European Polymer Journal, 1969, Vol. 5, pp. 575–585. Pergamon Press. Printed in England.

A STUDY OF INVERSIONS IN ETHYLENE–PROPYLENE COPOLYMERS

C. TOSI, A. VALVASSORI and F. CIAMPELLI

Centro Ricerche di Milano, Montecatini Edison S.p.A.
Via G. Colombo 81, 20133 Milano, Italy

(*Received* 8 *August* 1968)

Abstract—To account for the dependence of the amount of $(CH_2)_2$ groups contained in ethylene–propylene copolymers upon the composition and the product of reactivity ratios, we derived an equation containing two empirical parameters deduced from the i.r. spectrum of several copolymers, prepared by some vanadium based catalysts, and of the corresponding homopolymers of propylene. Our treatment shows that, with these catalysts, there is a probability of about 80 per cent for the entrance of an ethylene unit and of about 20 per cent of a normal propylene unit after an inverted propylene unit; it shows that two thirds of the propylene units in E–P diads add normally (i.e. at the methylene group).

INTRODUCTION

THE i.r. spectrum of most ethylene–propylene (E–P) copolymers, obtained by Ziegler–Natta catalysts through an anionic co-ordinated mechanism, shows a band at 752 cm^{-1}, characteristic of the rocking vibration of a sequence of two methylenes bound on both sides to tertiary carbon atoms.[1]

If all P units present in these copolymers had the normal head-to-tail arrangement, methylenic sequences should only contain an odd number of members. Thus the presence of the 752 cm^{-1} band proves the existence of "inversions" in the enchainment of P units, which can give rise to $(CH_2)_2$ groups formed either by tail-to-tail connection of two P units or by insertion of one E unit between two P units connected to it by the tertiary carbon atom.

On varying the copolymer composition, these two types of inversions behave in a different way, because the former is proportional to the amount of P sequences and the latter to that of isolated E units.

For molar concentrations of P higher than *ca.* 35 per cent, the amount of $(CH_2)_2$ groups, evaluated by the method of Bucci and Simonazzi,[2] is larger than in P homopolymer obtained by means of the same catalyst; the sequence distribution laws show that the number of long P sequences is not sufficient to account for such high values for $(CH_2)_2$ groups: this fact can be explained by assuming that the presence of E units favours, to some extent, the formation of inversions in the P units.[3]

No detailed study of this phenomenon has been made up to now, except for work by Lyubetzky *et al.*[4] who took into account the propagation steps connected with the formation and reaction of the "anomalous" growing chains: such an approach is equivalent to regarding the reaction as a terpolymerization of E and P entering the chain either head-first or tail-first.[5]

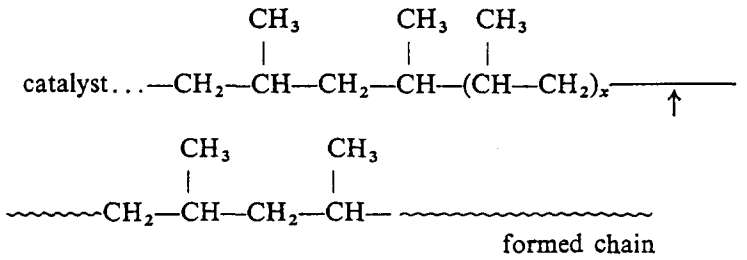
In this paper we show that a satisfactory description of the extent of inversions is obtained by means of an empirical equation containing three quantities, which can be deduced from the i.r. spectra of a series of E–P copolymers prepared by a

given catalyst and of the corresponding homopolymer P. These quantities are the composition of each copolymer, the amount of $(CH_2)_2$ groups contained therein and the product of reactivity ratios corresponding to that catalyst.

Our procedure is best understood on the basis of the following considerations.

