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Copolymerization of Olefins by Ziegler-Natta Catalyst. The Copolymerization of 1-Hexene and Propylene. Kinetic Study

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ABSTRACT

The copolymerization of 1-hexene and propylene in the presence of a Ziegler-Natta type catalyst ($AlEt_2Cl-TiCl_3$) has been studied. The gas chromatography method used for the kinetic study allowed determination of reactivity ratios of both monomers from the classical copolymerization equation which was found to be followed. The copolymers composition has been confirmed by NMR analyses and the theoretical sequence distribution computerized, thus giving an a priori description of the macromolecules useful for further studies of the properties of these copolymers. The drift in copolymer composition and thus in the distribution of monomer units occurring with conversion has been found important, and to avoid this heterogeneity in composition, some copolymers were prepared at constant monomer feed composition using a very simple manometric device.

INTRODUCTION

While the polymerization of olefins with Ziegler-Natta catalysts has been the object of many studies, very few studies have been devoted to their copolymerization [1-3] although this represents a means of controlling and modifying the properties of such polymers. However, the behavior of a copolymer is not only a function of its composition, which is too incomplete a picture, but it is also in relationship with the distribution of sequences of the monomer entities in the macromolecule. We have thus undertaken a precise kinetic study aimed at determining the reactivity ratio required for the a priori calculation of the distribution of monomer sequences; that is, the theoretical knowledge of the microstructure of copolymers.

EXPERIMENTAL

1-Hexene (Fluka ≥99%) was distilled under vacuum; propene (Fluka >98%) was trapped in a high-pressure glass tube at -30°C (5 atm) from a tank. The aluminum monochlorodiethyl (Texas Alkyl) was used in a dilute solution in n-heptane (1 mole/liter). The titanium trichloride (Stauffer AA) was used as a suspension in n-heptane (40 g/liter). Before being used as a solvent, n-heptane was first distilled, then passed through a column filled with molecular sieves, and distilled again under nitrogen in the presence of aluminum trihexyl.

The copolymerization runs were carried out at 60°C in heptane solution for 1 hr. The catalysts were used with a molar ratio of $TiCl_3/AlEt_2Cl = 1/3$ in order to be in a range where catalytic activity of the system $AlEt_2Cl$-$TiCl_3$ has been found to vary very little as a function of the ratio Al/Ti [4], the molar ratio $TiCl_3$/total monomer being fixed at 2.5×10^{-3} for each copolymerization run. The usual monomer molar concentration was 20%.

The variation in the composition of the reaction mixture was followed by a comparison of the monomer concentrations with the concentration of an internal standard (usually the solvent n-heptane) according to a method developed in this laboratory based on a gas-liquid chromatography (GLC) analysis of samples of the mixture [5, 6].

The high-pressure glass reactor (600 ml) was carefully washed and dried by heating at 120°C for 24 hr and repeated pumpings. The solvent and monomers were first introduced through high-pressure glass tubes, and when the equilibrium temperature was reached the solution of aluminum monochlorodiethyl was added with a hypodermic syringe. The first sample of the reaction mixture was picked to corresponding to the 0 point for GLC analysis. Finally, the suspension of titanium trichloride was introduced into the reactor which was magnetically stirred for the duration of the copolymerization (1 hr).

At regular time intervals (5 min), samples of the mixture were picked up from the liquid phase and stored at low temperature (0°C) to stop the reaction before they were analyzed as soon as possible by GLC. The chromatograph (Intersmat IGC 12 C) was equipped with a thermal conductibility detector and an electronic digital integrator

(LTT 4422) in order to obtain the required high accuracy. The column was packed with polyphenylsiloxane polymers [7] and heated to 150°C. The use of H_2 as the carrier gas permitted an analysis quick enough to obtain the conversion curves as the copolymerization proceeds. At the end of the reaction an antioxidizer (2,6-ditertiobutylparacresol) was added, and the copolymer was precipitated with methanol and dried under vacuum.

RESULTS AND DISCUSSION

Kinetic Study

All copolymerization runs have the same features. An example is given in Fig. 1 corresponding to an initial monomer feed of 0.416 mole hexene-0.143 mole propene. Each kinetic curve presents three ranges of different polymerizing activity. Nevertheless, in each part the ratio of the average rate of conversion is practically constant (Table 1). Thus, to obtain the maximum accuracy, the copolymer compositions (n) have been determined from the tangent at the inflection point. The charges of the reactors and the compositions of the copolymers are given in Table 2.

