Ethylene polymerization process with a highly active Ziegler-Natta catalyst: 2. Molecular weight regulation*

L. L. Böhm
Hoechst AG, Frankfurt/M 80, Germany

(Received 14 July 1977; revised 3 January 1978)

This paper deals with molecular weight regulation and molecular weight distribution in ethylene polymerization, using a highly active Ziegler–Natta catalyst. The molecular weight regulation can be described by equations derived in a previous paper. The development of the molecular weight distribution with reaction time showed that there must exist active sites with an overall propagation rate constant of at least 2.9 × 10^3 dm^3/mol sec at 85°C. This value is higher by a factor of approximately 40 than the value determined by kinetic experiments.

INTRODUCTION

In a previous paper[1] the kinetics of ethylene polymerization with a highly active Ziegler–Natta catalyst have been investigated. It has been pointed out that there are steady state conditions for which the kinetic behaviour depends only on chemical processes at the surface of the heterogeneous catalyst. This paper deals with molecular weight distributions (*MWD*) and molecular weight regulation to check the validity of a reaction model proposed elsewhere[2]. To decide how the different transfer processes given in the reaction model contribute to molecular weight regulation, the number-average degree of polymerization, which is reached after long reaction times, must be correlated with different process variables. In order to obtain these limiting values it is necessary to measure number-average degrees of polymerization as a function of reaction time or catalyst yield.

The number-average degree of polymerization or the number-average molecular weight are calculated from molecular weight distribution functions.

EXPERIMENTAL

The details of these investigations have been described in a previous paper[1]. If the polymerization process had to be stopped after short reaction times a large amount of isopropanol saturated with hydrogen chloride was added.

The molecular weight distributions were measured using a Waters 200 g.p.c. chromatograph with columns of different pore sizes (10^5, 10^4, 10^3 and 10^2 nm). The g.p.c. chromatograph was calibrated as described elsewhere[1]. The g.p.c. chromatogram has been transferred to molecular weight distribution functions without any corrections for longitudinal diffusion as proposed by Pickett, Cantow and Johnson[3]. The *MWD* established after long reaction times can be represented by a logarithmic normal distribution function according to the results of Wesslau[4]. It is important to emphasize that the moments of these distribution functions show a large error due to the scattering of the g.p.c. curve. This is demonstrated in *Figure 1*.

The average molecular weights thus have the following relative errors: $\Delta M_n/M_n = \pm 0.2$; $\Delta M_w/M_w = \pm 0.2$ and $\Delta M_v/M_v = \pm 0.1$. These errors also hold for the degrees of polymerization.

RESULTS

When the polymerization process starts, the degree of polymerization rises from 1 to higher values until it becomes constant after a certain reaction time. This constant value, $P_{n,\infty}$, depends on the ratio of propagation to transfer processes.

This means that the P_n values must be measured as a function of reaction time to obtain the asymptotic values $P_{n,\infty}$. On the other hand, the P_n *versus* reaction time curves give further information about the polymerization process.

The experimental results in *Figure 2* show that at the beginning of the polymerization process the degree of polymerization increases rapidly to high values, followed by a relatively long period in which the P_n values increase slowly

