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JOURNAL OF POLYMER SCIENCE: PART C NO. 16, PP. 2501–2516 (1967)

Some Aspects of the Polymerization Mechanism of α-Olefins to Isotactic Polymers

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Synopsis

Data on the behavior of different heterogeneous catalyst systems in the polymerization of α-olefins to isotactic polymer are reported and compared. The effect of substituents on the kinetic behavior of the catalyst complexes, which in the different systems yield polymeric chains having comparable steric regularities, was investigated. Moreover, hypotheses are put forth on the factors influencing the stereospecificity of the catalyst systems studied.

Heterogeneous catalytic systems stereospecific for polymerization of α-olefins to isotactic polymers have been extensively studied by several researchers in recent years.[1]

The following experimental facts can be pointed out. (*1*) Some heterogeneous catalytic systems containing only the transition metal, e.g., $TiCl_3$–$TiCl_3(CH_3)$ or $TiCl_3$–$TiCl_2(CH_3)_2$,[2] are stereospecific (at least in part) in the polymerization of α-olefins to isotactic polymers. (*2*) The bimetallic, e.g., violet $TiCl_3$–$Al(C_2H_5)_2Cl$, and the monometallic catalytic systems previously quoted, behave in a quite different manner: the former generally have a higher activity and (in the case of polypropylene) yield polymers containing a higher percentage of stereoregular material (boiling *n*-heptane-insoluble fraction).[3]

In order to clarify the behavior of the bimetallic catalytic systems, we take into consideration, in this paper, the variations in activity and stereospecificity observed for systems containing different organometallic compounds. The reported results have been obtained for polymerization of butene-1 or propylene in order to check the experimental conditions for both activity and stereospecificity measurements.

EXPERIMENTAL

Reagents Used

The types of reagents used and their purification have been given in previous papers.[3,4]

The δ-$TiCl_3$ (ARA, Al reduced $TiCl_4$ and activated by grinding; or HRA, H_2 reduced $TiCl_4$ and activated by grinding) and VCl_3 were obtained from Stauffer. The monomers used were pure grade butene-1 from Phillips Co. and propylene from Montecatini (over 99% pure); both monomers had been stored over $NaAl(C_2H_5)_4$.

Polymerization Runs

The polymerization runs for the determination of the propagation rate were carried out in glass reactors equipped with a stirrer and thermostatted at the desired temperature ±0.5°C. The reagents were introduced in the following order: the polymerization solvent (toluene), the organometallic

TABLE I
Polymerization of Butene-1 at 0°C. in the Presence of the Catalytic System Containing $TiCl_3$ (See Fig. 1)[a]

Catalyst system		Polymerization rate (average), g. polymer/g. $TiCl_3$-hr.	Time, sec.	$\bar{M}_v \times 10^{-6}$ [c]
$TiCl_3$, g.[b]	Organometallic compound (6.8 mmole)			
ARA 1–2	$Al(C_2H_5)_2Cl$	0.7	110	0.86
			180	1.12
			300	1.43
			480	1.67
ARA 2–4	$Al(C_2H_5)_2I$	0.9	60	0.57
			121	1.05
			180	1.29
			540	1.87
ARA 1–3	$Be(C_2H_5)_2$	110	55	0.28
			104	0.35
			290	0.48
ARA 2–4	$Al(i\text{-}C_4H_9)_2Cl$	0.3	60	0.81
			80	1.14
			120	1.40
			182	2.08
			230	2.06
			324	2.40
			480	3.39
HRA 1–3	$Al(C_2H_5)_2Cl$	0.4	90	0.79
			180	1.16
			300	1.92
			410	1.75
			626	2.50
HRA 0.75–1.5	$Be(C_2H_5)_2$	3.7	90	0.57
			160	0.71
			300	0.93

[a] Polymerization runs were performed at 0°C. with 180 ml. toluene, 60 g. butene-1.

[b] The amounts of transition metal halide used for each polymerization run range within the indicated values.

[c] $\bar{M}_v$ of the boiling pentane-insoluble fraction. The boiling pentane extraction residue varies from 70 to 100% with different catalyst sytems.

TABLE II

Polymerization Runs of Butene-1 with VCl_3 (See Fig. 2)[a]

Catalyst system					
VCl_3, g.[c]	Organometallic compound (6.8 mmole)	Polymerization rate (average), g. polymer/g. VCl_3-hr.	Time, sec.	$\bar{M}_v \times 10^{-6}$ [b]	Temperature, °C.
1	$Be(C_2H_5)_2$	19	33	1.82	0
			61	2.09	
			108	2.82	
			180	3.49	
0.6–1	$Al(C_2H_5)_3$	8	31	1.95	0
			58	2.82	
			60	2.69	
			111	2.89	
			180	3.40	
			297	3.62	
1–1.5	$Al(C_2H_5)_3$	6.5	35	1.62	−20
			61	2.11	
			120	2.51	
			240	3.16	
			363	3.28	
			490	3.47	
			606	3.72	
0.6–1.5	$Al(C_2H_5)_3$	2	60	1.84	−40
			120	2.02	
			131	2.38	
			242	2.72	
			420	2.81	
			600	3.10	
			900	3.23	
1.5–3.2	$Al(C_2H_5)_3$	n.d.	150	1.53	−78
			303	1.93	
			480	2.16	

[a] Polymerization runs were performed with 180 ml. toluene, 60 g. butene-1.