The reactivity ratios, as for radical copolymerization, have been

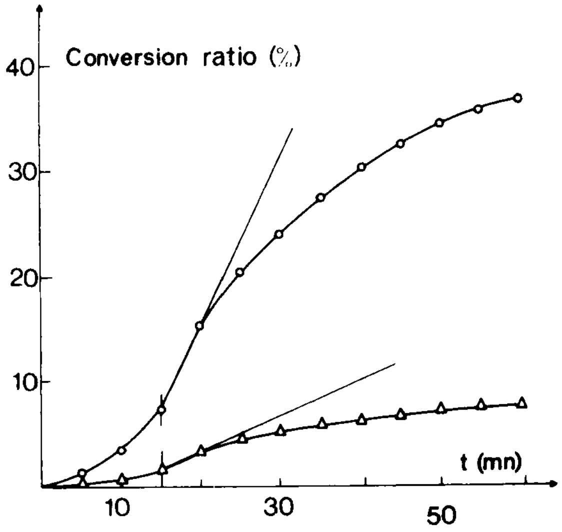

FIG. 1. Kinetic curves of 1-hexene—propylene copolymerization.

TABLE 1. Average Conversion Rate of Monomers in the Three Activity Areas of a Catalytic System

Average conversion rate (%/min)	Time (min)		
	$t_2 = 10, t_1 = 0$	$t_2 = 25, t_1 = 10$	$t_2 = 60, t_1 = 25$
1-Hexene	0.07	0.26	0.10
Propylene	0.35	1.13	0.47

TABLE 2. Initial Molar Concentration and Kinetic Results of 1-Hexene–Propylene Copolymerization

1-Hexene (mole)	Propylene (mole)	$x_H = \frac{H}{P}$	$n_H = \frac{dH}{dP}$
0.68	0.0475	14.3	2.50
0.57	0.0475	12.0	2.00
0.667	0.0667	10.0	1.88
0.69	0.095	7.25	1.20
0.357	0.0715	5.00	0.80
0.524	0.119	4.40	0.70
0.416	0.143	2.92	0.59
0.357	0.136	2.63	0.50
0.321	0.143	2.24	0.47
0.334	0.214	1.56	0.35
0.190	0.143	1.33	0.30
0.119	0.214	0.55	0.125
0.070	0.168	0.42	0.099

determined by both the linearization method (Fineman-Ross plot [8]) and the intersection method (Lewis and Mayo plot [9]). Figure 2 shows that whatever the monomer feed may be, all the experimental points are situated on a theoretical straight line from which is obtained r_H = 0.15 and r_P = 4.15 In Fig. 3 the curves intersect in a quite limited area, and the determination of the point closest to every line by the

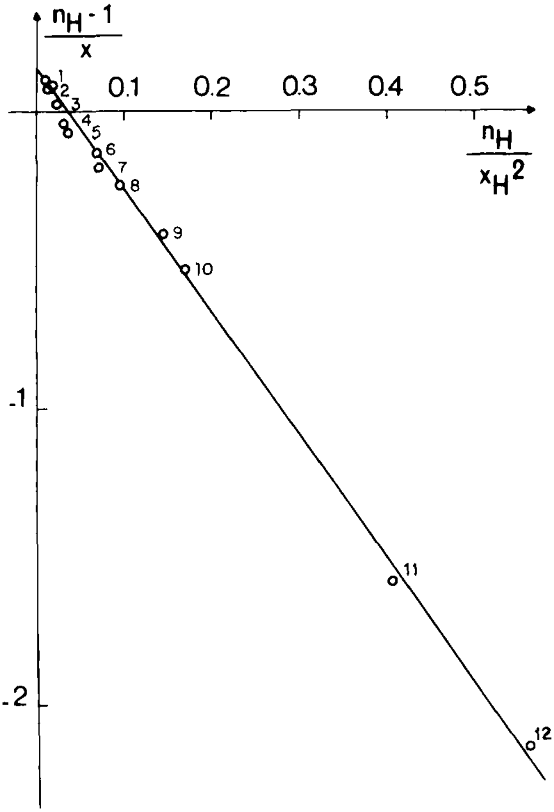

FIG. 2. 1-Hexene—propylene copolymerization: Fineman-Ross plot. x_H = 14.3 (1), 12.0 (2), 7.25 (3), 5.00 (4), 4.40 (5), 2.92(6), 2.63 (7), 2.24 (8), 1.56 (9), 1.33 (10), 0.55 (11), and 0.42 (12).

Joshi and Joshi [10] method gives $r_H = 0.16$ and $r_P = 4.18$. The agreement is quite good, and for further calculations these latter values were used.

