	0.07	100
	$\mathrm{C_3H_6}$	5.5	1.8	3.1

[a] Abstracted from Table I, ref 10. [b] Average of values at three different temperatures.

Comparison of Active Center Concentration Derived from ^{14}CO and ^{3}H-Alcohol Quench Methods. More recently,[19] active center concentrations in Ziegler–Natta systems have been determined by interaction of the propagating chains with ^{14}CO. This method appears advantageous in that the CO interacts specifically with the propagating chains (eq 5) and thus obviates the necessity of correction for the contribution by inactive MPB.



$$\mathrm{cat.{-}CH_2{\sim}P} + {}^{14}\mathrm{CO} \rightarrow \mathrm{cat.{-}}{}^{14}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_2{\sim}P} \qquad (5)$$

A comparison of the number of active centers obtained for various systems by the two methods (Table VIII) appears significant. In every case the tritium quench method gives higher results. Furthermore, the ratio ^{3}H/^{14}CO is higher for ethylene than propylene and for $\mathrm{AlEt_2Cl}$ than $\mathrm{AlEt_3}$. Both of these trends would be anticipated if interference by tritium exchange reactions were to occur.

The discrepancy between the two methods is of course capable of alternative explanations. Thus it has been suggested[20] that the insertion of carbon monoxide at the active center is nonquantitative. While certain experimental evidence for this view has been provided,[20] it seems unlikely that the magnitude of this effect and its variation with monomer and cocatalyst type could match the observations (Table VIII). Elsewhere,[10] it has been proposed that the much larger discrepancy in ethylene polymerization systems arises because of the high rates of MPB formation, which in turn lead to increased errors in extrapolation. Again, it seems unlikely that the errors involved in this extrapolation, of essentially linear plots,

Table IX
Effect of Various Parameters on Tritium Exchange Reactions

parameter	decreasing facility of exchange
catalyst	$VCl_4 \sim TiCl_4 > TiCl_3{\cdot}xAlCl_3 > TiCl_3, VCl_3$
cocatalyst	$AlRCl_2 > AlR_2Cl > AlR_3$
monomer	$CH_2 = C(Ph)H > CH_2 = CH_2 > CH_2 = C(CH_3)H > CH_2 = CH{\cdot}CH_2CH(CH_3)_2$
solvent	alkanes > aromatics

could lead to discrepancies of two orders of magnitude.

Limitations of the ^{3}H-Alcohol Quench Method by Tritium Exchange. From the preceding results and discussion it is evident that interference by tritium exchange reactions, during the course of tritiated alcohol quenching, may significantly affect the derived values of C_0. The extent of the interference will depend on the composite nature of the system investigated, in particular, on the nature of the catalyst, cocatalysts, monomer, and solvent (Table IX).

The effects of cocatalyst, monomer, and solvent have already been discussed and their order is self-evident. The order of catalysts is somewhat intuitive but arises on two grounds:

(i) Catalysts such as VCl_4 and $TiCl_4$ interact with cocatalysts to give very high yields of aluminum chloroalkyls, e.g.:

$$TiCl_4 + AlR_3 \rightarrow TiCl_3R + AlR_2Cl \qquad (6)$$

The aluminum chloroalkyls would then be expected to catalyze exchange reactions.

(ii) Many active titanium catalysts contain significant proportions of cocrystallized aluminium chloride. The aluminium chloride component would be expected to facilitate tritium exchange.

Examination of different systems, using the criteria summarized in Table IX, allows one to predict the likelihood of interference and thus the advisability of employing the tritium quench method.

In cases where all of the determining factors are on the right of Table IX, no serious interference would be anticipated. This inference is confirmed by the comprehensive study[7] of the VCl_3/AlR_3/4-methylpentene-1 system, employing benzene as solvent, where it was shown by a careful molecular weight analysis that no significant exchange reactions were occurring.

In cases where only one factor is on the left of Table IX, the outcome is less predictable. Thus in the polymerization of styrene by the $TiCl_3/AlEt_3$/benzene system, no interference was detected.[21] The determining factor in this system, where the polystyrene is very susceptible to exchange, would appear to be the absence of active exchange catalysts.

On the other hand, in the case of polymerizations where a number of factors are on the left of Table IX, interference through exchange reactions would be anticipated. An example of this is the polymerization of ethylene by the catalyst system $TiCl_3{\cdot}xAlCl_3/AlEt_2Cl$ in petroleum ether.[6,10] The massive discrepancy between the C_0 values determined by ^{14}CO and ^{3}H-alcohol quench methods, vide supra, would appear to be evidence that such complications are actually occurring.

Control Experiments. A good indication of the susceptibility of a polymerization system to exchange reactions may be obtained by appropriate control experiments. Typically, a sample of preformed polymer is treated with both catalyst components under normal polymerization conditions and subsequently quenched with active alcohol. The absence of tritium in the treated polymer demonstrates that interference is negligible, whereas the presence of radioactivity indicates either the presence of exchange reactions or inadequate purification procedures.