[b] $\bar{M}_v$ of the boiling pentane-insoluble fraction; the residue to the pentane extraction varies from 70 to 95% with varying reaction temperature.

[c] The amounts of transition metal halide used for each polymerization run range within the indicated values.

compound, the monomer, and the transition metal halide suspended in little toluene, thermostatted apart.

The starting time (±1 sec.) of the polymerization was taken as the moment when the transition metal halide was introduced. The polymerization was stopped by rapid introduction of acidified methanol.

The polymerization of propylene and the runs performed in order to determine the chain transfer constant with monomer in the polymerization of butene-1 were carried out in an autoclave, as described in previous papers.[3,4]

The experimental conditions of each run and the results obtained are reported in Tables I–III.

TABLE III
Polymerization of Butene-1 at 15°C. for the Determination of $\bar{M}_v$ for a Long Polymerization Time (See Fig. 4)[a]

Catalyst system	Amt. organometallic compound, mmole	$[\eta]$ pentane residue, dl./g.
$TiCl_3$(ARA)–$Be(C_2H_5)_2$	2.25	9.00
	9.00	6.92
$TiCl_3$(HRA)–$Be(C_2H_5)_2$	4.00	7.50
	5.75	7.45
	6.25	7.12
	10.80	5.96
$TiCl_3$(ARA)–$Al(C_2H_5)_2Br$	12.20	11.80
$TiCl_3$(HRA)–$Al(C_2H_5)_2Br$	4.00	10.86
	12.00	9.80
$TiCl_3$(HRA)–$Al(i\text{-}C_4H_9)_2Cl$	3.00	9.50
	9.00	10.35
	12.30	9.30
	16.00	9.65
$TiCl_3$(ARA)–$Al(i\text{-}C_4H_9)_2Cl$	2.25	11.22
	6.25	10.41
	12.20	11.80
$TiCl_3$(HRA)–$Al(C_2H_5)_2Cl$	2.25	11.60
	4.85	11.25
	8.40	12.30
	13.00	12.10

[a] The polymerization runs were performed with 100 ml. toluene 135 g. butene-1, and $TiCl_3$ in an amount varying from 0.02 to 0.4 g.

Polymer purification and extraction were as described in previous papers.[3,4]

Determination of $\bar{M}_v$

The molecular weights of the polybutenes were determined by viscometric methods in tetralin at 100°C.[5]

Though polybutene is soluble at lower temperatures than polypropylene (this is why the latter monomer was preferably used), the intrinsic viscosities were subject to systematic errors, due to unavoidable polymer degradation.

The extent of polymer degradation for a given thermal treatment depends on the polymer molecular weight and on the traces of inorganic substances produced by the catalyst. Therefore, error involved in the values of k'_p/k'_m differs in different systems. These errors are always negative.

On the other hand, it can be demonstrated that the slopes of the curves $1/\bar{M}_v$ versus $1/t$ were not altered by systematic errors, provided that the polymer degradation is not too high.

Degradation is more marked for the polymers that contain traces of V or I.

In the determination of the propagation rates, we did not encounter the difficulties, attributed to diffusion phenomena, met by other authors.[6] This might depend on the fact that polybutene can swell in the polymerization solvent, more than polypropylene, or that in all our tests the polymer yield per gram of catalyst was very low (Table I).

NMR Analysis of Polymers

The NMR analysis of polymers was carried out at 100 Mc./sec. as described in the literature.[7] The spectra are calibrated in ppm referred to hexamethyldisiloxane as internal reference. The definition of R and of the heterotactic methyl groups has been given elsewhere.[7] R allows one to evaluate the percentage of permanence* of steric configuration present in a given sample of polypropylene, i.e., $R = 0$ for isotactic polypropylene (100% permanence*); $R \simeq 2.2$ for syndiotactic polypropylene (100% alternances*); R assumes intermediate values in the case of not perfectly ordered polymers. R does not give any indication of the distribution of permanences* and alternances* in the macromolecules. However, qualitative information can be obtained from the NMR spectrum at 100 Mc./sec. of the methyl groups.[7]

RESULTS

Propagation Rate in the Polymerization of Butene-1

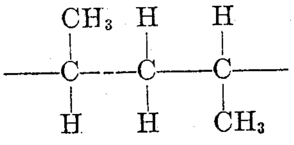
In a previous paper,[8] the following relationship was proposed to relate the number-average molecular weight with the concentration of the reagents, the number of active centers, and the polymerization time.

$$\frac{1}{\bar{M}_n} = \frac{C^* + \int_0^t C^* k_{t,i}(x_i)^\alpha \, dt}{\int_0^t k_p C^* m dt} \qquad (1)$$

where $\bar{M}_n$ is the number-average molecular weight, C^* is the number of active centers, $k_{t,i}$ is a generic chain transfer constant, x_i is the concentration of a generic chain transfer agent, α is a suitable exponent, m is monomer concentration, and t is reaction time.

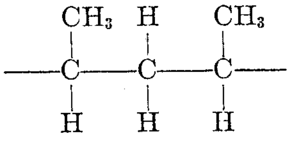
By supposing that the concentration of the reagents and the number of

* Alternances and permanences are the following structural units, respectively:



$$-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-$$

and



$$-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-$$

(planar projection).