The sampling in the first period (from 0 up to 10 min) shows a transformation of the catalyst $TiCl_3$. From an initial pulverulent violet state, it turns after 10 min to a fleecy reddish precipitate. This is accompanied by an important modification of the whole reaction mixture which, starting from slightly colored and translucent, becomes deep colored (purple) and then totally opaque after 10 min. This first period might correspond to the formation of active sites by the reaction of the

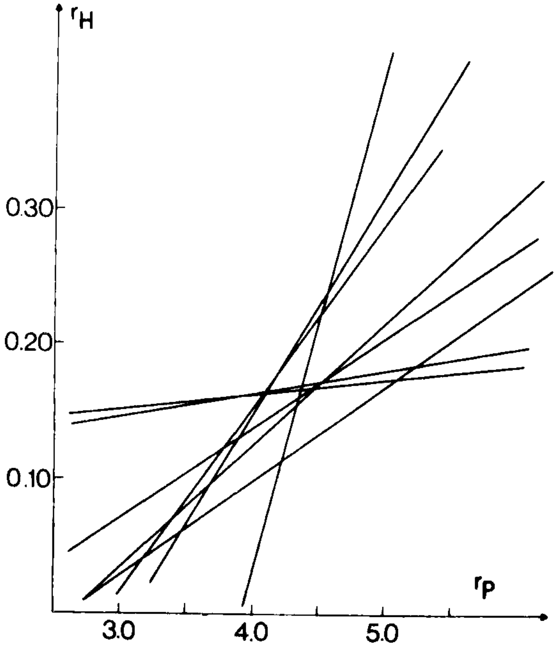

FIG. 3. 1-Hexene—propylene copolymerization: Lewis and Mayo plot.

components of the catalyst which is, from microscopic studies [11], an aggregate of elemental particles. Jones and Thorne [12] suggested that at the beginning of the process, the polymer formed causes the solid catalyst to deagglomerate and give accessibility to new sites. This phenomenon, also observed by Bulls and Higgins [13], offers an explanation for the kinetic data of the first two periods: the formation of the first active sites triggers the polymerization which induces the bursting of the aggregates and brings about the progressive increase of the active sites and consequently of the conversion rate. The evolution of the reaction mixture aspect corroborates this hypothesis. The decrease of the rate is generally attributed either to the formation of aluminum dichloroethyl [13] or to the destruction of active sites by isomerization in the presence of monomers [11] or again at the soiling of the catalyst by polymer. It seems, according to our results, that the catalyst modifications have the same influence on both monomers since the ratio of the conversion rates remains constant.

To our knowledge, no work concerning the kinetic study of 1-hexene—propene copolymerization has been reported in the literature. However, we have compared our results with those obtained by other authors for the copolymerization of some α-olefines (propylene—1-butene, ethylene-propylene, and ethylene—1-butene) (Table 3).

The reactivity ratios for ethylene-propylene and ethylene—1-butene copolymerization have been determined by Mazzanti and co-workers [1] in the presence of VCl_4-$Al(C_6H_{13})_3$ and VCl_3-$Al(C_6H_{13})_3$ catalysts. The reported values are, respectively, $r_e = 7.08$ - $r_p = 0.088$, $r_e = 29.60$ - $r_b = 0.019$, and $r_e = 5.61$ - $r_p = 0.145$, $r_e = 26.96$ - $r_b = 0.043$. Thus it seems with ethylene copolymerizations that comonomer reactivity is influenced by the steric hindrance. Likewise, if we compare the reactivity ratios obtained at the time of our study with those contained in Table 3, we observe the same phenomenon: with propylene the comonomer reactivity decreases as the steric hindrance becomes more important.

Copolymers Composition

Because the initial concentration of copolymer (% 1-hexene) is different from that of the initial mixture, a drift in copolymer composition occurs during copolymerization (Fig. 4).

For this reason and in order to confirm our kinetic results, we have determined the copolymer average compositions by a NMR (high resolution) study utilizing a Varian DA 60 IL apparatus (Fig. 5).

Copolymers were dissolved in the proportion of 2 or 3% in 1,2-dichlorobenzene. At 60 MHz frequency and 140°C the methyl protons spectrum is suitably separated from that of methylene and methine protons which practically overlap each other. The area of methylene methine and methyl spectra are named, respectively, A and B. A is proportional to 9 hexene protons and 3 propylene protons; B to 3 hexene protons and 3 propylene protons.

The hexene and propylene fractions in the copolymer can then be expressed by the formulas

$$H = \frac{A - B}{2\,B} \qquad P = \frac{3\,B - A}{2\,B}$$

The NMR results are in good agreement with those obtained in the kinetic study (Table 4). The drift in copolymer composition is very small (the average copolymer composition is just a little higher than the initial one). However, the importance of this phenomenon is strongly dependent on the conversion and also on the duration of copolymerization. For our experiments the average conversion at the end of copolymerization is rather slight (15 to 20%), and so the drift in copolymer composition is of little importance.