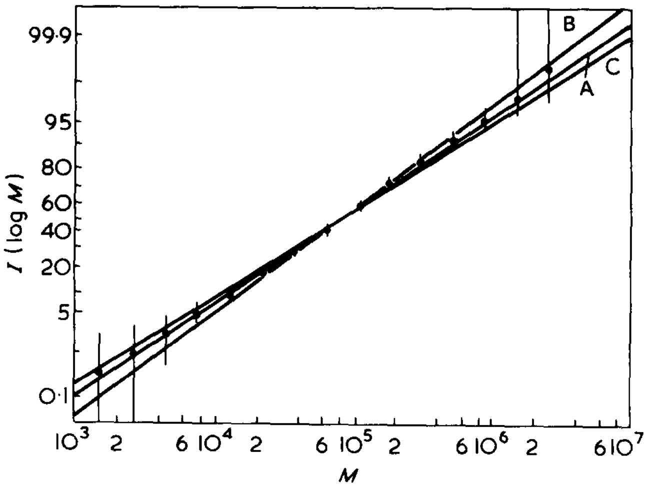

Figure 1 Molecular weight distribution function: ●, experimental point with error, A: M_n = 3.0 × 10^4, M_w = 2.3 × 10^5, M_v = 1.7 × 10^5. B: M_n = 3.6 × 10^4, M_w = 1.9 × 10^5, M_v = 1.5 × 10^5. C: M_n = 2.5 × 10^4, M_w = 2.6 × 10^5, M_v = 1.9 × 10^5

---

* Paper presented at the 'Makromolekulares Kolloquium' in Freiburg, 3–5 March 1977.

0032–3861/78/1905–0562 $02.00

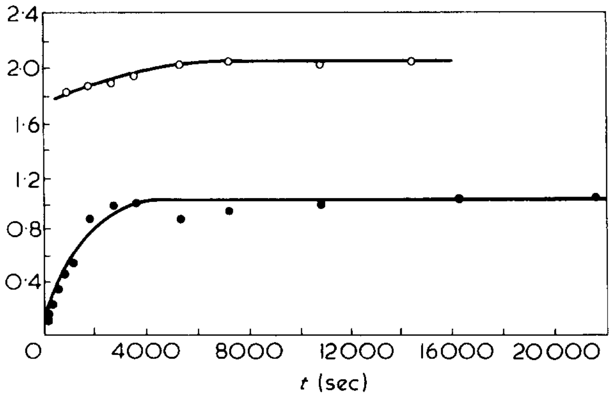

Figure 2 Number-average degree of polymerization, P_n, as a function of reaction time, t: 1 dm^3 reaction vessel: 0.6 dm^3 diesel oil; 750 rpm; 85°C; $n_K = 2.5 \times 10^{-5}$ mol Ti compound. ○, $[M] = 0.52$ mol/dm^3, $n_{AlR_3}/n_K = 80$; ●, $[M] = 0.086$ mol/dm^3, $n_{AlR_3}/n_K = 80$

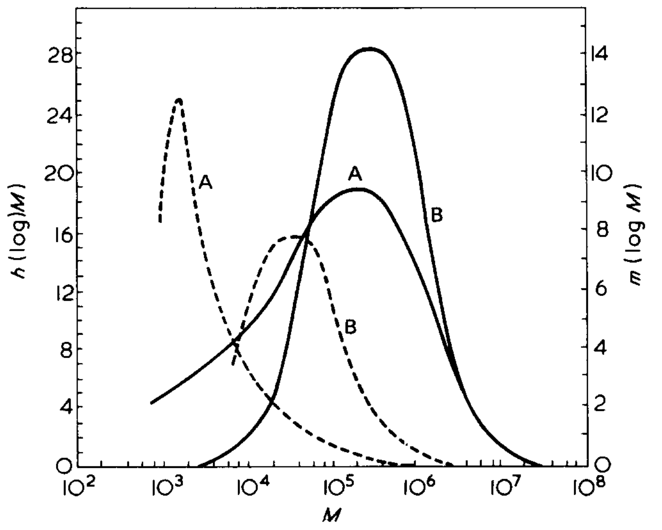

Figure 3 Molecular weight distributions as functions of reaction time: 1 dm^3 reaction vessel; 0.6 dm^3 diesel oil; 750 rpm; 85°C; $n_K = 2.5 \times 10^{-5}$ mol Ti compound; $[M] = 0.086$ mol/dm^3, $n_{AlR_3}/n_K = 80$. Reaction time: A, 15 sec; B, 7200 sec. — — —, Frequency distribution function (left scale); ———, weight distribution function (right scale)

to reach the asymptotic value. This corresponds to some extent to the results of Reichert and Meyer[5]. The result implies that there must be active centres, with high propagation rate constants, capable of producing macromolecules with high molecular weights immediately after the beginning of the polymerization process.