THEORETICAL CONSIDERATIONS

Let us first consider homopolymer P, prepared by the catalysts giving rise to inversions in copolymers, and represent the growing chains with the methylene group of P units directed toward the catalyst:



At a given point, indicated by the arrow, an inverted unit enters the chain, originating the $(CH_2)_2$ group revealed by the i.r. spectrum. This unit can be followed either by a normal P unit or by another inverted unit. The "straightening" represented by the entrance of a normal unit is jeopardized by the steric hindrance of the adjacent methyl groups; nonetheless, after a number x ($\geqslant 1$) of consecutive inverted units, the "straightening" must necessarily take place, since the number of $(CH_2)_2$ groups should be otherwise of the same order as that of chain terminals and the molecular weight of this polymer could not be higher than a few hundreds: measurements of both viscosity and unsaturation content prove that this is not the case.

On the other hand, as there are no physical means capable of differentiating the inverted units after the first from the normal units, we may suppose $x = 1$, i.e. assume that, in polypropylene, any inversion is immediately followed by a straightening. As will be clearly shown subsequently, such an assumption does not affect the results of our calculations although it gives a description of the arrangement of P units which probably differs from the actual one.

The situation is quite different in copolymers: a straightening like that of the homopolymer is still possible; but, owing to the presence of E in the feed mixture, it is reasonable to suppose that more probably an inverted P unit is followed by an E unit.

If so, one should expect that the distribution of sequence length of the monomers is different from that existing when all P units are normally arranged, as if the catalyst acted with a different product of reactivity ratios. When no inversions are present, we evaluate this quantity by measuring, on the i.r. spectrum of E–P copolymers, the so-called "distribution index" ϕ of P units.[6] The same procedure may be also followed when inversions are present; in this way we obtain a value of $r_1 r_2$ defining a sequence distribution which can be thought of as representative, to a first approximation, of the actual distribution in the copolymer. From this distribution, we calculate the amount of the groupings, such as triads P–E–P and diads P–P, which in the case

of inversion may give rise to $(CH_2)_2$ groups and assign them two "probability factors" P_E and P_P, characteristic of the catalytic system and independent of composition, and accounting for the possibility of entrance of an E or a normal P unit after an inverted P unit.

It is then possible to represent the amount G of $(CH_2)_2$ groups as a function of four quantities (the composition—expressed as the molar ratio (f) of P to E–, the product of reactivity ratios and the aforesaid parameters P_P and P_E) and to find these latter by introducing into the equation the values of f, r_1r_2 and G deduced from the i.r. spectra.

It should be pointed out that our procedure, which essentially consists in regarding the inversions as a "perturbation" to the normal copolymerization process, is an approximate one; but we believe that a rigorous treatment, probably implying a larger number of variables and more complicated mathematical calculations, would hardly give a better description of the experimental results.

CALCULATION OF THE AMOUNT OF $(CH_2)_2$ GROUPS

Let us consider an E–P copolymer containing a certain amount of $(CH_2)_2$ groups, and indicate by ‾ the E units, by ⌋ the normal P units and by ⌊ the inverted ones.

We may distinguish four different types of inversions:

(1) Internal inversion in a P sequence of three or more units:*

..... ‾ ⌋ ⌋ ⌋ ⌊ ⌋ ⌋ ‾ .....

(2) Terminal† inversion in a P sequence of two or more units:

..... ‾ ⌊ ⌋ ⌋ ⌋ ‾ .....

(3) Initial† inversion in a P sequence of two or more units:

..... ‾ ⌋ ⌋ ⌊ ‾ .....

(4) Inversion in a P sequence containing one unit only:

..... ‾ ⌊ ‾ .....

These four situations may be characterized by four "probability factors" P_1, P_2, P_3 and P_4, defined as the ratio between the number of inverted units of each type and the total number of units of the same type. With respect to the formation of the 752 cm^{-1} band,

Type (1) gives rise to one $(CH_2)_2$ group for each inverted unit;

Type (2) gives rise, in all cases, to one $(CH_2)_2$ group; a further $(CH_2)_2$ group arises when the P sequence is followed by an isolated E unit and then by a normal P unit;

Type (3) never gives rise to any $(CH_2)_2$ group;

* This means that the inverted unit can occupy any place in the chain except the first and the last.

† It should be noted that, in our notation, chains grow from right to left.

