A kinetic study of 'living' coordination polymerization of propene with the soluble $V(acac)_3$–$Al(i\text{-}C_4H_9)_2Cl$ system

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The soluble $V(acac)_3$–$Al(i\text{-}C_4H_9)_2Cl$ system initiated living polymerization of propene at −78°C affording monodisperse polymers ($\bar{M}_w/\bar{M}_n = 1.15 \pm 0.10$). A kinetic study (of the living polymerization) was carried out to evaluate the rate coefficients for propagation. The equilibrium constant K_M for a propene monomer coordinated to an active vanadium and the rate constant k_p for a subsequent insertion of coordinated monomer into a living polymer chain were determined and compared with the values for the polymerization of propene with other soluble vanadium-based catalyst systems. The relation between K_M and k_p revealed that a strong interaction between vanadium and propene is unfavourable for the insertion of the coordinated propene into a living polymer chain. The mechanism of an initiation reaction involving alkylation and complexing of $V(acac)_3$ with $Al(i\text{-}C_4H_9)_2Cl$ has been proposed.

Keywords Polymerization; kinetics; catalyst; propagation; vanadium; complexing; alkylation

INTRODUCTION

An ideal living polymerization takes place when propagation of all chains is initiated simultaneously and chain transfer and termination are absent. Such limiting conditions have been achieved in the anionic polymerization of vinyl monomers by the organic derivatives of alkali metals[1,2]. The living anionic polymerization has proved useful in the preparation of monodisperse polymers and block copolymers and also effective in the determination of the rate coefficients for chain propagation, since the chain ends remain active for long periods of time[3]. In the field of the coordination polymerization of α-olefins with Ziegler-type catalysts, the development of a catalyst exhibiting 'living' character comparable with the anionic polymerization catalysts has been desired[4]. Recently, we have found that the soluble catalyst system of $V(acac)_3$ (acac = acetyl acetonate) with $Al(C_2H_5)_2Cl$ initiates a living polymerization of propene to afford monodisperse polymers ($\bar{M}_w/\bar{M}_n = 1.05 \sim 1.20$)[5]. A kinetic study proved that the polymerization of propene proceeds without any chain termination and transfer reactions at temperatures below −65°C[6]. This was the first Ziegler-type catalyst meeting all the requirements for an ideal living polymerization. In a further investigation we found combinations of $V(acac)_3$ with some other dialkyl-aluminium halides initiate the living polymerization of propene at −78°C. The purpose of this study is to examine the kinetics of the living polymerization of propene with the $V(acac)_3$–$Al(i\text{-}C_4H_9)_2Cl$ system and to elucidate the mechanism of initiation and propagation steps in the living polymerization.

EXPERIMENTAL

Reagents

$V(acac)_3$ (Alfa Division Ventron Co.) and alkylaluminiums (Japan Aluminium Alkyl Co.) were used without further purification. Propene (purity 99.8%; the impurity was propane) supplied from Mitsubishi Petrochemical Co. was used after passage through columns of sodium hydroxide and phosphorus pentoxide. Pentene-1 (extra pure grade) was dried by refluxing over phosphorus pentoxide under a nitrogen atmosphere after distillation. A reagent grade of toluene was dried by refluxing over sodium metal under a nitrogen atmosphere prior to use.

Polymerization procedure

A three-necked glass flask with a magnetic stirrer was used as the reactor. Propene was condensed into toluene in the reactor which was kept at −78°C with methanol–dry ice. The amount of toluene used was adjusted to 100 cm^3 for the total volume. Prescribed amounts of alkylaluminium and $V(acac)_3$, in that order, were charged under a nitrogen stream. The polymerization was timed from the addition of the $V(acac)_3$ component, and quenched at a given time by introducing an ethanol solution of hydrochloric acid (100 cm^3) cooled at −78°C. The polymers obtained were washed several times with ethanol (200 cm^3) and dried *in vacuo* at room temperature.

