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COPOLYMERIZATION WITH ZIEGLER–NATTA CATALYSTS—III.

RATES OF COPOLYMERIZATION FOR SEVERAL OLEFIN PAIRS

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Abstract—Dilatometry was used to measure the rates of copolymerizations of styrene with hex-1-ene, hept-1-ene, 4-methylpent-1-ene and 4-methylhex-1-ene, in the catalyst system, $AlEt_3$–$\alpha TiCl_3$ in toluene.

The copolymerizations were found to be first order with respect to $TiCl_3$ and independent of Al/Ti ratio. Increased temperature produced a rapid increase in rate; variation of monomer feed, over the whole range, resulted in a gradual change from one homopolymerization rate to the other. The nature of the α-$TiCl_3$ sample was found to have considerable effect on the rate of copolymerization.

The order of reactivity, both from rate measurements and reactivity ratios, implies that, for the polymerization of α-olefins by heterogeneous Ziegler–Natta catalysts, steric effects outweigh electronic consideration.

IN PREVIOUS papers[1,2] the copolymerizations of styrene with several α-olefins have been described, with special reference to reactivity ratios and copolymer structure.

This paper presents the kinetic results from these copolymerizations to show how the relative emphasis of steric and electronic factors in determining (a) copolymer composition and (b) overall rates of copolymerization results in two different patterns of reactivity in the olefins studied. The kinetic results also provide a means of testing various kinetic schemes proposed for Ziegler–Natta heterogeneous polymerization catalysts.

Since the α-olefins, all of which were copolymerized with styrene, are liquids at room temperature the experimental technique developed for styrene can be used.[3] Two linear olefins, n-hex-1-ene and n-hept-1-ene, and their branched isomers, 4-methylpent-1-ene and 4-methylhex-1-ene, were used to study the effect of moving in a homologous series and the effect of branching. It was found that 2-methylpent-1-ene did not undergo homopolymerization nor copolymerization with styrene. This behaviour was attributed to the considerable steric hindrance of the methyl group on the β-carbon atom, so indicating the importance of steric consideration in this type of polymerization.

MATERIALS AND EXPERIMENTAL TECHNIQUE

The purification of solvent, catalyst components and monomers is described in previous papers.[1,2] The experimental methods have also been outlined.[1]

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Density measurements

To calculate absolute rates from dilatometric measurements it is essential to know the densities of the monomers and polymers. The copolymer densities were measured by a modified flotation method. Small particles of the copolymer were outgassed thoroughly on a high vacuum line and a known quantity of ethanol distilled on to the particles. The vessel was then transferred to a thermostat, the temperature of which was identical to the copolymerization temperature. Outgassed, distilled water was then run in until the copolymer particle floated. False readings were avoided by ensuring that no air bubbles adhered to the copolymer particles. The densities of the ethanol–water mixtures were obtained from tables.[4]

RESULTS

The initial settling period, characteristic of Ziegler–Natta homopolymerization[3,5] was also evident in the copolymerization reactions but it was impossible to establish any relationship between the time taken for the rate to reach a constant value and the reaction variables. Once over this initial period, the rate was constant with time for the first 5 per cent conversion, except for one notable case (styrene/heptene = 80/20), where the reactivities and concentration of the monomers were such that the monomer feed did change slightly over the first 5 per cent conversion. The values given in subsequent tables are all taken from the linear part of the curve below 4–5 per cent conversion.

In the polymerization system under question there are four variables (a) monomer feed ratio, (b) titanium trichloride concentration, (c) aluminium triethyl concentration (expressed as Al/Ti ratio) and (d) temperature.

The effect of (b) and (c) were determined for the styrene/4-methylpent-1-ene system and conclusions drawn from the results were assumed to hold for the other three systems.

Dependence of rate on titanium trichloride concentration

A series of copolymerization was carried out at 45° with constant monomer feed ratio and constant Al/Ti ratio while the titanium trichloride concentration was varied from 0·05 mole/l. to 0·14 mole/l. The values of the rates in Table 1 show the first order dependence of rate on titanium trichloride concentration.