Mechanism of Exchange. The present results, while indicating the importance of this effect, unfortunately do not shed much light on the actual mechanism of the exchange reactions. However, the observations do not appear to be compatible with the mechanism of tritium exchange proposed for the analogous *n*-heptane/$AlCl_3$/TOH system.[12] In that case exchange was considered to occur via carbonium ion intermediates, although the exact pathway was not delineated. Three features mitigate against such an explanation: (i) the observed variation of activity with polymer structure;[18] (ii) the very significant incorporation of tritium using CH_3O^3H;[22] and (iii) the high rate of the exchange reaction, and rapidity of catalyst deactivation, which argues against a slow attainment of exchange equilibrium as normally envisaged for the cationic mechanism.

Work is in hand to further probe the nature of the exchange reaction.

Conclusion

It is apparent from the preceding results and discussion that interference by tritium exchange reactions in the tritiated alcohol quench method of active center determination is potentially highly significant. The actual magnitude of the effect is dependent on the nature of the polymerization system and polymerization conditions.

It should be noted, however, that these results may only be indicative of the order of magnitude of these effects, since the physical nature of the "polymer gels" used in this work may differ considerably from that of the "as-polymerized" polymers encountered in actual polymerization systems. Thus the possibility of even more extensive tritium exchange reactions cannot be discounted.

References and Notes

(1) C. F. Feldman and E. Perry, *J. Polym. Sci.*, **46**, 217 (1960).
(2) E. Kohn, H. J. L. Schuurmans, J. V. Cavender, and R. A. Mendelson, *J. Polym. Sci.*, **58**, 681 (1962).
(3) G. Bier, W. Hoffmann, G. Lehmann, and G. Seydel, *Makromol. Chem.*, **58**, 1 (1963).
(4) W. Cooper, D. E. Eaves, G. D. T. Owen, and G. Vaughan *J. Polym. Sci., Part C*, **4**, 211 (1966).
(5) H. W. Coover, J. E. Guillet, R. L. Combs, and F. B. Joyner, *J. Polym. Sci., Part A*, **4**, 2583 (1966).
(6) K. A. Jung and H. Schnecko, *Makromol. Chem.*, **154**, 227 (1972).
(7) D. R. Burfield and P. J. T. Tait, *Polymer*, **13**, 315 (1972).
(8) D. R. Burfield, P. J. T. Tait, and I. D. McKenzie, *Polymer*, **13**, 321 (1972).
(9) A. A. Baulin, V. N. Sokolov, A. S. Semenova, N. M. Chirkov, and L. F. Shalayeva, *Polym. Sci. USSR (Engl. Transl.)*, **17**, 51 (1975).
(10) G. D. Bukatov, N. B. Chumaevskii, V. A. Zakharov, G. I. Kuznetsova, and Y. I. Yermakov, *Makromol. Chem.*, **178**, 953 (1977).
(11) See, E. A. Evans, "Tritium and its Compounds", 2nd ed., Butterworths, London, 1974, and references contained therein.
(12) C. Mantescu, A. Genunche, D. Duta-Cristu, and A. T. Balaban, *J. Labelled Compd.*, **2**, 267 (1966).
(13) D. R. Burfield, K. H. Lee, and R. H. Smithers, *J. Org. Chem.*, **42**, 3060 (1977).
(14) D. R. Burfield, G. H. Gan, and R. H. Smithers, *J. Appl. Chem. Biotechnol.*, **28**, 23 (1978).
(15) I. D. McKenzie, P. J. T. Tait, and D. R. Burfield, *Polymer*, **13**, 307 (1972).
(16) See, T. Mole and E. A. Jeffery "Organoaluminium Compounds", Elsevier, Amsterdam, 1972, and references contained therein.
(17) This evaluation neglects the concomittant tritium exchange with solvent which is known to occur.
(18) Since the ease of carbonium ion formation decreases in the order tertiary > secondary > primary.
(19) N. B. Chumaevskii, V. A. Zakharov, G. D. Bukatov, G. I. Kuznetzova, and Y. I. Yermakov, *Makromol. Chem.*, **177**, 747 (1976), and preceding references.

(20) J. Mejzlik and M. Lesna, *Makromol. Chem.*, **178**, 261 (1977).
(21) G. Ayrey and R. J. Mazza, *Makromol. Chem.*, **176**, 3353 (1975).
(22) It would be anticipated that the carbonium ion would interact preferentially with the methoxide fragment, viz., $R^+ + CH_3OT \rightarrow ROCH_3 + T^+$. Indeed ^{14}C labeled alcohols have been used as a diagnostic test for cationic polymerization. See L. S. Bresler, I. Ya. Poddubnyi, and V. N. Sokolov, *J. Polym. Sci., Part C*, **16**, 4337 (1969), and references contained therein.