The further slow increase of the degree of polymerization with reaction time cannot be caused by a diffusional hindering of monomer transport to the active sites because in this case the P_n values should become smaller or even reach a minimum[6]. A possible explanation for this behaviour is that there are different types of active sites with different propagation rate constants.

To obtain more information on how the polymer molecules are built up during the polymerization process, it is necessary to measure molecular weight distributions as functions of reaction time. This is shown in *Figure 3*.

At small reaction time the weight distribution function is broad. There is a large number of macromolecules with high molecular weights which do not further increase with time. This means that the maximum of the weight distribution function is not shifted to a higher molecular mass with increasing reaction time. At small reaction times, the weight distribution function contains amounts of low molecular mass. Although this quantity is small there are a lot of macromolecules with low molecular weights as demonstrated by the frequency distribution function in *Figure 3*. With increasing reaction time the amount of molecules with low molecular weights decreases.

This result can be interpreted in the following way: as there are molecules with very high molecular weights formed immediately after the beginning of the polymerization process there must exist highly active sites. A minimum value for the overall propagation rate constant $\bar{k}_p$ of these highly active sites can be calculated according to the following equation[2]:

$$P_{n,0} = \frac{M_{n,0}}{M_m} = \bar{k}_p [M]_0 t = \bar{k}_p [M]\, t \qquad (1)$$

Equation (1) only holds if no transfer processes have occurred. As the development of the *MWD* with time shows that the molecular mass of the high molecular fraction does not increase, it is significant that even after a reaction time of 15 sec, transfer processes have taken place to a great extent. So the $\bar{k}_p$ value for the highly active site must be greater as calculated by equation (1).

To calculate $\bar{k}_p$ with equation (1), $M_{n,0}$ must be known. As the molecular mass of the high molecular fraction remains constant with time it is possible to assume that the *MWD* of this fraction is identical with the *MWD* of the polymer after long reaction times (see *Figure 4*). As this *MWD* can be approximated within experimental error by a logarithmic normal distribution function, $M_{n,0}$ can be calculated using an equation given by Wesslau[6,7]. With $M_{n,0} = 1.05 \times 10^5$ it was found that $\bar{k}_p > 2.9 \times 10^3$ dm^3/mol sec. This is a high value compared with values so far published. On the other hand, this value is of the same order of magnitude as values published by Zakharov and coworkers[8,9] (see also Mejzlik and Lesná[10]). Such a high value has also been reported by Reichert and Meyer[5].

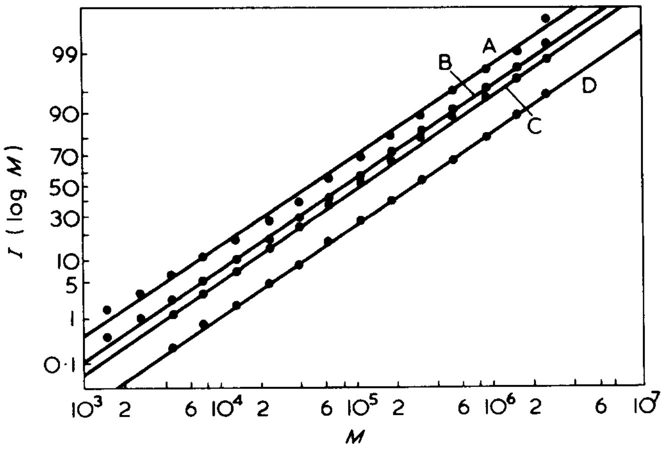

Figure 4 Integral weight distribution functions. A: $M_n = 1.7 \times 10^4$, $M_w = 1.2 \times 10^5$, $M_v = 9.2 \times 10^4$. B: $M_n = 3.1 \times 10^4$, $M_w = 2.2 \times 10^5$, $M_v = 1.6 \times 10^5$. C: $M_n = 4.2 \times 10^4$, $M_w = 2.9 \times 10^5$, $M_v = 2.2 \times 10^5$. D: $M_n = 1.05 \times 10^5$, $M_w = 7.4 \times 10^5$, $M_v = 5.5 \times 10^5$