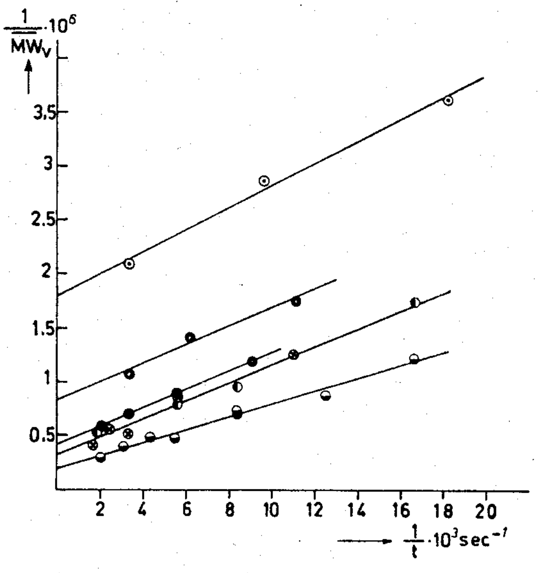


Fig. 1. Comparison among some catalytic systems containing δ-$TiCl_3$ (HRA or ARA) and different organometallic compounds: (⊙) $TiCl_3$(ARA)–$Be(C_2H_5)_2$; (○) $TiCl_3$(HRA)–$Be(C_2H_5)_2$; (●) $TiCl_3$(ARA)–$Al(C_2H_5)_2Cl$; (⊗) $TiCl_3$(HRA)–$Al(C_2H_5)_2Cl$; (◐) $TiCl_3$-(ARA)–$Al(C_2H_5)_2I$; (◒) $TiCl_3$(ARA)–$Al(i\text{-}C_4H_9)_2Cl$. The polymerization conditions are reported in Table I.

active centers are practically constant during the whole polymerization, and that:

$$\chi \bar{M}_v = \bar{M}_n \tag{2}$$

where χ is a constant and $\bar{M}_v$ is the viscosity-average molecular weight, eq. (1) becomes:

$$\frac{1}{\bar{M}_v} = \frac{1}{k'_p m t} + \frac{\sum k'_{t,i} x_i^{\alpha}}{k'_p m} \tag{3}$$

This relationship (by choosing reaction times lower than the mean lifetime of the macromolecules), enables us to determine $k'_p m$ (the propagation rate excepting the χ factor) for different catalytic systems, from the variations in $\bar{M}_v$.

Figure 1 reports $1/\bar{M}_v$ for the polymer residues after pentane extraction (isotactic fraction) versus $1/t$ for a series of catalytic systems consisting of δ-$TiCl_3$ (HRA and ARA) and different organometallic compounds. All polymerization runs were carried out at the same temperature (0°C.) and with the same concentration of reagents. In order to obviate the differences in the overall polymerization activity of the various catalytic systems, only the amount of $TiCl_3$ introduced was varied.

It can be observed that every catalytic system gives rise to a linear dependence of $1/\bar{M}_v$ versus $1/t$; the slopes $(1/k'_p m)$ of the different straight lines are practically coincident. On the contrary, the intercepts with the abscissas $(\sum k'_{t,i} x_i^{\alpha}/k'_p m)$ are different.

Figure 2 shows analogous results obtained from polymerizations carried out under the same conditions as in Figure 1 in the presence of the catalytic systems VCl_3–$Al(C_2H_5)_3$ and VCl_3–$Be(C_2H_5)_2$. k'_pm is far higher when catalytic systems containing VCl_3 have been used. As in Figure 1, the k'_pm is not appreciably influenced by the nature of the organometallic compound.

Activation Energy of Propagation in the Polymerization of Butene-1

Polymerization of butene-1 was carried out at different temperatures (from −78 to 0°C.) in the presence of VCl_3–$Al(C_2H_5)_3$ catalytic systems (Fig. 2). Also in this case, we observed the variation of $\bar{M}_v$ of the boiling n-pentane-insoluble fractions obtained for different polymerization times.

For the catalytic systems containing VCl_3 the energy of activation for pure chain propagation (Fig. 3) was determined as $E_{VCl_3} = 2.3$ kcal./mole. The pure propagation activation energy of the systems containing VCl_3 is far lower than the overall polymerization activation energy;[9] our preliminary results showed that the propagation activation energy of the systems containing $TiCl_3$ is higher than the value measured for systems with VCl_3.

Transfer with the Monomer

It is known[10] that, at low temperatures and with high polymerization times, eq. (1) becomes:

$$1/\bar{M}_v = (k'_mm + k'_{MR}MR^{\alpha})/k'_pm \qquad (4)$$

where k'_m is the chain transfer constant with the monomer, k'_{MR} is the chain transfer constant with the organometallic compound, MR is the