TABLE 3. Reactivity Ratio of 1-Butene—Propylene Copolymerization

Authors	Catalytic system			
	$TiCl_4$-$Al(C_2H_5)_3$	$TiCl_3$-$Al(C_2H_5)_3$	VCl_4-$Al(C_6H_{13})_3$	VCl_3-$Al(C_6H_{13})_3$
Laputte and Guyot [3]	$r_p = 2.4 \pm 0.4$ $r_b = 0.5 \pm 0.2$			
Hayashi and Ohno [2]		$r_p = 1.62$ $r_b = 0.50$		
Mazzanti and co-workers [1]			$r_p = 4.39$ $r_b = 0.227$	$r_p = 4.04$ $r_b = 0.252$

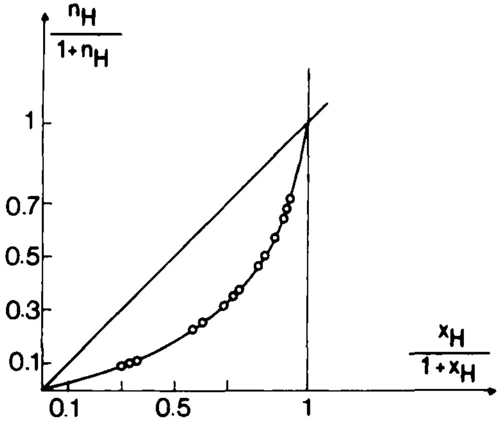

FIG. 4. Initial concentration of copolymer (% 1-hexene) vs concentration of initial mixture (% 1-hexene).

Theoretical Sequence Distribution

A complete description of the macromolecule is clearly impossible. Nevertheless, by resorting to statistical methods it is possible to evaluate the probability of finding any given sequences or linkages. The macromolecule is better described on the basis of the run number of Harwood and the Ito-type functions [14, 15]. Because some of these are very complex, we have used an IBM 1130 electronic computer for their calculation. The probability method is based on the hypothesis that the copolymerization reaction propagates very rapidly and that it always exists as a chain of given length (steady state). It should be noted that the calculation always involves the existence probability or unconditional probability which is directly related to the conditional probability. The latter is determined by the degrees of reactivity and the monomer ratio $x = M_1/M_2$ in the reaction medium. Although the reactivity ratios remain constant, x changes during the copolymerization. Consequently, there are two cases to be considered: a low degree of conversion, in which the x variation is negligible, and a high degree of conversion. It is necessary to take into account the evolution of the monomer concentration in the reaction medium.

We have therefore adopted a two-step approach. First, the calculations are performed, neglecting the variation of monomer concentration (initial microstructure of copolymers). Second, we calculate the influence of this parameter on the sequence distribution.

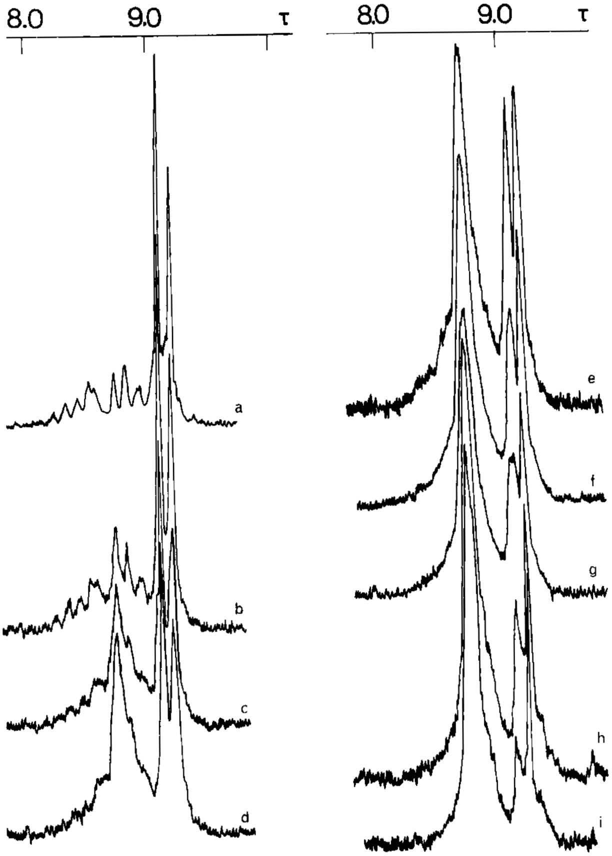

FIG. 5. NMR spectra of polypropylene, polyhexene, and some copolymers: (a) polypropene, (b) 8% hexene, (c) 22% hexene, (d) 29% hexene, (e) 40% hexene, (f) 54% hexene, (g) 63% hexene, (h) 83% hexene, and (i) poly-1-hexene.