Table 1 Number-average degree of polymerization $P_{n,\infty}$ as a function of bulk monomer and cocatalyst concentration; 1 dm^3 reaction vessel; 0.6 dm diesel oil, 750 rpm; 85°C; $n_K = 2.5 \times 10^{-5}$ mol

$[AlR_3] \times 10^3$ (mol/dm^3)	$[al] \times 10^3$ (mol/dm^3)	[M] (mol/dm^3)	$P_{n,\infty} \times 10^{-3}$	$1/P_{n,\infty} \times 10^4$	$[al]/[M] \times 10^3$
3.6	1.58	0.516	7.3	1.37	3.04
5.0	1.94	0.516	8.0	1.25	3.73
8.3	2.64	0.516	6.1	1.64	5.08
10.0	2.95	0.516	6.1	1.64	5.67
16.6	3.95	0.516	4.5	2.22	7.60
20.0	4.38	0.516	5.4	1.85	8.42
9.1	2.79	0.516	8.0	1.25	5.37
8.3	2.64	0.344	5.0	2.00	7.67
8.3	2.64	0.344	5.0	2.00	7.67
8.3	2.64	0.258	4.6	2.17	10.23
8.3	2.64	0.172	3.9	2.56	15.35
8.3	2.64	0.172	3.9	2.56	15.35
1.0	0.65	0.086	4.6	2.17	7.56
4.0	1.69	0.086	3.2	3.13	19.65
4.0	1.69	0.086	3.8	2.67	19.65

This result also means that there is a discrepancy in the kinetic results[1]. It has been found that about 70% of the titanium atoms form active sites, and that the overall propagation rate constant $\bar{k}_p$ has a value of 80 dm^3/mol sec. A possible interpretation is that there are different active sites with extremely different $\bar{k}_p$ values, or the active sites are reversibly blocked by the cocatalyst as pointed out in the reaction scheme[2]. This would mean that only a small amount of active site would take part in the polymerization process. It is possible to estimate that about 2% of active sites, as a minimum, are highly active sites. The major amount, about 68% of the active sites, has $\bar{k}_p$ values smaller than 80 dm^3/mol sec, or if the active sites are reversibly blocked the $\bar{k}_p$ value is 0.

After a long reaction time of about 2 h the P_n values become constant and time independent. This also holds for molecular weight distributions, irrespective of whether the molecular mass is regulated by hydrogen or not. Hydrogen is usually used to control the molecular weight in Ziegler–Natta polymerization processes[11–13]. The *MWD* functions of polymers with different average molecular weights are plotted in *Figure 4*.

In all cases the *MWD* can be described by a logarithmic normal distribution function[4,7]. The dispersion ratio M_w/M_n is 7.5 ± 2. This means that the $M_{n,\infty}$ values can be calculated by equation (2):

$$M_{n,\infty} = 0.19 M_{v,\infty} \tag{2}$$

where $M_{v,\infty}$ is the viscosity-average molecular weight. The factor 0.19 implies an exponent of the Mark–Houwink–Sakurada equation α of 0.71. All $M_{n,\infty}$ values have been calculated using equation (2), if the *MWD* has not been established.

In a previous paper[2] it was pointed out that different transfer processes exist. Equations have been derived to describe the dependence of the number-average degree of polymerization on different process variables. If there is no hydrogen in the system the following equation should hold:

$$\frac{1}{P_{n,\infty}} = \bar{A} + \bar{B}\frac{1}{[M]_0} + \bar{C}\frac{[al]_0}{[M]_0} \tag{3}$$

The constants $\bar{A}$, $\bar{B}$ and $\bar{C}$ are given elsewhere[2]. As there is no indication of diffusion processes, the concentration at the surface of the catalyst are substituted by bulk concentrations. The concentration of the monomeric form of the organoaluminium compound was calculated using the data published by Smith[14]. To obtain K_c from K_x, the molecular mass 142.29 ($C_{10}H_{22}$) and the density 0.962 g/cm^3 of diesel oil at 85°C were used. With these values, K_c was found to be 2.46×10^{-3} mol/dm^3. As the cocatalyst concentrations are about two orders of magnitude higher than the 'catalyst concentration', the concentrations of the organoaluminium compound have not been corrected due to the loss of cocatalyst by the activation reaction. *Table 1* summarizes the experimental results. *Figure 5* demonstrates that the experimental data in *Table 1* are arranged along a straight line if $1/P_{n,\infty}$ is plotted as a function of [al]/[M].