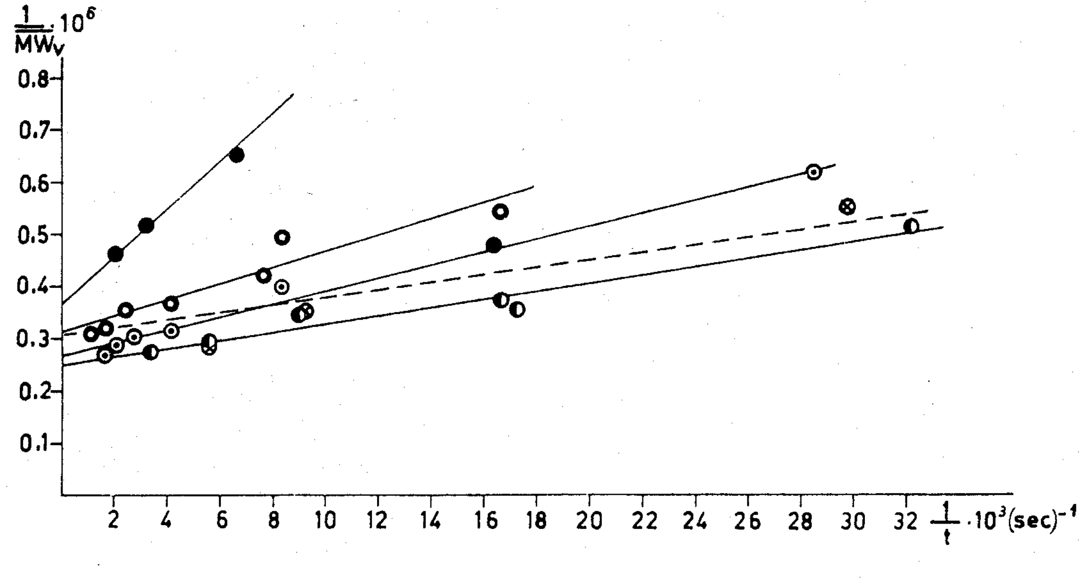


Fig. 2. Behavior of the VCl_3–$Al(C_2H_5)_3$ catalyst system in the polymerization of butene-1 at different temperatures, and comparison with the VCl_3–$Be(C_2H_5)_2$ system at 0°C.: (⊗) VCl_3–$Be(C_2H_5)_2$ at 0°C.; (◐) VCl_3–$Al(C_2H_5)_3$ at 0°C.; (⊙) VCl_3–$Al(C_2H_5)_3$ at −20°C.; (○) VCl_3–$Al(C_2H_5)_3$ at −40°C.; (●) VCl_3–$Al(C_2H_5)_3$ at −78°C. The polymerization conditions are reported in Table II.

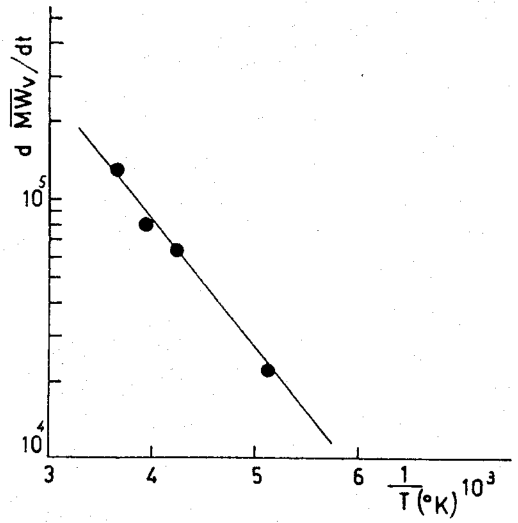


Fig. 3. Arrhenius plot (propagation rate) for the VCl_3–$Al(C_2H_5)_3$ catalyst system; $E \simeq$ 2.3 kcal./mole.