TABLE 1. RATE DEPENDENCE ON [$TiCl_3$] STYRENE/4-METHYLPENT-1-ENE

[$TiCl_3$] (mole/l.)	Mole % styrene in feed	Rate × 10^2 (% conversion/min)	Rate (% conversion/min/[$TiCl_3$])
0·054	65	0·99	0·183
0·080	65	1·66	0·207
0·138	65	2·42	0·175
0·083	35	2·59	0·312
0·117	35	3·59	0·307

Temperature = 45°; Al/Ti = 3·00.

Use is made of this first order relationship in defining the standard units of rate used in this paper as percentage conversion/min/[$TiCl_3$]. From the scatter of results it follows that such a treatment will produce errors in the rate measurements of the order of 3–7 per cent.

Dependence of rate on aluminium/titanium ratio

With constant monomer and titanium trichloride concentration, a number of copolymerizations were carried out at 45°, with varying concentration of aluminium triethyl, effectively varying the Al/Ti ratio from 1·5 to 7·5.

The results in Table 2 show that the rate is approximately zero order with respect to aluminium triethyl concentration, but falls off very slightly with increasing concentration, as has also been observed and explained in homopolymerization.[6]

TABLE 2. RATE DEPENDENCE ON Al/Ti RATIO
STYRENE/4-METHYLPENT-1-ENE

$[TiCl_3]$ (mole/l.)	$[AlEt_3]$ (mole/l.)	Al/Ti	Rate (% conversion/min/$[TiCl_3]$)
0·086	0·645	7·5	0·355
0·083	0·498	6·0	0·390
0·083	0·249	3·0	0·390
0·117	0·351	3·0	0·369
0·086	0·129	1·5	0·437

Temperature = 45°; mole % styrene = 35.

Dependence of rate on temperature

In order to cover a wide range of temperature, the constant monomer feed chosen for the temperature dependence series was one with a high styrene content to minimize the formation of vapour bubbles from the more volatile α-olefins which interrupt dilatometric mesaurements.

The results in Table 3 indicate a rapid increase in rate as the temperature increases.

TABLE 3. RATE DEPENDENCE ON TEMPERATURE

Temperature (°C)	Rate (% conversion/min/$[TiCl_3]$)			
	Styrene/Hexene = 65/35	Styrene/Heptene = 65/35	Styrene/4 Me.pentene = 80/20	Styrene/4 Me.hexene = 65/35
25	0·170	0·173	—	0·120
30	0·221	—	0·095	—
35	0·232	0·242	0·118	0·177
40	—	0·270	—	0·270
45	—	0·327	0·130	—
50	0·593	—	0·236	—

Al/Ti = 3·00.

However an Arrhenius plot of log rate against T^{-1} does not give the expected straight line (slope $= -E/R$). It can be shown that the theoretical expression for the rate of copolymerization contains several temperature dependent factors, the combination of which need not necessarily give a straight line Arrhenius plot.

Dependence of rate on monomer feed

The effect of altering the monomer feed ratio was studied at constant temperature, titanium trichloride concentration, aluminium/titanium ratio and total monomer concentration. All four systems (Table 4 and Fig. 1) show similar rate-monomer feed curves with minima at or near the 100 per cent styrene axis, styrene being the monomer in each case with the lower homopolymerization rate.

TABLE 4. RATE DEPENDENCE ON MONOMER FEED

Hex-1-ene		Hept-1-ene		4-methylpent-1-ene*		4-Methylhex-1-ene	
% Styrene†	Rate‡	% Styrene	Rate	% Styrene	Rate	% Styrene	Rate
100	0·082	100	0·082	100	0·147	100	0·082
80	0·153	80	0·120	80	0·134	80	0·093
65	0·280	65	0·237	65	0·180	72	0·087
50	0·395	50	0·478	50	0·272	65	0·103
35	0·581	35	0·582	35	0·305	50	0·085
20	0·830	25	0·669	20	0·530	35	0·095
0	1·821	0	1·560	0	1·462	0	0·306

Temperature = 35°; Al/Ti = 3·00.