Type (4) gives rise to one $(CH_2)_2$ group only when the inverted P unit is followed by an isolated E unit and then by a normal P unit.*

According to this classification, the number g of $(CH_2)_2$ groups (per monomeric unit) present in a copolymer may be expressed as

$$g = P_1\,\alpha + P_2\,\beta\,(1 + \gamma) + P_4\,\delta\gamma, \tag{1}$$

where α is the fraction of P units internal to sequences of three or more units; β is the fraction of P sequences containing two or more units; γ is the fraction of E sequences containing one unit only and followed by a normal P unit; and δ is the fraction of P sequences containing one unit only.

By applying, to a first approximation, the distribution formulae relevant to the product of reactivity ratios experimentally found, Eqn. (1) takes the form:†

$$\begin{aligned} g = {} & P_1 \left[\frac{(K^3 + 6K^2)m_1}{(K+2)^3} - \frac{4K^2 m_1}{(K+2)^3}\right] \\ & + P_2 \frac{2Km_1}{(K+2)^2}\left[1 + \frac{K}{K + 2r_1 r_2}\,\frac{K(1-P_3) + 2(1-P_4)}{K+2}\right] \\ & + P_4 \frac{4m_1}{(K+2)^2}\,\frac{K}{K+2r_1 r_2}\,\frac{K(1-P_3) + 2(1-P_4)}{K+2} \end{aligned} \tag{2}$$

where m_1 is the molar fraction of P in the copolymer and $K = f - 1 \div \sqrt{[(f-1)^2 + 4r_1 r_2 f]}$, with $f = m_1/1 - m_1$.

Equation (2) may be simplified from the following considerations. In the homopolymerization of P, the entrance of an inverted unit may be thought of as an "easy" step, there being no steric hindrances against it; the subsequent straightening can be regarded as a "difficult" step, because of the steric hindrance of adjacent methyls; thus the number of $(CH_2)_2$ groups in P homopolymer is determined by the probability P_P of occurrence of the difficult step. It may be assumed that, in copolymers also, this step has the same probability as in polypropylene: therefore, in a copolymer, the probability of entrance of a normal P unit after an inverted P unit is given by $P_P = P_1 = P_3$.

On the other hand, a much easier step and an alternative to the straightening is the entrance of an E unit after an inverted P unit, defined by P_2 and P_4; also these factors may be then thought of as equal:

$$P_2 = P_4 = P_E.$$

Therefore, Eqn. (2) becomes:

$$\frac{g}{m_1} = \frac{K}{(K+2)^2}\left\{K P_P + 2P_E\left[1 + \frac{K(1-P_P) + 2(1-P_E)}{K + 2r_1 r_2}\right]\right\}. \tag{3}$$

* The direction of growth of P chains assumed here is in agreement with the usual hypotheses on the mechanism of coordinated anionic polymerization. However, it may be easily shown that our procedure need not be modified, should the chains grow in the opposite direction (i.e. with the tertiary carbon atom of P units pointing to the catalyst). It must be observed that in this model the hindered step of polymerization is the *entrance of the inverted unit*, whereas in the model assumed in the text the hindered step is *the straightening*, i.e. the step immediately following the entrance of the inverted unit.

† A full account of the calculations leading to Eqn. (2) is given in the Appendix.

In Eqn. (3), g/m_1 represents the ratio between the number of $(CH_2)_2$ groups and the number of P units. In order to transform this ratio into the weight fraction G of $(CH_2)_2$ groups in the copolymer, we multiply by

$$\frac{28}{42} \times \frac{3m_1}{2 + m_1} = \frac{2f}{3f + 2}.$$

Thus we obtain:

$$G = \frac{2fK}{(3f + 2)(K + 2)^2} \left\{ KP_P + 2P_E \left[1 + \frac{K(1 - P_P) + 2(1 - P_E)}{K + 2r_1 r_2} \right] \right\}. \quad (4)$$

In this way we have a quantity, G, which can be experimentally deduced from the intensity of the 752 cm^{-1} band.