The experimental data can be described with the following equation:

$$\frac{1}{P_{n,\infty}} = \bar{A} + \bar{C}\frac{[al]}{[M]} \tag{4}$$

Comparison with equation (3) reveals that $\bar{B}$ must be small or zero, which implies that spontaneous β-elimination as proposed in the reaction scheme[2] is less important. This agrees well with results of Grievenson[15] and Henrici-Olivé and Olivé[16]. The intercept $\bar{A}$ was found to be 1.0×10^{-4} which means that 10^4 propagation steps occur until a β-elimination process followed by a dissociation of the vinyl group from the active site takes place. *Figure 5* also shows that the transfer process with the cocatalyst takes place to approximately the same extent. This result corresponds to results of Zakharov and coworkers[17] for a classical Ziegler–Natta catalyst.

In Ziegler–Natta catalysis hydrogen is usually used as transfer agent[11–13] to control the average molecular weight over a wide range. On the other hand, hydrogen strongly inhibits the polymerization process. Both effects are observed with a highly active catalyst as well.

It has been pointed out in a previous paper[2] that the asymptotic value of the degree of polymerization after long reaction times should depend on the hydrogen concentration at the surface of the catalyst, according to equation (5):

$$\frac{1}{P_{n,\infty}} = \bar{A} + \bar{B}\frac{1}{[M]_0} + \bar{C}\frac{[al]_0}{[M]_0} + \bar{D}\frac{[H_2]_0}{[M]_0} \tag{5}$$

The experimental data to check the validity of equation (5) are given in *Table 2*. As in other cases, $P_{n,\infty}$ was determined as a function of bulk concentrations. The hydrogen concentration was calculated according to Henry's law $(H_2) = \lambda_H p$;

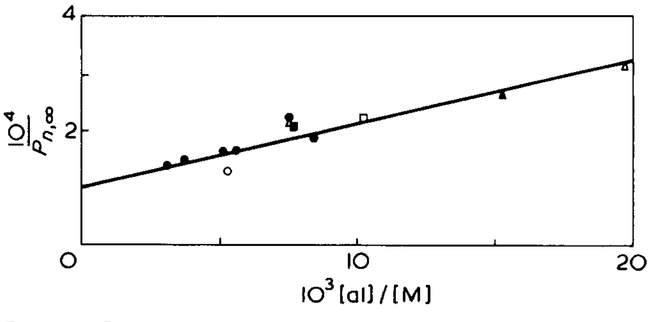

Figure 5 Plot of $1/P_{n,\infty}$ as a function of [al]/[M]

Table 2 Number-average degree of polymerization $P_{n,\infty}$ as a function of bulk hydrogen and monomer concentration.

(a) 85°C; 100 dm^3 diesel oil, 6 h; $n_K = 9 \times 10^{-3}$ mol, $[AlR_3] = 4 \times 10^{-3}$ mol/dm^3; $[M] = 0.172$ mol/dm^3; $pC_2H_4 = 2$ bar

$P_{n,\infty}$	$1/P_{n,\infty} \times 10^3$	pH_2/pC_2H_4	$[H_2]/[M]$
2.41×10^2	4.15	2.04	0.109
3.39×10^2	2.95	1.39	0.074
5.71×10^2	1.75	0.83	0.044
6.79×10^2	1.47	0.54	0.029
7.14×10^2	1.40	0.49	0.026
1.00×10^3	1.00	0.45	0.024
1.04×10^3	0.96	0.37	0.020
1.21×10^3	0.83	0.26	0.014
1.29×10^3	0.78	0.23	0.012
1.55×10^3	0.65	0.21	0.011
1.79×10^3	0.56	0.17	0.009
2.23×10^3	0.45	0.11	0.006
2.96×10^3	0.34	0.06	0.003