Initial Distribution of Monomer Units

Run number (Harwood) (Fig. 6)

This is the alternation number for 100 monomer units:

$$R = 200(M_1M_2) = 200\,\frac{p_{m_1m_2}\,p_{m_2m_1}}{p_{m_1m_2} + p_{m_2m_1}}$$

TABLE 4. Initial Concentration (GLC) and Average Concentration (NMR) (% 1-Hexene)

x_H	14.3	12.0	10.0	7.25	5.00	4.40	2.92	2.63	2.24	1.56	1.33	0.42
Initial concentration (% 1-hexene)	71	68	64	57	50	46	37	35	32	25	22.5	9
Average concentration (% 1-hexene)	83	80	73	63	54	53	40	35	30	29	22	8

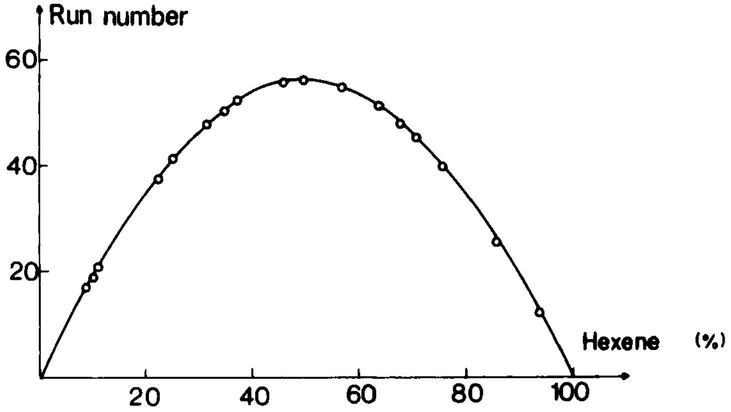

FIG. 6. Run number evolution vs copolymer concentration (% 1-hexene).

where (M_1M_2) is the unconditional probability and $p_{m_1m_2}$ is the conditional probability.

Number-Average Length of 1-Hexene Sequences ($\overline{\mathrm{In\ H}}$)

$$\overline{\mathrm{In\ H}} = \frac{\sum_{1}^{\infty} nN_{H(n)}}{\sum_{1}^{\infty} N_{H(n)}}$$

where $N_{H(n)}$ is the number fraction of 1-hexene units in sequences of n unit length (Fig. 7).

Weight Fractions of 1-Hexene Sequences of n Unit Length ($W_{H(n)}$)

$$W_{H(n)} = \frac{nN_{H(n)}}{\sum_{1}^{\infty} nN_{H(n)}}$$

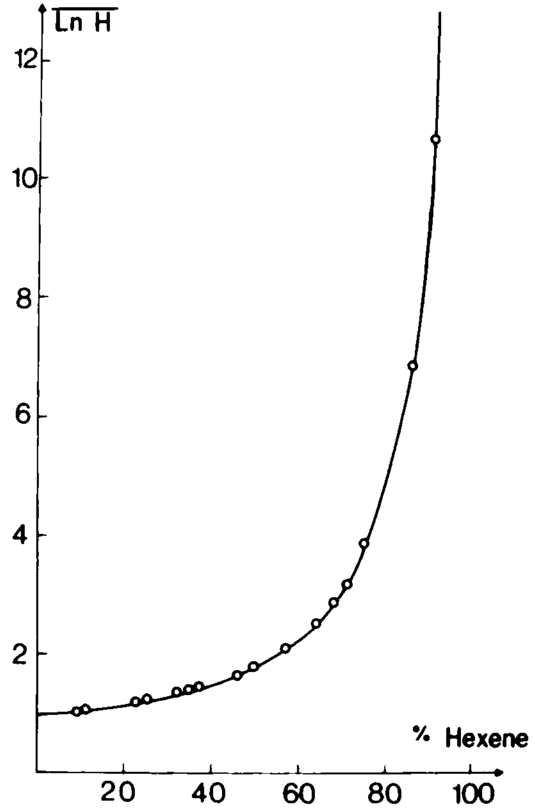

FIG. 7. Evolution of number-average length of 1-hexene sequences vs copolymer concentration (% 1-hexene).

The weight fractions of 1-hexene sequences $W_{H(n)}$ of n = 1, 2, 3, 4, 5, and >10 length were calculated (Fig. 8).

Composition Drift. Influence of the Conversion

From the composition diagram (Fig. 4) it appears that the drift is maximum when copolymerization is carried out from a mixture containing 75% of 1-hexene [$(x_H)_0 = 3$] and with a copolymer initially containing 40% of the same monomer.