Equation (4) is plotted in Fig. 1 for two arbitrary values of P_P and P_E, in the simplest case of a random distribution of P and E sequences ($r_1 r_2 = 1$). The plot also shows

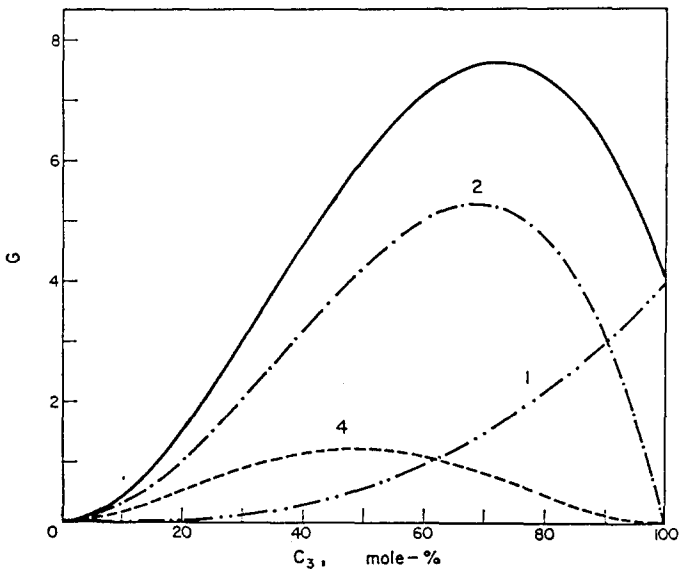


FIG. 1. Contribution to the total amount of $(CH_2)_2$ groups of the various types of inversions (designated by the same numbers as in the text).

The curves reported here refer to $r_1 r_2 = 1$ and to probability factors (arbitrarily chosen) $P_P = 0{\cdot}06$ and $P_E = 0{\cdot}30$.

the contribution of the various types of inversions to the total amount of $(CH_2)_2$ groups.

EXPERIMENTAL RESULTS

In order to check the validity of the treatment worked out in the previous section, we examined the i.r. spectra* of four sets of E–P copolymers.

* The i.r. spectra were recorded on a Perkin-Elmer 221 Spectrophotometer, with NaCl optics. The samples were examined as sheets, approximately 0·01 cm thick, pressed by die-casting.

The products of reactivity ratios found for these copolymers by the method of Fineman and Ross were:

(A)	VCl_4–$Al(C_2H_5)_3$	$r_1r_2 = 1{\cdot}00 \pm 0{\cdot}04$
(B)	$V(acac)_3$–$Al(C_2H_5)_2Cl$	$0{\cdot}35 \pm 0{\cdot}05$
(C)	$VOCl_3$–$Al(C_2H_5)_2Cl$	$0{\cdot}37 \pm 0{\cdot}05$
(D)	VCl_4–$Al(C_2H_5)_2Cl$	$0{\cdot}26 \pm 0{\cdot}01$

For each sample, we determined the amount of $(CH_2)_2$ groups by the aforesaid method of Bucci and Simonazzi[2] and plotted this value against the P mole content (Fig. 2). Afterwards, we introduced into Eqn. (4) the values of P_P calculated from the