* Temperature = 45°.
† Rate = % conversion/min/[$TiCl_3$].
‡ Mole % styrene in feed.

Dependence of rate on titanium trichloride sample

It is widely recognized that the rate of polymerization in this type of heterogeneous system is proportional to the number of active sites which in turn is some function of the surface area of the titanium trichloride and the amount of cleavage and dislocations. Thus it is possible that two samples of titanium trichloride from different sources may give entirely different rates.

The polymerizations described so far in this paper have all been achieved using the same sample of titanium trichloride, making it possible to compare data obtained from the various monomer pairs. However, the styrene/4-methylhex-1-ene system was repeated using a new sample of $TiCl_3$ (sample B) with a vastly different reactivity. The effect of change of sample on the reactivity ratios has already been discussed[2] and the effect on rate of copolymerization is shown in Table 5 and Fig. 2.

DISCUSSION

The kinetics of copolymerization of α-olefins using $AlEt_3$-α-$TiCl_3$ as catalyst and toluene as diluent, appear to follow the same general principles as are observed in homopolymerization,[3,5] the rate being first order in titanium trichloride concentration and approximately zero order in aluminium triethyl concentration, with the characteristic settling period and irreproducibility of different titanium trichloride samples.

Such behaviour is consistent with current ideas on reaction mechanisms. The first order dependence on titanium trichloride concentration and importance of sample

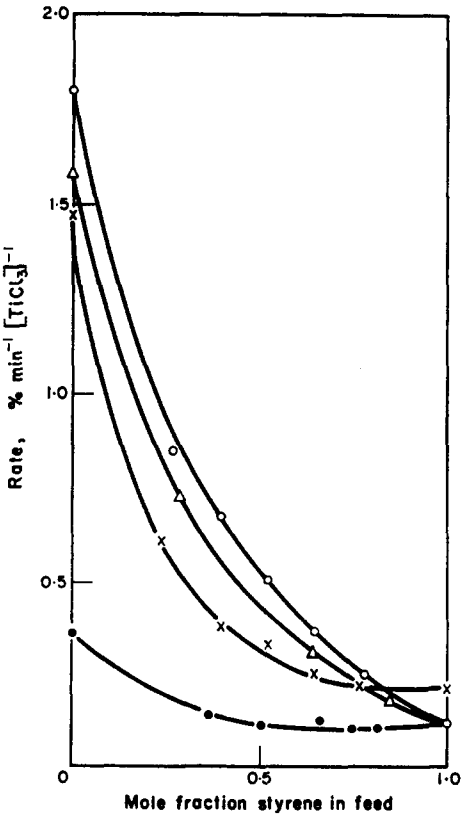


FIG. 1. Rate of copolymerization (% conversion/min/[$TiCl_3$]) vs. monomer feed composition. ○ Styrene-hex-1-ene; Temp. = 35°. △ Styrene-hept-1-ene; Temp. = 35°. × Styrene-4-methylpent-1-ene; Temp. = 45°. ● Styrene-4-methylhex-1-ene; Temp. = 35°.

TABLE 5. EFFECT OF $TiCl_3$ SAMPLE ON RATE

Sample A		Sample B	
% Styrene	Rate	% Styrene	Rate
100	0·082	100	0·037
80	0·093	65	0·025
72	0·087	60	0·041
65	0·013	45	0·030
50	0·085	28	0·023
35	0·095	15	0·057
0	0·306	0	N.D.

Temperature = 35°; Al/Ti = 3·00.

history and preparation, implies a relationship between the surface area and the number of active propagation sites. On the Cossee picture,[7] Arlman[8] has suggested that active sites are formed by the interaction of aluminium alkyl with a chlorine vacancy on the surface of the titanium trichloride to produce a titanium atom with a chlorine vacancy and an alkyl group in adjacent octahedral positions.