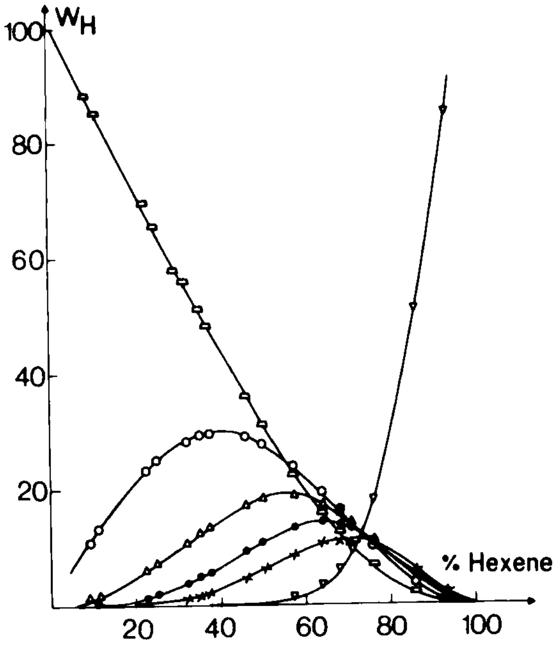

FIG. 8. Evolution of weight fractions of 1-hexene sequences of n units length vs copolymer concentration (% 1-hexene). W_H = 1(□), 2(○), 3(△), 4(●), 5(×), and >10(▽).

In order to check on this phenomenon, we have determined the x_H variations vs average conversion rate, as well as the corresponding changes in copolymer composition, from the kinetic curves (Fig. 9).

For an average conversion rate of 10%, the most important drift occurs for an initial concentration of 1-hexene in copolymers around 40%. These results are in good agreement with composition diagram results (Table 5 and Fig. 10).

Regarding the sequences distribution, the number-average length 1-hexene sequence grows faster the richer in hexene the reaction mixture becomes (Fig. 11).

The weight fractions of 1-hexene sequences of n unit length change substantially, particularly at extreme compositions (Fig. 12).

At higher degrees of conversion, the rate the drift in copolymer composition becomes much larger and the resulting copolymer will be very different from the initial product. It is often interesting to

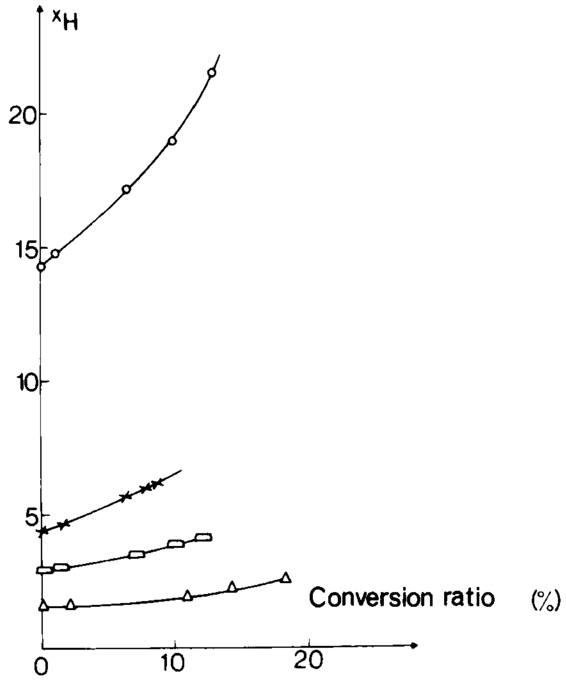

FIG. 9. Evolution of reaction mixture vs average conversion rate.

TABLE 5. Drift in Copolymer Composition at a Conversion Rate of 10%

$(x_H)_0$	$[H]_0 = \frac{(n_H)_0}{(n_H)_0 + 1} \times 100$	Drift in copolymer composition, $\frac{[H] - [H]_0}{[H]_0} \times 100$
14.3	71	4
4.40	46	10
2.90	37	9
1.56	25	5.5

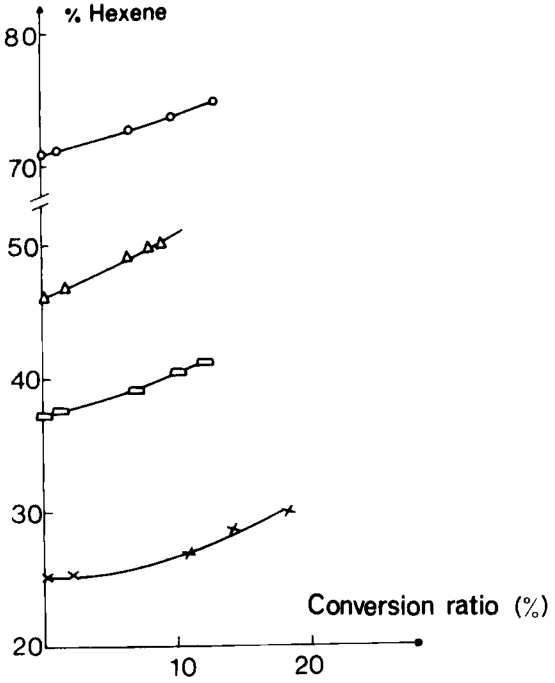

FIG. 10. Evolution of copolymer concentration vs average conversion rate. $(X_H)_0$ = 14.3 (○), 4.40 (△), 2.90 (□), and 1.56 (×).

have the copolymerization reaction proceed further until a higher conversion rate is obtained. In order to obtain a copolymer of good definite composition in this case, it will be necessary to keep the monomer ratio in the reaction mixture constant. Such an objective was achieved by the copolymerization under constant propylene pressure.