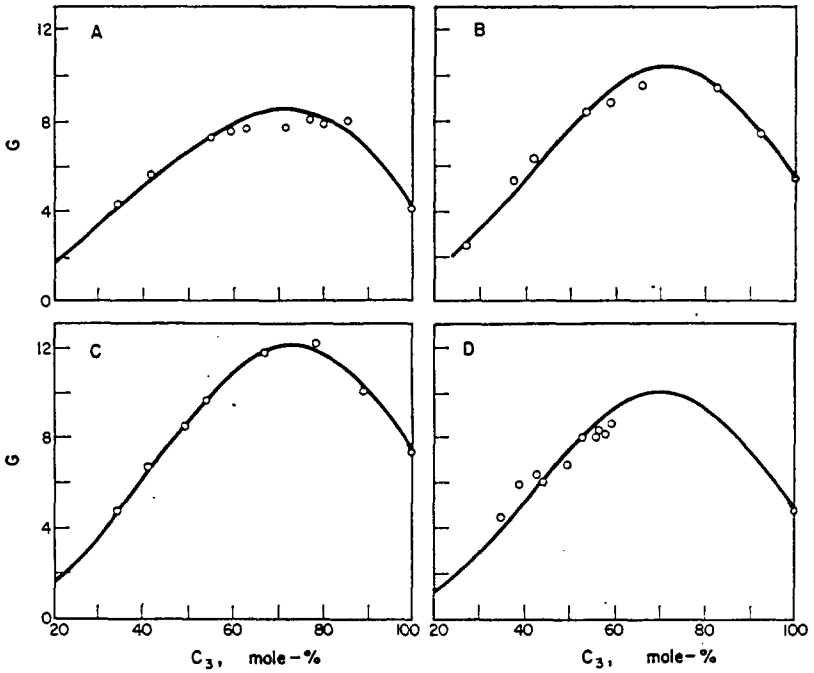


FIG. 2. Plot of Eqn. (4) for various sets of E–P copolymers prepared by different catalysts (see text). The circles represent the experimental points; the solid lines correspond to P_E values obtained from the data of Table 1.

amount of $(CH_2)_2$ groups found in homopolymers* and of r_1r_2 previously determined; in this way G depended on one parameter only, P_E, which was found as the arithmetic average among the values corresponding to experimental points (see Table 1): the four curves of Fig. 2 were thus obtained.

The probability factors for the various catalysts are reported in Table 2.

The examination of these values allows us to draw two important conclusions.

First, in our E–P copolymers, there is a probability of about 80 per cent for the entrance of an E unit, and of about 20 per cent for the entrance of a normal P unit,

* Equation (4) gives: $$P_P = \frac{2}{3} \lim_{f \to \infty} (G).$$

TABLE 1

A		B		C		D	
f	$G\%$	f	$G\%$	f	$G\%$	f	$G\%$
0·53	4·3	0·36	2·4	0·53	4·8	0·53	4·5
0·71	5·6	0·59	5·3	0·70	6·7	0·63	5·9
1·22	7·2	0·71	6·3	0·95	8·5	0·74	6·3
1·47	7·5	1·13	8·3	1·18	9·6	0·79	6·0
1·70	7·6	1·41	8·7	2·03	11·7	0·97	6·8
2·51	7·7	1·90	9·5	3·65	12·1	1·10	8·0
3·35	8·0	4·56	9·4	8·1	10·0	1·25	8·0
4·0	7·8	11·5	7·4	∞	7·3	1·27	8·2
5·9	7·9	∞	5·3			1·35	8·1
∞	3·9					1·44	8·6
						∞	4·7

TABLE 2

Catalyst	P_P	P_E	$\frac{P_P}{P_P + P_E}$	$\frac{P_E}{P_P + P_E}$
A	0·06	0·335±0·008	0·15	0·85
B	0·08	0·346±0·012	0·19	0·81
C	0·11	0·401±0·005	0·22	0·78
D	0·07	0·328±0·016	0·18	0·82

after an inverted P unit.* This fact confirms the assumption, put forward in the second section, that in copolymers the probability that an inversion is followed by an E unit is much higher than that of a straightening.

Second, P_E is approximately 1/3 in all cases; this means that *ca.* 1/3 of the P–E diads are of the type _ ⌊_ and *ca.* 2/3 of the type ¯ _⌋. Now, the ratio between the amounts of these diads is the quantity

$$a = \frac{K'_{12}}{K_{12}}$$

introduced by Lyubetzky *et al.*,[4] where K'_{12} and K_{12} are the propagation rate constants for the reactions

$$\ldots \text{E} + \text{P} \rightarrow \_ \lfloor\_ \text{ and}$$

$$\ldots \text{E} + \text{P} \rightarrow \_ \_\rfloor$$

respectively: the value they give ($a = 0{\cdot}5 \pm 0{\cdot}1$) from the intensity ratio of the i.r. bands characterizing the sequences $(CH_2)_2$ and $(CH_2)_3$ is just the same as the ratio (1/3)/(2/3) deduced with our procedure.

A further independent check of the validity of this procedure was provided by

* These probabilities may be expressed as $\frac{P_E}{P_P + P_E}$ and $\frac{P_P}{P_P + P_E}$, respectively.