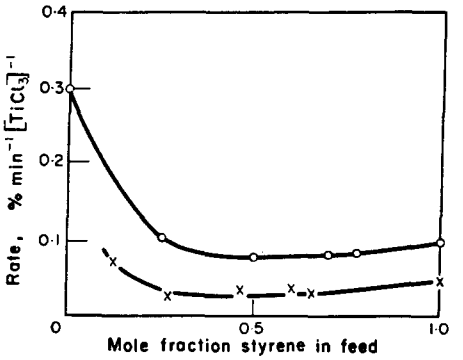
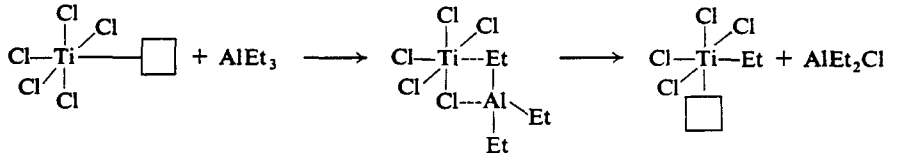


FIG. 2. Rate of copolymerization (% conversion/min/[$TiCl_3$]) vs. monomer feed composition for styrene-4-methylhex-1-ene. ○ $TiCl_3$ Sample A. × $TiCl_3$ Sample B.



On this basis aluminium alkyl is only required for setting up active sites and once the aluminium alkyl concentration exceeds the value which will provide the maximum number of possible sites, the excess alkyl will be preferentially adsorbed on the titanium trichloride surface, effectively preventing adsorption of monomer adjacent to active sites, which in turn will tend to decrease the rate slightly at high Al/Ti ratios.

Several workers[9–11] have observed distinct maxima in plots of rate against Al/Ti ratios in systems such as AlR–$TiCl_4$ but in this system measurements at low Al/Ti ratios were impossible so that only the decreasing half of the curve was obtained.

The second function of aluminium alkyl is as a transfer agent to give a polymer chain with an aluminium atom at one end and an active site with an alkyl group in place of the polymer chain. The polymer chain which is not "dead" but only "dormant" can be readsorbed at another propagation site with an even chance of inversion or it can be terminated at another type of active site.[12] The former procedure will lead to stereo-block polymers and the aluminium alkyl will influence both the stereospecificity and the molecular weight of the products.

Further evidence of the non-participation of aluminium alkyl in the propagation step is provided by Carrick's investigation of the copolymerization of ethylene with propylene using a series of metal alkyls and a series of transition metal compounds.[13] He found that the relative reactivity of the propylene increases as the electronegativity of the transition metal centre increases but no differences were observed when the metal alkyl was varied.

The rate/monomer feed composition curves (Fig. 1) are similar in shape to free radical copolymerization curves[14] but little work has been published on rate of copolymerization in the field of heterogeneous catalysts. In the copolymerization of ethylene with propylene using aluminium trihexyl and vanadium tetrachloride or trichloride, Natta[15] found that the rate of copolymerization was a linear function of the monomer feed composition at high ethylene fractions (20–100%) and a slight curve at the propylene

(less reactive) end. The difference in reactivities in these monomers is far greater than any of the monomer pairs mentioned above and it must be emphasised that the shape of the curve depends to a large extent on the constitution of the catalyst and especially on the nature of the solid phase. The latter observation makes direct comparisons with other workers invalid and only an internal comparison of the four systems in question, investigated using identical reaction conditions, can be used in evaluating the steric and electronic effects.