Copolymers at Constant Monomer Feed Composition

Apparatus

The copolymerization runs carried out in the high-pressure glass reactor described previously involved fixing a photocell on a manometer connected to the reactor [16]. Depending on the pressure and by means of an electrovalve, the device permits propylene to be

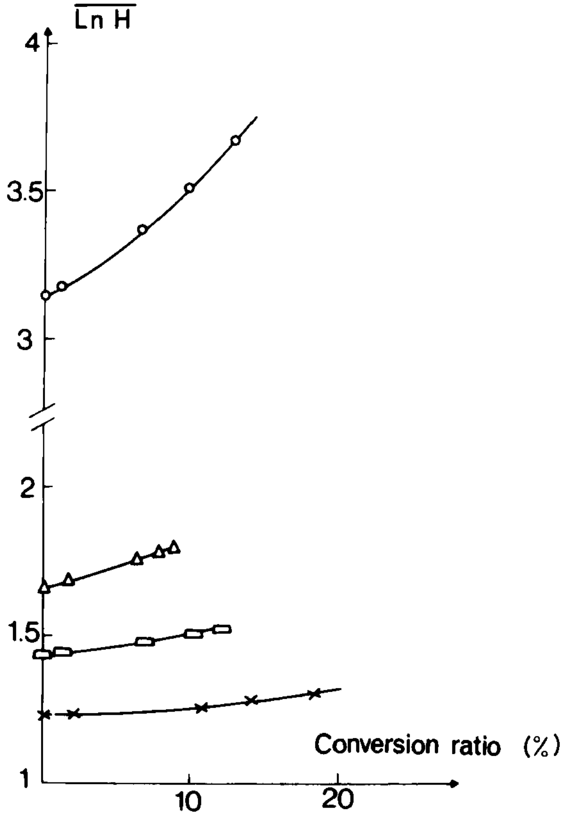

FIG. 11. Variation of number-average length of 1-hexene sequencies vs average conversion rate. $(X_H)_0$ = 14.3 (○), 4.40 (△), 2.90 (□), and 1.56 (×).

put into the reactor during the copolymerization reaction and thus maintain a nearly constant propylene concentration in the reaction mixture.

Such a device, given the slow conversion rate of 1-hexene, permits the maintenance of a relatively constant monomer ratio in the reaction mixture, provided that a too high degree of conversion is not reached.

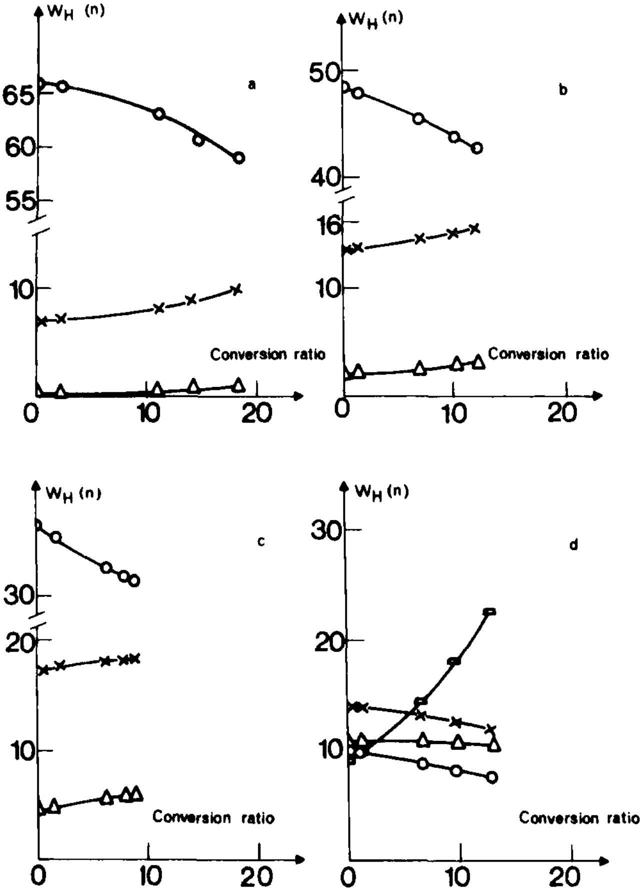

FIG. 12. Evolution of weight fractions of 1-hexene sequencies of n units length vs average conversion rate. $(X_H)_0 = 1.56$ (a), 2.90 (b), 4.40 (c), and 14.30 (d), where n = 1 (○), n = 2 (×), n = 5 (△), and n > 10 (□).