Gel-permeation chromatography analysis

Molecular weight distributions of polymers were measured by gel-permeation chromatography (g.p.c.) (Waters Associates, Model 200) equipped with five polystyrene gel columns (10^7, 10^6, 10^5, 10^4, and 10^3 Å pore sizes) at 135°C. The solvent was *o*-dichlorobenzene, and the flow rate was 1.0 $cm^3\ min^{-1}$. A molecular weight calibration curve was obtained on the basis of the universal calibration[7,8] with ten monodisperse polystyrene samples (Pressure Chemical Co.) of molecular weights 2100 to 2610000. From the g.p.c. data, the number-average and weight-average molecular weights ($\bar{M}_n$,$\bar{M}_w$) were obtained by standard procedures. The correction of the g.p.c. peak spreading (zone spreading)

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Table 1 Polymerization results obtained at −78°C under different conditions with the $V(acac)_3$–$Al(i–C_4H_9)_2Cl$ system[a]

Run	$[Al(i–C_4H_9)_2Cl]$ (mol. dm^{-3})	$[C_3H_6]$ (mol. dm^{-3})	Time (h)	Yield (g)	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$[b]	$[N]$[c] (mol/mol of V)
1	0.10	8.3	1	0.08	1.21	1.19	0.007
2	0.10	8.3	2	0.26	1.86	1.16	0.014
3	0.10	8.3	2	0.26	2.34	1.16	0.011
4	0.10	8.3	3	0.44	3.50	1.13	0.013
5	0.10	8.3	4	0.44	3.02	1.15	0.015
6	0.10	8.3	5	0.80	5.85	1.11	0.014
7	0.10	8.3	6	0.76	6.67	1.17	0.011
8	0.10	8.3	8	1.06	8.23	1.15	0.013
9	0.10	8.3	10	1.16	9.94	1.22	0.012
10	0.10	8.3	12	1.39	10.7	1.19	0.013
11	0.10	8.3	15	1.86	14.7	1.13	0.013
12	0.03	8.3	6	0.09	3.62	1.26	0.003
13	0.05	8.3	6	0.10	4.60	1.07	0.002
14	0.05	8.3	6	0.27	4.56	1.17	0.006
15	0.07	8.3	6	0.34	4.80	1.07	0.004
16	0.08	8.3	6	0.52	4.83	1.10	0.011
17	0.20	8.3	6	1.43	4.80	1.09	0.030
18	0.30	8.3	6	2.70	5.20	1.05	0.052
19	0.40	8.3	6	2.56	4.44	1.06	0.058
20	0.10	1.7	6	0.24	2.56	1.19	0.010
21	0.10	2.4	6	0.35	3.38	1.22	0.010
22	0.10	2.9	6	0.47	3.83	1.24	0.012
23	0.10	4.7	6	0.65	4.63	1.29	0.014
24	0.10	10.7	6	0.72	–	–	–

[a] Polymerization conditions: −78°C, $[V(acac)_3]$ = 0.01 mol. dm^{-3} and [toluene solution] = 0.1 dm^3
[b] Corrected for g.p.c. peak spreading
[c] Number of polymer chains per vanadium atom