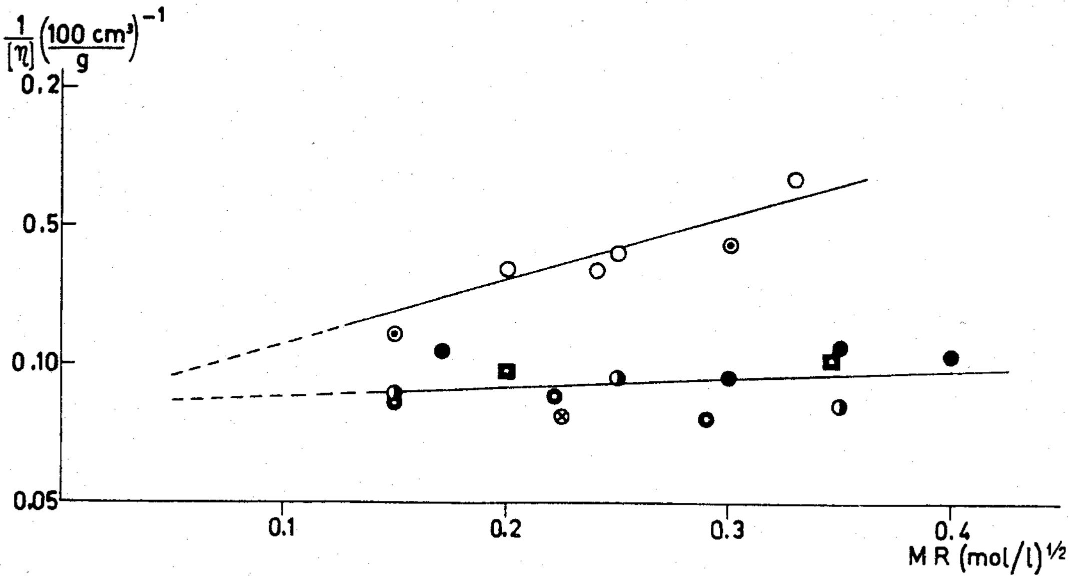


Fig. 4. Comparison among some catalytic systems containing δ-$TiCl_3$ (ARA or HRA) in the polymerization of butene-1 at 15°C.: (⊙) $TiCl_3$(ARA)–$Be(C_2H_5)_2$; (○) $TiCl_3$-(HRA)–$Be(C_2H_5)_2$; (⊗) $TiCl_3$(ARA)–$Al(C_2H_5)_2Br$; (■) $TiCl_3$(HRA)–$Al(C_2H_5)_2Br$; (●) $TiCl_3$(HRA)–$Al(i\text{-}C_4H_9)_2Cl$; (◑) $TiCl_3$(ARA)–$Al(i\text{-}C_4H_9)_2Cl$; (○) $TiCl_3$(HRA)–$Al(C_2H_5)_2Cl$. The polymerization conditions are reported in Table III.

concentration of the organometallic compound, and α is a generally unknown exponent, which for $Al(C_2H_5)_3$ is equal to $^1/_2$.

Polymerizations of butene-1 were carried out at 15°C. in the presence of different catalytic systems containing $TiCl_3$ (HRA) or $TiCl_3$ (ARA); use was made of high monomer concentrations, of high polymerization times, and increasing concentrations of the organometallic compound.

Figure 4 shows the inverse of the intrinsic viscosity of the boiling n-pentane-insoluble fractions of polymers obtained with different catalytic systems versus the square root of the concentration of the organometallic compound.

It is observed that with all catalytic systems containing δ-$TiCl_3$, $\bar{M}_v$ of the different polymers approaches the same value as the concentration of the organometallic compound decreases.

When $[\eta]$ can be extrapolated to zero concentration of the organometallic compound, the resulting values (k'_p/k'_m) coincide to a good approximation ($[\eta] \simeq 12$).

Therefore, it can be concluded that, for the catalytic systems containing δ-$TiCl_3$, the chain transfer constant with the monomer does not vary when varying the organometallic compound used.

Figure 2 also shows that, in the case of systems based on VCl_3, the values of $\bar{M}_v$ for a long polymerization time are far higher than in the case of catalytic systems containing δ-$TiCl_3$.

Stereospecificity of the Different Catalytic Systems

As previously mentioned, $\bar{M}_v$ values were determined on the *n*-pentane-insoluble fractions of the different polymers. This choice depended on the fact that we wanted to study the kinetics of the isotactic polymer formation by the stereospecific active centers. Actually, x-ray analysis revealed that the boiling *n*-pentane-soluble fraction is either amorphous or very slightly crystalline. Yet, as already known, the stereospecificity of the different catalytic systems in the polymerization of propylene varies on varying either the transition metal halide or the organometallic compound.[3] In this respect, butene-1 shows a similar behavior to that of propylene,[11] except for the higher solubility of its polymers. For this reason, we thought it convenient to make a survey of the stereospecificities of some catalytic systems, also taking into account the properties of the polymer fractions soluble in the different solvents. However, we thought it more convenient to take the stereospecificity data for the polymerization of propylene, as the fractionation methods have been studied more extensively[12] for this monomer, and more spectroscopic data are available.

We compared the behavior of some catalytic systems in the polymerization of propylene at 70°C. Many of the data obtained from boiling solvent extractions have already been reported.[3] In any case they are reported in Table IV. Regarding the stereoisomeric composition of the soluble fraction, Table IV also reports the x-ray crystallinity, the $\bar{M}_v$, the melting points, and some indexes of permanences and alternances (*R*) obtained by NMR analysis at 100 Mc./sec.[7] A qualitative NMR estimate of the heterotactic methyl content is also given.

The results show that the polymers obtained with the different catalytic systems not only differ in the relative amount of the various fractions, but also in their stereoisomeric composition, as indicated by the melting point and by the NMR analysis. The boiling diethyl ether-soluble fractions often differ from the *n*-heptane-soluble ones more owing to the greater amounts of heterotactic methyl groups present than to the NMR index of alternances and permanences; in particular, it may happen that two fractions, i.e., the ether and heptane fractions, have very close indexes of al-

TABLE IV

Stereospecificity of Some Catalyst Systems in the Polymerization of Propylene to Isotactic Polymer at 70°C.[a]

		Ether extract				Heptane extract						Heptane residue	
Run no.	Catalytic system	%	[η], dl./g.	*R*	Heterotactic methyl group content	%	[η], dl./g.	X-ray crystallinity, %	M.P., °C.	R	Heterotactic methyl group content	%	X-ray crystallinity, %
1	γ-$TiCl_3$–$Al(C_2H_5)_2Cl$	6.5	0.57	1.8	High	2.1	1.05	—	—	1.2	Low	91.4	66.3
2	γ-$TiCl_3$–$Al(C_2H_5)_3$	10.3	0.71	—	—	6.8	1.07	38.0	—	—	—	82.9	58.0
3	γ-$TiCl_3$–$Ga(C_2H_5)_3$	9.4	0.68	—	—	5.1	1.22	32.0	150°	1.1	Low	85.5	67.8
4	γ-$TiCl_3$–$Al(C_2H_5)_2I$	—	—	—	—	—	—	—	—	—	—	98.6	70.0
5	γ-$TiCl_3$–$Be(C_2H_5)_2$	2.1	0.63	—	—	2.6	0.91	43.0	—	—	—	95.3	65.0
6	γ-$TiCl_3$–$Al(C_2H_5)_2Br$	3.1	—	—	—	1.3	—	—	—	—	—	95.6	—
7	β-$TiCl_3$–$Ga(C_2H_5)_3$	12.0	0.88	1.5	High	8.0	1.80	32.0	155°	1.3	Very low	80.0	63.0
8	VCl_3–$Al(C_2H_5)_2Cl$	41.4	2.02	1.9	High	21.2	4.3	28.6	147°	0.9	Medium	37.4	59.0