Sequence Distributions of Inverted Propylene Units in Polypropylenes Measured by ^{13}C NMR

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ABSTRACT: Predominantly syndiotactic, stereoirregular and predominantly isotactic polypropylene samples were prepared at −78 °C with different vanadium-based catalyst systems. The ^{13}C NMR resonances arising from propylene unit inversion were observed in the spectra of all polypropylene samples. The mole fractions of different dyads and triads of propylene units and the reactivity ratio product, r_0r_1, were determined directly from ^{13}C NMR peak areas. The sequence distributions of inverted propylene units have been accounted for in terms of first-order Markov statistics.

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy has been employed successfully in the structural studies of polypropylenes[1-8] and ethylene–propylene copolymers.[9-14] Some of these studies have been directed toward the elucidation of the mechanistic features of the stereospecific polymerization of propene with Ziegler–Natta catalysts. From the analysis in the methyl region of the ^{13}C NMR spectra of polypropylenes[6,7] and ethylene–propylene copolymers,[11] an important conclusion concerning the origin of the stereospecificity of the catalysts has been derived: the isotactic specific chain propagation is controlled by the asymmetry of the catalyst sites, whereas the syndiotactic specific chain propagation is controlled by the asymmetry of the last unit in the growing chain. Zambelli et al.[5,12,15] have suggested that the syndiotactic propagation takes place by the secondary insertion of propene into a secondary metal–carbon bond:

--- —● Mt + C_3H_6 → --- —● —● Mt

whereas the primary insertion of propene into a primary metal–carbon bond results in either stereoirregular or isotactic propagation.

--- ●— Mt + C_3H_6→ --- ●— ●— Mt

Here, Mt, —●, and ●— indicate the metal atom in the catalyst site bound to the polymer chain and the propylene units in the orientation $-CH_2CH(CH_3)-$ and $-CH(CH_3)CH_2-$, respectively. However, to date the driving force in the selection of the type of insertion is still open to discussion.

In the polymerization of propene with vanadium-based catalyst systems, the polypropylenes produced have been frequently found to involve the irregular linkages of the propylene units in the chain, i.e., a head-to-head arrangement (—●●—) and a tail-to-tail arrangement (●——●).[16-18] From a structural viewpoint, these systems may be considered a binary copolymerization[5] involving head-to-tail and tail-to-head propylene units. Recently, we have demonstrated that ^{13}C NMR is sensitive to a specific sequence structure of propylene units resulting from propylene inversion along the chain of polypropylene. Chemical shift assignments of ^{13}C resonances in these spectra have been made using the basic relationships established by Lindeman and Adams[19] which is applicable in a wider range by improving the Grant and Paul relationship.[20] However, the assignment for all resonances has been limited because of the low content of propylene inversion.

In the present study we have observed ^{13}C NMR spectra of the polypropylenes prepared at −78 °C by combining VCl_4 with different types of aluminium alkyls and have attempted to make the chemical shift assignments for all ^{13}C resonances arising from propylene inversion. The area of each resonance will be accounted for in terms of sequence distribution of inverted propylene units.

Experimental Section

^{13}C NMR spectra of polypropylene samples were measured at 140 °C using a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25.149 MHz. Instrument conditions were: $\pi/4$ pulse of 9.7 μs, 6.0-s repetition rate, and 4000 Hz sweep width. The numbers of transients accumulated were 5000. Solutions were made up in *o*-dichlorobenzene to 20–30% (w/v).

Polypropylene samples were prepared at −78 °C by combining VCl_4 with different types of aluminium alkyls. The polymerization procedures are as below. Propylene (40 g) was condensed into heptane (50 mL) in a glass reactor kept at −78 °C. The given amounts of aluminium alkyl and VCl_4 were charged at the beginning of the polymerization. The polymerization was quenched by adding 100 mL of an ethyl alcohol solution of hydrochloric acid thermostated at −78 °C prior to use. The produced polymers were washed several times with 200–300 mL of ethyl alcohol and dried in vacuo at room temperature. The catalyst systems used in this experiment are given in Table I, together with the stereoregularities and molecular weights of the polypropylene samples obtained.

Results and Discussion

As mentioned in the introductory section we previously succeeded in observing several ^{13}C NMR resonances arising from propylene inversions in the predominantly syndiotactic polypropylenes obtained with the VCl_4–$AlEt_2Cl$ system.[8] In the present study the existence of propylene inversions was verified in ^{13}C NMR spectra of the polypropylene samples prepared with the other vanadium-based catalyst systems. A ^{13}C NMR spectrum of sample T-5, obtained with the VCl_4–$AlEt_2I$ catalyst system, is reproduced in Figure 1. The ^{13}C chemical shift assignments made using the Lindeman and Adams relationship[19] are shown in Table II. We denote each tertiary carbon as T with two Greek subscripts indicating its position relative to the nearest tertiary carbons in both directions along the polymer chain, as suggested by Carman.[9] Each

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