In such a system the order of reactivity from homopolymerization rates is hex-1-ene > hept-1-ene > 4-methylpent-1-ene > 4-methylhex-1-ene > styrene, whereas the apparent order from reactivity ratios is hex-1-ene > hept-1-ene > 4-methylpent-1-ene > styrene >

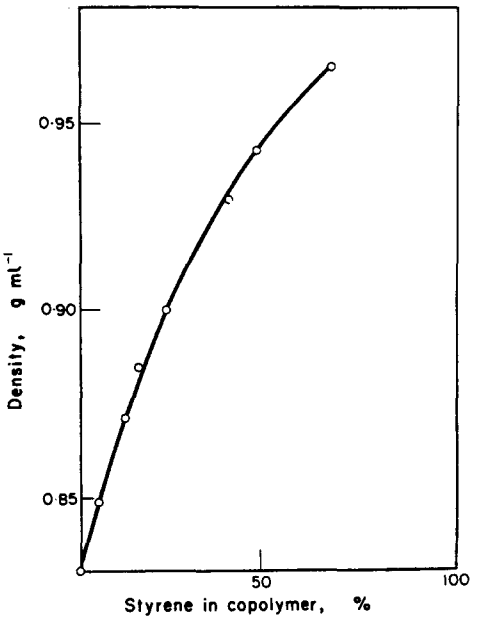


FIG. 3. Density (g/ml) vs. copolymer composition for styrene-4-methylpent-1-ene. Temp. = 45°.

4-methylhex-1-ene. This latter is, however, only an apparent order since it will be shown in a later paper that the measured reactivity ratios are not the true values, although the differences are small.

It has already been shown that the order of overall rates of homopolymerization for the lower members of the linear α-olefins series is ethylene > propylene > but-1-ene > pent-1-ene,[16] with an identical pattern from copolymer reactivity ratios.[17] The decline in rate on moving up the homologous series is attributed to a combination of decrease in the inductive effect of the methyl group with distance from the double bond (negligible after one or two intervening methylene groups) and the actual bulk of the side chain of the growing polymer chain tending to obscure the active catalyst site. Fitting the monomer into the active chain end presents no great difficulty as the molecule would be in the adsorbed position, adjacent to the active site, with the double bond

attached to the surface and the hydrocarbon tail in the solution. Thus, in the longer chain homologues, physical size is the governing factor in deciding the rate of polymerization.

Turning to the branched isomers, one would expect a less straight-forward pattern. The effect of chain length is the underlying factor but the position of branching influences the polarity of the double bond and produces steric hindrance both in the approaching monomer and in the growing chain. Methyl branching nearer the double bond enhances the affinity of the olefin for the electron deficient catalyst surface but, at the same time, the increased bulk in the vicinity of the active end inhibits the growth reaction. In the $TiCl_3/AlEt_3$ system, the latter is the deciding factor and branched olefins have lower rates than their linear parents, further support of which is provided by Ketley[18] in the copolymerization of but-1-ene and 3-methylbut-1-ene using a catalyst composed of titanium trichloride and aluminium triisobutyl. Overberger[19], with vanadium oxytrichloride and aluminium triisobutyl, found the order of overall rate to be 4-methylpent-1-ene > styrene > 3-methylbut-1-ene, which corresponds to the behaviour of the $TiCl_3/AlEt_3$ system.

The factors, which determine the order of reactivities from copolymerizations, follow the general principles of polarity and steric hindrance outlined for rate of homopolymerization. However, this is complicated by the heterogeneous nature of the catalyst which results in sites which have a preference for one monomer or the other, so that one does not obtain a true, representative picture from the overall copolymer composition and reactivity ratios. Also, since the reaction is highly stereospecific, it is possible that monomer A does not fit well in the polymer B structure, which will distort the apparent affinity of A for chain end B. Models show that the 7_2 helix of isotactic poly-4-methylpent-1-ene is more open than the 3_1 helix of isotactic polystyrene, making it relatively simple to fit a unit of styrene into the 7_2 helix but very difficult to fit a 4-methylpent-1-ene unit into the 3_1 helix.