(b) 85°C; 1 dm^3 reaction vessel; 750 rpm; 0.60 dm^3 diesel oil; $n_K = 2.5 \times 10^{-5}$ mol; $[AlR_3] = 8.3 \times 10^{-3}$ mol/dm^3, $[M] = 0.172$ mol/dm^3; $pC_2H_4 = 2$ bar

$P_{n,\infty}$	$1/P_{n,\infty} \times 10^3$	pH_2/pC_2H_4	$[H_2]/[M]$
3.57×10^2	2.80	1.40	0.074
5.0×10^2	2.00	0.79	0.042
7.32×10^2	1.37	0.41	0.022
8.21×10^2	1.22	0.36	0.019
1.0×10^3	1.00	0.28	0.015
1.21×10^3	0.83	0.21	0.011
1.29×10^3	0.78	0.19	0.010

Henry's constant λ_H as a function of temperature is given by $\log \lambda_H = -0.819 - (543/T)$; $[\lambda_H] = \text{mol/dm}^3\ \text{bar}$. The data of *Table 2* are plotted in *Figure 6*.

Figure 6 shows that the experimental data can be described by the following equation:

$$\frac{1}{P_{n,\infty}} = \bar{E} + \bar{D}\frac{[H_2]}{[M]} \qquad (6)$$

Comparison with equation (5) reveals that the intercept $\bar{E}$ is given by:

$$\bar{E} = \bar{A} + \bar{C}\frac{[al]}{[M]}$$

$\bar{B}$ was found to be very small or zero. A value of 2.5×10^{-4} was calculated for the intercept, $\bar{E}$. This value agrees with the value given in *Table 1* for $[AlR_3] = 8.3 \times 10^{-3}$ mol/dm^3 and $[M] = 0.172$, which are the corresponding process variables established in this series. *Figure 6* further shows that the $P_{n,\infty}$ values strongly depend on the ratio $[H_2]/[M]$, which means that the average molecular weight can be regulated over a wide range. For example, if there is a hydrogen content of 50 vol % in the gaseous phase, 456 propagation steps take place until a transfer reaction with hydrogen occurs. The ratio of transfer to propagation processes thus rises approximately by a factor of 20 in comparison to polymerization without hydrogen.

DISCUSSION

Although the experimental results show that this polymerization process is complex and there should exist different active sites to explain the development of the *MWDs* as functions of reaction time, the polymerization process[1] and the molecular weight regulation can be described by simple equations. On the other hand, it has not been possible to evaluate the rate constants of a reaction model proposed elsewhere[2], because all equations contain only complex constants due to the fact that different processes interfere in a complex manner. It is important to emphasize that these investigations do not show any significant influence of diffusion processes on polymerization. This result is also supported by the results in this paper. It is scarcely possible to imagine that the experimental data as presented in *Figures 5* and *6*, should be arranged along straight lines if there are strong influences of diffusion. On the other hand, these plots agree well with equations derived from a reaction model proposed elsewhere[2].

According to these results, in the absence of hydrogen, 2 transfer processes occur, namely β-elimination including a monomer molecule and transfer to the cocatalyst. Both processes contribute approximately to the same extent to the termination of the propagation of a chain. From these results it is also evident that spontaneous β-elimination is an unimportant process and can be neglected. This agrees with results of other authors[15,16]. It may be concluded from the data in *Figure 5* that β-elimination and transfer to the cocatalyst $Al(C_2H_5)_3$ take place to the same extent. This result was also found by Zakharov and coworkers[17] for a classical Ziegler–Natta catalyst. It may be that this occurs by accident, but it could also show that both catalysts operate in the same manner. As with classical Ziegler–Natta catalysts, the molecular weight can be controlled with hydrogen over a wide range, which is important for technical processes.