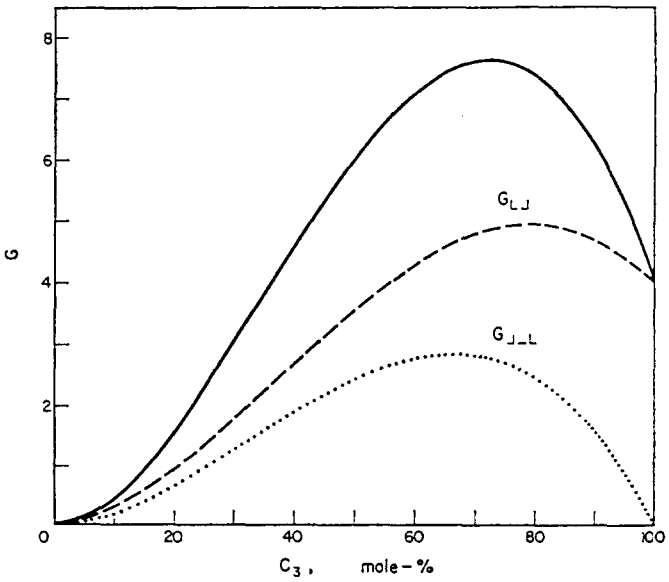


FIG. 3. Contribution, to the total amount of $(CH_2)_2$ groups, of $(CH_2)_2$ groups formed by two tail-to-tail P units ($G_{\lfloor\rfloor}$) and of $(CH_2)_2$ groups formed by one E unit lying between two head-to-head P units ($G_{\rfloor\_\lfloor}$). The three curves correspond to $r_1r_2 = 1$, $P_P = 0{\cdot}06$ and $P_E = 0{\cdot}30$.

the examination of a set of copolymers of P and fully deuterated E, where the $(CH_2)_2$ groups can be originated by P units only.

In fact, the contribution of $(CH_2)_2$ groups formed by P units (designated as $G_{\lfloor\rfloor}$) and by E units ($G_{\rfloor\_\lfloor}$) may be obtained by decomposing Eqn. (4) in the sum of two terms (see Fig. 3):

$$G = G_{\lfloor\rfloor} + G_{\rfloor\_\lfloor} =$$

$$= \frac{2fK}{(3f+2)(K+2)^2}(KP_P + P_E) + \frac{4fKP_E}{(3f+2)(K+2)^2} \cdot \frac{K(1-P_P) + 2(1-P_E)}{K + 2r_1 r_2}. \quad (5)$$

Assuming that the substitution of deuterium for hydrogen does not modify the monomer reactivities, the quantity $G_{\lfloor\rfloor}$ can be just obtained from the 752 cm^{-1} band in the above copolymers.

We have then examined two C_3H_6–C_2D_4 copolymers prepared by the catalyst D.* Also in this case the composition was determined radiochemically. The application of our method of determination of the product of reactivity ratios[6] to these copolymers† gave a value of r_1r_2 (0·25) equal, within experimental errors, to that found for C_3H_6–C_2H_4 copolymers prepared using the same catalyst. Thus we were

* The i.r. spectrum of a C_3H_6–C_2D_4 copolymer with P = 83·5 mole % is shown in Fig. 4.

† A band at about 975 cm^{-1} is observed in the spectrum of poly-C_2D_4. The absorptivity of this band, however, is low, so that it does not hinder, in copolymers with a molar content of P higher than about 40 per cent, the application of our method, based on the absorption ratio of the bands at 973 and 935 cm^{-1}.