This phenomenon is borne out by the density measurements, where there is no marked lowering from the extrapolated density, at the 4-methylpent-1-ene end of the copolymer composition curve, as the styrene content increases, implying that the crystallinity of the poly-4-methylpent-1-ene is not appreciably decreased by the introduction of up to 30 per cent styrene.

For the study of copolymerizations of styrene and several α-olefins, achieved using the titanium trichloride-aluminium triethyl Ziegler–Natta system, it appears that both rates of polymerization and copolymer reactivity ratios are determined by a combination of electronic and steric factors, with the latter proving to be the more important.

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Résumé—On a utilisé la méthode dilatométrique pour mesurer les vitesses de copolymérisation du styrène avec l'hexène-1, l'heptène-1, le méthyl-4-pentène-1 et le méthyl-4-hexène-1 avec le système catalytique Al Et_3–$\alpha TiCl_3$ dans le toluène.

Ces réactions étaient de ler ordre par rapport à $TiCl_3$ et leurs vitesses étaient indépendantes du rapport Al/Ti. Une élévation de la température produisait une importante augmentation de la vitesse. En faisant varier la composition du mélange des monomères on a observé que la vitesse de la réaction variait graduellement entre les valeurs obtenues pour les homopolymérisations de chacun des monomères. La nature de l'échantillon de $TiCl_3$ avait une influence notable sur la vitesse de copolymérisation. L'ordre des réactivités obtenu à la fois d'après les vitesses et les rapports de réactivités implique que les effets stériques sont prépondérants par rapports aux facteurs électroniques pour déterminer les réactivités dans la polymérisation des α-oléfines amorcée par des catalyseurs Ziegler–Natta hétérogènes.

Sommario—Per misurare le velocità di copolimerizzazione dello stirene con esene-1, eptene-1, 4-metilpentene-1 e 4-metilesene-1 col sistema catalitico $AlEt_3$–$\alpha TiCl_3$ in toluolo, è stata usata la dilatometria.

Si è visto che la copolimerizzazione è del I ordine rispetto al $\alpha TiCl_3$ ed è indipendente dal rapporto Al/Ti. Un aumento di temperatura produce un rapido aumento della velocità; una variazione della concentrazione, in tutto il campo, corrisponde ad un passaggio graduale da une velocità di omopolimerizzazione all'altra. È stato trovato che la natura del campione di α-$TiCl_3$ ha notevoli effetti sulla velocità di copolimerizzazione.

L'ordine di reattività, ricavato sia dalle misure di cinetica che dai rapporti di reattività, implica che, per la polimerizzazione di α-olefine con catalizzatori eterogenei Ziegler–Natta, gli effetti sterici predominano su considerazioni elettroniche.

Zusammenfassung—Die Geschwindigkeiten der Copolymerisation von Styrol mit Hex-1-en, Hept-1-en, 4-Methylpent-1-en und 4-Methylhex-1-en mit dem Katalysatorsystem $AlEt_3$—α $TiCl_3$ in Toluol wurden dilatometrisch gemessen.

Es erwies sich, daß die Copolymerisation nach der ersten Ordung in Bezug auf $TiCl_3$ und unabhängig vom Al/Ti Verhältnis verlaufen. Mit steigender Temperatur nimmt die Geschwindigkeit rasch zu. Eine Variation der Monomerzugabe über den gesamten Bereich bewirkte einen kontinüierlichen Übergang von einer Homopolymerisationsgeschwindigkeit zur andern. Es wurde gefunden, daß die Art der α-$TiCl_3$ Probe einen beträchtlichen Einfluß auf die Geschwindigkeit der Copolymerisation hat.

Die Reihenfolge der Reaktivität, sowohl aus Geschwindigkeitsmessungen als aus den Reaktivitätsverhältnissen abgeleitet, lässt darauf schließen, daß bei der Polymerisation von α-Olefinen durch heterogene Ziegler–Natta Katalysatoren, sterische Effekte gegenüber elektronischen Einflüssen überwiegen.