Summarizing the kinetic results[1] and the results presented in this paper, it is evident that at least this highly active catalyst works in the same way as classical Ziegler–Natta catalysts. There is only one significant difference, namely the high amount of active sites.

As the development of the molecular weight distribution shows, there must exist different types of active sites. The molecular weight distribution established after short reaction times of 15 sec indicates active sites with an overall propagation rate constant of 2.9×10^3 dm^3/mol sec as a minimum. Comparison with the overall propagation rate constant from kinetic measurement[1] shows that only a small amount of the active sites, i.e. in the range of 2% as a maximum, are such highly active sites. However, the experimental data do not allow us to give an interpretation of this effect. On the other hand, these results confirm the existence of active sites with extremely high propagation rate constants, as pointed out by Zakharov and coworkers[8,9].

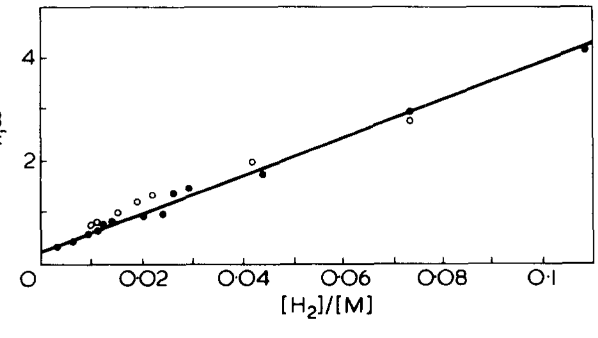

Figure 6 Plot of $1/P_{n,\infty}$ as a function of $[H_2]/[M]$

ACKNOWLEDGEMENT

The author is very indebted to Dr Gann for g.p.c. measurements. The author wants to thank Dr M. Fleissner for helpful discussions, and Professor Dr H. Cherdron for his permission to publish this paper.

REFERENCES

1 Böhm, L. L. *Polymer* 1978, **19**, 553

2 Böhm, L. L. *Polymer* 1978, **19**, 562

3 Pickett, H. E., Cantow, M. J. R. and Johnson, J. F. *J. Appl. Polym. Sci.* 1966, **10**, 917

4 Wesslau, H. *Makromol. Chem.* 1956, **20**, 111

5 Meyer, H. and Reichert, K. H. *Angew. Makromol. Chem.* 1977, **57**, 211

6 Crabtree, J. R., Grimsby, F. N., Nummelin, A. J. and Sketchley, J. M. *J. Appl. Polym. Sci.* 1973, **17**, 959

7 Peebles, L. H. in *Polym. Rev.* (Eds. H. F. Mark and E. H. Immergut) 1971, **18**

8 Chumaevskii, N. B., Zakharov, V. A., Bukatov, G. D., Kuznetzova, G. I. and Yermakov, Y. I. *Makromol. Chem.* 1976, **177**, 747

9 Zakharov, V. A., Chumaevskii, N. B., Bukatov, G. D. and Yermakov, Y. I. *Makromol. Chem.* 1976, **177**, 763

10 Mejzlik, J. and Lesna, M. *Makromol. Chem.* 1977, **178**, 261

11 Natta, G., Mazzanti, G., Longi, P. and Bernardini, F. *Chem. Ing. (Milan)* 1958, **41**, 519

12 Vandenberg, E. J. US Pat, 30 51 690 (1962)

13 Hofmann, A. S., Fries, B. A. and Condit, P. C. *J. Polym. Sci. (C)* 1963, **1**, 109

14 Smith, M. B. *J. Phys. Chem.* 1967, **71**, 364

15 Grievenson, B. M. *Makromol. Chem.* 1965, **84**, 93

16 Henrici-Olivé, G. and Olivé, S. *Polym. Lett.* 1974, **12**, 39

17 Bukatov, G. D., Chumaevskii, N. B., Zakharov, V. A., Kuznetzova, G. I. and Yermakov, Y. I. *Makromol. Chem.* 1977, **178**, 953