[a] Polymerizations were performed at 70°C. with the use of 200 ml. *n*-heptane and 30 g. propylene. The concentration of organometallic compound was always 8.3×10^{-3} mole/l. The amount of $TiCl_3$ and the polymerization time were changed in each run in order to obtain always 5–10 g. of polymer.

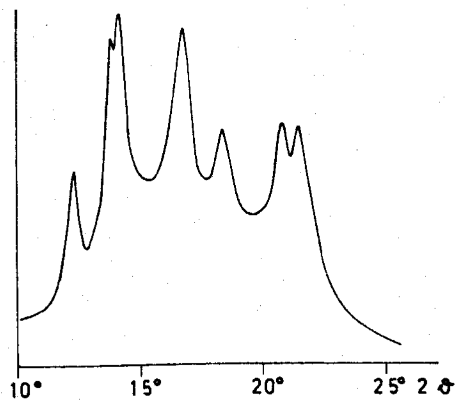


Fig. 5. Geiger spectrum (CuKα) of the boiling n-heptane-soluble and boiling diethyl ether-insoluble polymer fraction (product from run 7 of Table IV).

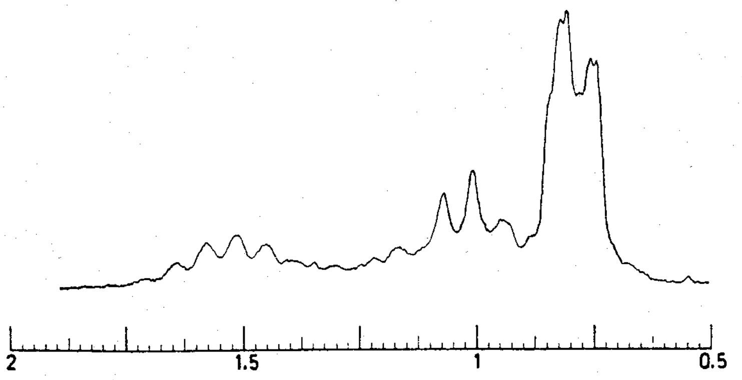


Fig. 6. NMR spectra (100 Mc./sec.) of the boiling diethyl ether-soluble polymer fractions (product of run 1 of Table IV).

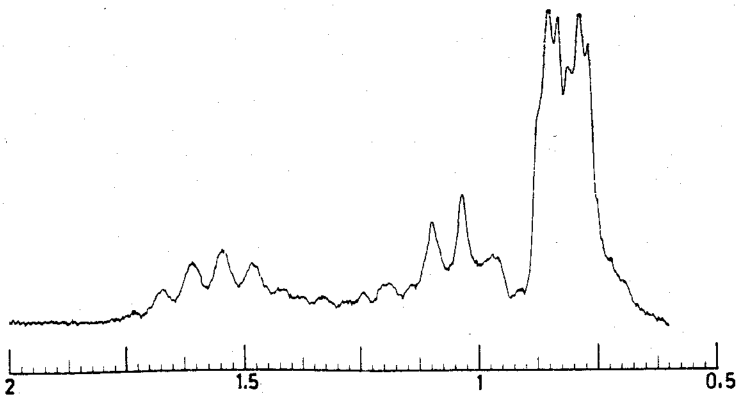


Fig. 7. NMR spectra (100 Mc./sec.) of the boiling diethyl ether-soluble polymer fractions (product of run 8 of Table IV).

ternances and permanences. The ether fractions consist, with a few exceptions, of macromolecules containing comparable amounts of permanences, alternances, and heterotactic methyl groups. In other words, these are head-to-tail polymers, in which the monomeric units follow one another with a randomly variable steric configuration. The heptane extracts obtained by the catalytic systems containing $TiCl_3$ have generally a relatively

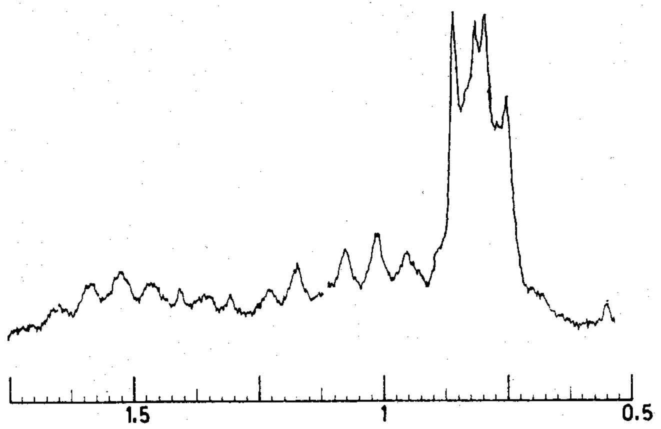


Fig. 8. NMR spectra (100 Mc./sec.) of the boiling *n*-heptane-soluble and boiling diethyl ether-insoluble polymer fractions (product of run 1 of Table IV).