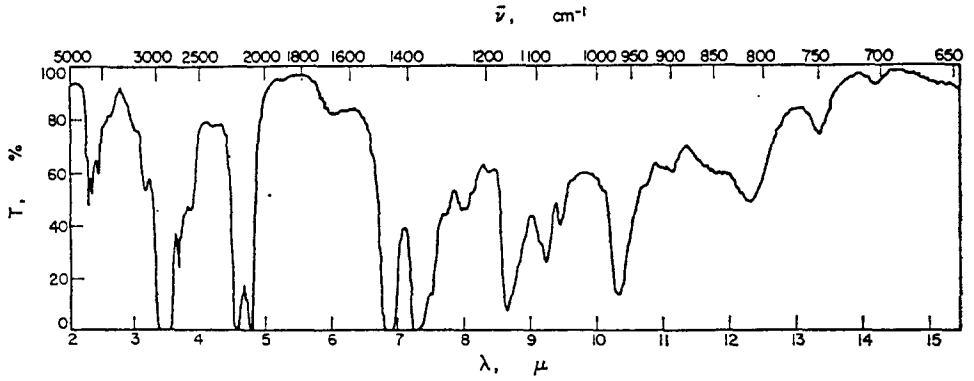


FIG. 4. Infra-red spectrum of a P-perdeuteroethylene copolymer (P = 83·5 mole%), recorded on a Perkin-Elmer 221 Spectrophotometer.

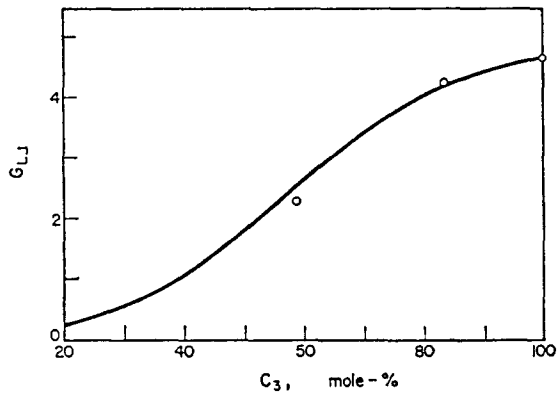


FIG. 5. Plot of $G_{[-]}$, according to Eqn. (5), vs. composition for two P–perdeutero E copolymers prepared by the catalytic system VCl_4–$Al(C_2H_5)_2Cl$.

able to apply Eqn. (5) and obtained the results plotted in Fig. 5. The fitting of the experimental points with the "theoretical" curve is very good.

CONCLUSIONS

The treatment proposed in the present work accounts very well for the amount of $(CH_2)_2$ groups found in all E–P copolymers studied by us, and throws more light upon a phenomenon that is not foreseen in the usual copolymerization theories.

We are right to believe that simplifications introduced in our procedure reflect with good fidelity the actual physical situation of these copolymers: therefore, the origin of $(CH_2)_2$ groups may be partly attributed to the entrance in the chain of an inverted P unit and to a greater extent to the fact that this unit is generally followed by an E unit.

Acknowledgements—The authors wish to thank Professor P. Corradini for many fruitful discussions and Professor A. Zambelli for the preparation of deuterated copolymers.

REFERENCES

(1) F. Ciampelli and C. Tosi, *Spectrochim. Acta* **24A**, 2157 (1968).
(2) G. Bucci and T. Simonazzi, *J. Polym. Sci.* C7, 203 (1964).
(3) F. Ciampelli and A. Valvassori, *J. Polym. Sci.* C16, 377 (1967).
(4) S. Lyubetzky, B. Erussalimsky and A. Goldenberg, International Symposium on Macromolecular Chemistry, Tokyo 1966, Preprint 1.1.10.
(5) J. Van Schooten and S. Mostert, *Polymer* **4**, 135 (1963).
(6) C. Tosi, A. Valvassori and F. Ciampelli, *Europ. Polym. J.* **4**, 107 (1968).
(7) C. Tosi, *Adv. Polym. Sci.* **5**, 451 (1968).

Résumé—Pour tenir compte de la dépendence de la quantité de groupes $(CH_2)_2$ présents dans les copolymères éthylène–propylène de la composition et du produit des rapports de réactivité, on a formé une équation contenant deux paramètres empiriques. Ceux-ci sont déduits des spectres infra-rouges de plusieurs copolymères, préparés au moyen de quelques catalyseurs au vanadium, et d'homopolymères du propylène correspondants. Notre traitement montre qu'au moyen de tels catalyseurs, la probabilité pour l'introduction après une unité propylénique inversée est d'environ 80 pour cent pour une unité éthylénique et d'environ 20 pour cent pour une unité propylénique normale. Il montre aussi que, dans les diades E–P, 2/3 des unités propyléniques s'additionnent normalement (c'est-à-dire sur le groupement méthylénique).