Results

The variation of reaction mixture composition was followed by gas chromatography. The evolution of the x_H ratio is much slower than in the usual copolymerization (Fig. 13). Samples of copolymer were taken during the reaction and their composition determined by NMR

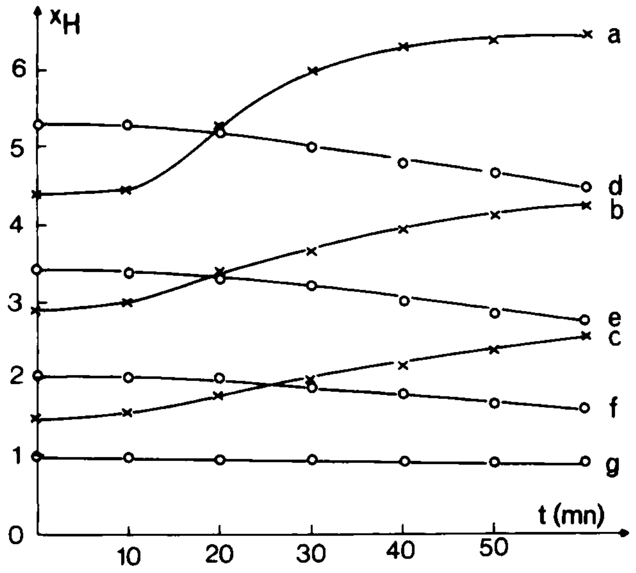

FIG. 13. Evolution of reaction mixture (X_H) as a function of the reaction duration: (×) regular copolymerization, and (o) copolymerization at constant monomer feed composition, where $(X_H)_0$ is 4.40 (a), 2.90 (b), 1.56 (c), 5.3 (d), 3.40 (e), 2.05 (f), and 1 (g).

(high resolution). Given the accuracy of these measurements (of the order of ±5%), there is no significant difference in copolymer composition whether they are obtained after 20 or 60 min (Table 6).

CONCLUSION

The copolymerization of 1-hexene and propylene has been realized in the presence of a Ziegler-Natta type catalyst ($AlEt_2Cl$, $TiCl_3$).

For operative conditions (solvent, n-heptane; temperature, 60°C, $AlEt_2Cl/TiCl_3$ molar ratio = 3) the reactivity ratios are 0.16 and 4.18 for 1-hexene and propylene, respectively. The copolymerization proceeds with a drift in composition, the importance of which changes with the reaction mixture composition. The calculation of theoretical

TABLE 6. Initial Concentration and Average Concentration (% 1-Hexene) of Some Copolymers

Initial concentration (% 1-hexene, GLC)	Average concentration (% 1-hexene, NMR)	
	After 20 min	After 60 min
18	16	16
30	26.5	28
40.5	40	38
50	54	52

sequence distribution has been made on the basis of an a priori description of the macromolecules. The influence of the drift in copolymer composition on the distribution of monomer units has been evaluated. Some copolymers have been prepared under constant propylene pressure.

Owing to the low drift copolymer composition, this technique leads to copolymers of rather constant monomer feed composition as long as the conversion ratio does not exceed 15 to 20%.

REFERENCES

[1] G. Mazzanti, A. Valvassori, G. Sartori, and G. Pajaro, Chim. Ind. (Milan), 42, 468 (1960).
[2] I. Hayashi and K. Ohno, Kobunshi Kagaku, 22, 243 (1965).
[3] R. Laputte and A. Guyot, Makromol. Chem., 129, 234 (1969).
[4] H. Schnecko, W. Lintz, and W. Kern, J. Polym. Sci., A-1, 5, 205 (1967).
[5] A. Guyot and J. Guillot, J. Chim. Phys., 61, 1434 (1964).
[6] J. Guillot, Ann. Chim., 3(5), 441 (1968).
[7] J. Guillot, C. Janin, and A. Guyot, J. Chromatogr. Sci., 11, 375 (1973).
[8] M. Fineman and J. D. Ross, J. Polym. Sci., 5, 259 (1950).
[9] F. R. Mayo and F. M. Lewis, J. Amer. Chem. Soc., 66, 1594 (1944).
[10] R. M. Joshi and S. G. Joshi, J. Macromol. Sci.—Chem., A5(8), 1329 (1971).
[11] E. Kohn, H. J. L. Schurmans, J. V. Calender, and R. A. Mendelson, J. Polym. Sci., 58, 681 (1962).
[12] H. H. Jones and M. P. Thorne, Can. J. Chem., 40, 1510 (1962).

[13] V. W. Bulls and T. L. Higgins, J. Polym. Sci., Polym. Chem. Ed., 11, 925 (1973).
[14] H. J. Harwood, Amer. Chem. Soc., Div. Polym. Chem. Preprint, 8(1), 199 (1967).
[15] K. Ito and Y. Yamashita, J. Polym. Sci., A, 3, 2165 (1965).
[16] C. Pichot, Thèse, Lyon, 1971.

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