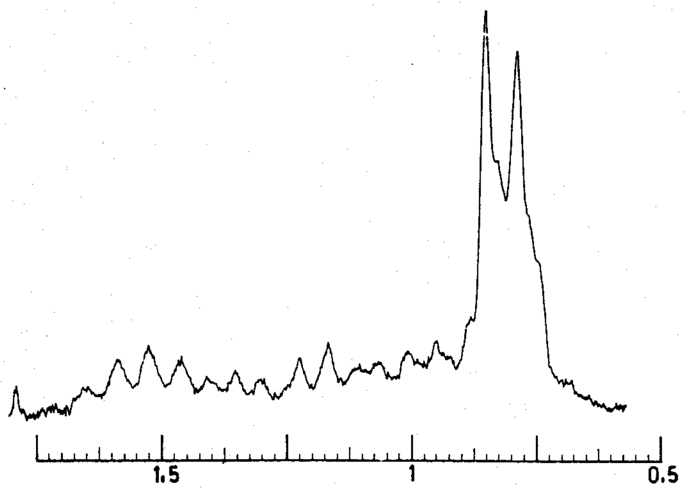


Fig. 9. NMR spectra (100 Mc./sec.) of the boiling *n*-heptane-soluble and boiling diethyl ether-insoluble polymer fractions (product of run 8 of Table IV).

small heterotactic methyl content[7]; therefore, sometimes, they predominantly consist of isotactic and syndiotactic type stereoblock macromolecules.

Stereoblocks are connected by one or few units that follow one another in a sterically disordered manner (heterotactic methyl groups).

As revealed by x-ray analysis, the heptane extracts sometimes present crystallinity of the two types: i.e., isotactic and syndiotactic (see Fig. 5). The relative amount of syndiotactic type segments in the heptane fraction can be qualitatively evaluated from the NMR spectrum of the methyl groups and, with regard to the catalytic systems based on γ-$TiCl_3$, it increases in the following order: $Al(C_2H_5)_2I < Al(C_2H_5)_2Cl < Al(C_2H_5)_3 \simeq Be(C_2H_5)_2 < Ga(C_2H_5)_3$.

The catalytic system $Ga(C_2H_5)_3$–β-$TiCl_3$ seem to contain a greater amount of syndiotactic segments.

The heptane extract of product obtained with the catalytic system VCl_3–$Al(C_2H_5)_2Cl$, on the contrary, has a low syndiotactic segment content.

The isotactic segments are connected by sterically disordered segments. The ether extract of polymer obtained with the VCl_3–$Al(C_2H_5)_2Cl$ catalyst system contains the lowest amount of permanences ($R = 1.9$). Though the heptane extracts can be further fractionated, according to the type of steric regularity,[13] they certainly consist of stereoblock macromolecules having a different composition and are not mechanical mixtures of isotactic and amorphous or syndiotactic macromolecules.

In fact, as revealed by NMR analysis, many heptane fractions contain syndiotactic portions, which are not crystalline by x-rays. If such portions were not chemically bound to the boiling diethyl ether-insoluble isotactic type portion, it would be impossible to explain why they are insoluble in boiling diethyl ether, being amorphous by x-ray examination.

As an example, we report NMR spectra of some particularly interesting fractions (Figs. 6–9).

DISCUSSION OF THE EXPERIMENTAL RESULTS

With regard to all the catalytic systems containing the same transition metal halide, evidence was accumulated proving that the stereospecific active centers are, at least to a first approximation, kinetically equivalent.

When passing from $TiCl_3$ (HRA) to $TiCl_3$ (ARA), some slight discrepancies were observed, especially about the chain transfer constants. However, in our opinion, this is a spurious effect, due to the fact that very pure $TiCl_3$ (ARA) can be hardly obtained, owing to its very high reactivity. On the contrary, the kinetic constants of the stereospecific active centers are quite different in the catalytic systems containing different transition metal halides.

The variations in the polymerization rates with different organometallic compounds (see Table I) can be substantially ascribed to variations in the number of stereospecific active centers.

It is convenient to note that, due to the type of results obtained, the validity of these statements, with regard to the equality in kinetic behavior of the active centers present in the different catalytic systems containing δ-$TiCl_3$, holds even when the preliminary hypotheses (independence of χ of the catalytic system and constancy of the number of active centers during the whole polymerization run) were not fully satisfied.

The same observations can be made for the catalytic systems containing VCl_3, i.e., the kinetic constants of the stereospecific active centers are in this case actually different from those of the δ-$TiCl_3$-containing systems.

The relative values of the propagation activation energies prove that k_p is higher for VCl_3 than for δ-$TiCl_3$ (taking into account that steric factors cannot be very different in the two cases), even if it can happen that χ varies when passing from the systems containing δ-$TiCl_3$ to those containing VCl_3. However, it would be an oversimplification to conclude on the basis of this kinetic behavior that the stereospecific active centers are monometallic. In fact, the reported experimental data prove only that the kinetically determining stage of propagation is an interaction between the transition metal and the olefin.

For instance, it could be assumed that the kinetically determinant stage in the chain propagation is the formation of a complex of the α-olefin on the transition metal.