Sommario—Allo scopo di rendere conto della dipendenza della quantità di gruppi $(CH_2)_2$ contenuti nei copolimeri etilene–propilene dalla composizione e dal prodotto dei rapporti di reattività, abbiamo stabilito un'equazione contenente due parametri empirici dedotti dallo spettro infrarosso di svariati copolimeri preparati con alcuni catalizzatori a base di vanadio e dei corrispondenti omopolimeri del propilene. Il nostro procedimento mostra che con questi catalizzatori c'è una probabilità di circa 1'80% per l'ingresso di un'unità etilenica, e di circa il 20% per l'ingresso di un'unità propilenica normale, dopo un'unità propilenica invertita, e che i due terzi delle unità propileniche nelle diadi E–P si addizionano normalmente (cioè sul gruppo metilenico).

Zusammenfassung—Für die in Äthylen–Propylen Copolymeren enthaltene Zahl an $(CH_2)_2$ Gruppen wird deren Abhängigkeit von der Zusammensetzung und dem Produkt der Reaktivitätsverhältnisse durch eine Gleichung dargestellt. Die Gleichung enthält zwei empirische Parameter, abgeleitet von den Infrarot-Spektren verschiedener Copolymerer—hergestellt mit einigen Katalysatoren auf Vanadiumbasis—und von den entsprechenden Homopolymeren des Propylens. Nach unserer Berechnung ergibt sich für diese Katalysatoren eine Wahrscheinlichkeit von etwa 80 Prozent für den Einbau einer Äthyleneinheit und von etwa 20 Prozent für den Einbau einer normalen Propyleneinheit im Anschluß an eine invertierte Propyleneinheit. Dies zeigt, daß zwei Drittel der Propyleneinheiten in E–P Diaden sich normal addieren (d.h. an der Methylen-gruppe).

APPENDIX

Consider a copolymer containing m_1 moles of P and $m_2 = 1-m_1$ moles of E (the weight fractions are $(3m_1)/(2+m_1)$ for P and $(2-2m_1)/(2+m_1)$ for E). Let r_1 be the reactivity ration of P, r_2 that of E, F and f the molar ratios of P to E in the feed and in the copolymer, respectively.

In order to evaluate the quantities α, β, γ and δ, we must take into account some relationships deduced from the sequence distribution laws:[7]

(a) fraction of P units belonging to sequences of three or more units† $= \dfrac{K^3 + 6K^2}{(K+2)^3}$,

(b) fraction of first and last units belonging to P sequences of length $\geqslant 3$ (which is twice the ratio of P sequences containing three or more units to the total number of P units) $= \dfrac{4K^2}{(K+2)^3}$,

(c) ratio of P sequences containing two or more units to the total number of P units $= \dfrac{2K}{(K+2)^2}$,

(d) fraction of E sequences containing one unit only† $= \dfrac{K}{K + 2r_1 r_2}$,

† Quantities a and d are given in Ref. 7 the symbols $U_3(m_1)$ and $S(m_2)_1$, respectively.

(*e*) ratio of P sequences containing one unit only to the total number of P units $= \frac{4}{(K+2)^2}$.

To transform these amounts into mole fractions in the copolymer, *a*, *b*, *c* and *e* must be multiplied by m_1 and *d* by $1-m_1$. By considering the above relationships and the conditions for the formation of $(CH_2)_2$ groups, we obtain then:

$$\alpha = \frac{(K^3 + 6K^2)\, m_1}{(K+2)^3} - 2 \cdot \frac{2K^2 m_1}{(K+2)^3}$$

$$\beta = \frac{2\,K\, m_1}{(K+2)^2}$$

$$\gamma = \frac{K}{K + 2r_1 r_2} \cdot \frac{K(1 - P_3) + 2(1 - P_4)}{K+2}$$

$$\delta = \frac{4m_1}{(K+2)^2}.$$