On the contrary, if, as some authors think,[14] the kinetically determining stage is the addition of the α-olefin to the metal–carbon bond, the data obtained show that the reacting bond in the polymerization is the transition metal–carbon bond.

However, the active centers might contain the organometallic compound of a light metal, or exchange with it one or more substituents in addition to the alkyl radical.

As a matter of fact, many experimental findings cannot be understood now only on the basis of the second hypothesis, i.e., that the active centers simply are surface alkylation products of transition metal halide.

As observed in a previous paper,[15] the alkylation of the surface of the transition metal halide alone cannot explain the changes in the number of active centers when changing the organometallic compound in the catalytic system.

Moreover, the activity of the different catalytic systems containing $TiCl_3$ depends little on the concentration of the organometallic compound.[16,17] If the second hypothesis were true, instead, activity would increase with the concentration of the organometallic compound (at least when the organometallic compounds have low alkylating power and low catalytic activity), because in this case, the surface of $TiCl_3$ cannot be considered as wholly covered by active centers.

Moreover, in general, the number of active centers increases with the increase in temperature (from -78 to 0°C.), in a less marked manner for $TiCl_3$, and very markedly for VCl_3, as is seen from the comparison between the propagation and overall polymerization activation energies. Also the data of stereospecificity of the different catalyst systems hardly agree with the hypothesis that the catalytic complexes are all monometallic.

The composition of the heptane extracts (stereoblocks) shows that the nonstereospecific active centers interact with the stereospecific ones. During the chain growth, the isotactic type stereospecificity of the active centers can turn into syndiotactic; in other cases, active centers lose and regain their stereospecificity.

Experimental evidence shows that these phenomena are associated closely with the organometallic compound initially introduced in the catalytic system; in fact they are quite insignificant in the case of the catalytic system violet $TiCl_3$–$Al(C_2H_5)_2I_7$ and variously significant in the other systems examined.

Therefore, even if it was established that some catalytic systems[2,18] contain monometallic stereospecific active centers, in our opinion, no generalization is possible, before clarification of the various experimental findings concerning the quite complex behavior of the bimetallic catalytic systems.

CONCLUSION

The data obtained so far from the study of the kinetic behavior of the stereospecific active centers and of the stereospecificity of the bimetallic catalytic systems do not seem to allow a simple assimilation of the bimetallic catalytic systems with the monometallic ones, from the point of view of the constitution of the stereospecific active centers.

The kinetic behavior of the stereospecific active centers present in the bimetallic systems is independent of the organometallic compound used. This could indicate that the growth of the macromolecules occurs on the transition metal–carbon bond or else that the kinetically determining stage is the complexation of the olefin with the transition metal, and, according to our data, we believe that this hypothesis is the most probable.

If the overall catalytic activity of the different catalytic systems is examined and compared with the alkylating power of the organometallic compound used,[15] an interpretation of the experimental findings seems easier if the stereospecific active centers are considered in this case bimetallic. This opinion is also supported by the stereospecificity of the different bimetallic catalytic systems, as it can be deduced either by extraction or by the stereoisomeric composition of the different polymer fractions, determined by NMR analysis.

In our opinion, a more detailed study of the stereospecificity of the different catalytic systems will be of help in solving this problem.

These hypotheses agree with the data reported by other authors on the reactions of growing macromolecules with deuterium[19] and take into account both the variations in stereospecificity (which induced some of us to attribute the reactivity to a light metal–carbon bond[20]) and the unity requirements for a mechanism of the stereospecific catalysis of α-olefins to isotactic polymers.

Apart from their meaning about the constitution of the active centers, the following points seem to be established: (*1*) the different activities of catalytic systems containing the same transition metal halide and different organometallic compounds depend, exclusively or predominantly, on the variations in the number of active centers; (*2*) the average constant of chain propagation of the active centers present in the different catalytic systems varies appreciably only when varying the transition metal halide; (*3*) the different catalytic systems polymerize propylene with different stereospecificities also with regard to the steric regularity of the fractions soluble in boiling hydrocarbons; (*4*) the soluble polypropylene fractions, e.g., soluble in boiling *n*-heptane, often consist of stereoblock macromolecules of different types (isotactic, syndiotactic, atactic), and in some cases, present a x-ray crystallinity of the isotactic and syndiotactic type, in comparable amounts.

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Résumé

Des résultats concernant le comportement de différents systèmes catalytiques hétérogènes pour les polymérisations d'α-oléfines en vue d'obtenir des polymères isotactiques sont rapportés et comparés entre eux. L'effet des substituants sur le comportement cinétique des catalyseurs complexes qui dans différents systèmes fournissent des chaînes polymériques ayant des régularités stériques comparables a été étudié. En outre, des hypothèses sont présentées concernant les factuers qui influencent la stéréospécificité des systèmes catalytiques étudiés.

Zusammenfassung

Daten über das Verhalten verschiedener heterogen-katalytischer Systeme bei der Polymerisation von α-Olefinen zu isotaktischen Polymeren werden mitgeteilt und verglichen. Der Einfluss von Substituenten auf das kinetische Verhalten der Katalysatorkomplexe welche in den verschiedenen Systemen Polymerketten mit vergleichbarer sterischer Regelmässigkeit liefern, wurde untersucht. Hypothesen über die Faktoren, welche die Stereospezifität der untersuchten Katalysatorsysteme beeinflussen, werden aufgestellt.