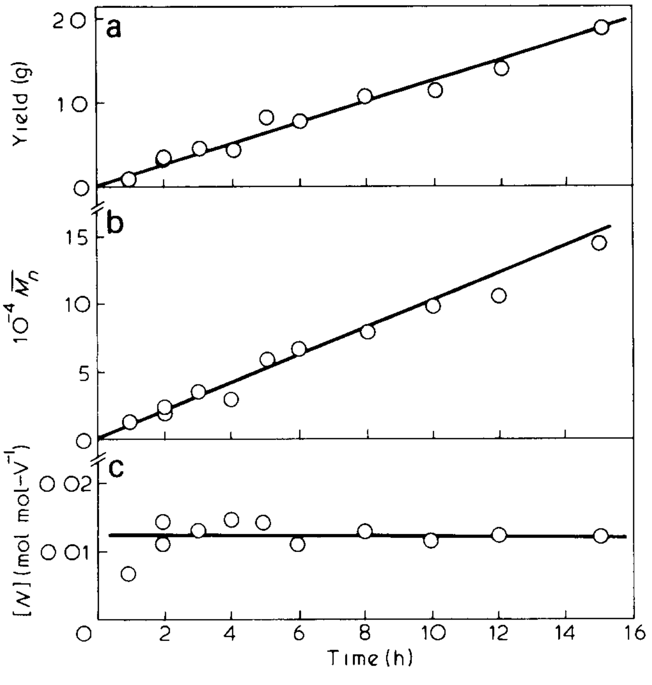


Figure 1 Time dependences of yields and number-average molecular weights $\bar{M}_n$ of the resulting polymers and of the number of polymer chains produced per vanadium atom $[N]$ in the polymerization of propene at −78°C with $V(acac)_3$–$Al(i–C_4H_9)_2Cl$ system. Polymerization conditions are given in *Table 1* (Run no. 1–11)

for the polydispersity parameters ($\bar{M}_w/\bar{M}_n$) was made on the basis of the method of Hamielec and Ray[9].

RESULTS AND DISCUSSION

Kinetic analysis

Table 1 shows the polymerization results obtained at −78°C under various conditions with the $V(acac)_3$–$Al(i$-$C_4H_9)_2Cl$ system. Polymerization was carried out in the range of a low conversion of propene monomer up to several percent. The concentration of monomer may be regarded as constant during the course of polymerization. Kinetic analysis for the polymerization was made from the data given in the Table.

The time dependence of the yield of the polymers produced in the course of polymerization is shown in *Figure 1a*. The yield of polymer was proportional to the polymerization time, the appropriate plot passing through the origin. This indicates that formation of propagation centres is complete just after polymerization starts and that the subsequent polymerization proceeds without deactivation of the centres. The time dependence of the number-average molecular weight, $\bar{M}_n$, of polymers is shown in *Figure 1b*, and *Figure 1c* shows the relation between the polymerization time and the number of polymer chains produced per vanadium atom, $[N]$, being calculated from the relation $[N]$ = polymer yield/$\bar{M}_n$. The $\bar{M}_n$ of polymers was proportional to the polymerization time. Consequently, the number of polymer chains produced per vanadium atom remained almost constant during the course of the polymerization. From these results, we have concluded that the soluble $V(acac)_3$–$Al(i$-$C_4H_9)_2Cl$ system initiates a living polymerization of propene at −78°C. This is confirmed by the narrow molecular weight distributions of the polymers produced. The polydispersity ($\bar{M}_w/\bar{M}_n$) of polymers is 1.15 ± 0.10 (see *Table 1*), which is close to the theoretical value ($\bar{M}_w/\bar{M}_n$ = 1.0) for an ideal living polymerization.

The polymer yield at a given polymerization time was first order with respect to the concentration of $V(acac)_3$ at a constant concentration of $Al(i$-$C_4H_9)_2Cl$. In contrast, the effect of the concentration of $Al(i$-$C_4H_9)_2Cl$ on the polymer yield was complex. As *Figure 2a* shows, the yield of polymers produced in 6 h increased to a constant value with an increase in the concentration of Al(i-$C_4H_9)_2$Cl. The $\bar{M}_n$ of the polymers was negligibly dependent on the concentration of Al(i-$C_4H_9)_2$Cl (see *Figure 2b*), confirming that the chain transfer reaction with Al(i-$C_4H_9)_2$Cl does not exist in the present polymerization system. *Figure 2c* shows the relation between the concentration of Al(i-$C_4H_9)_2$Cl, [A], and the number of polymer chains produced per vanadium atom, [*N*]. The relation could be expressed by the following equation.

$$[N]=\alpha\left(\frac{K_A[A]^2}{1+K_A[A]^2}\right) \tag{1}$$

The values of the constants, α and K_A, at −78°C were 0.08 mol/mol of V and 17 dm^6 (mol of Al)$^{-2}$, respectively. It is characteristic of a living polymerization that the number of polymer chains [*N*] is consistent with the number of propagation centres. The influence of the concentration of Al(i-$C_4H_9)_2$Cl on the polymer yield is thus understandable as a result of the change in the number of propagation centres.

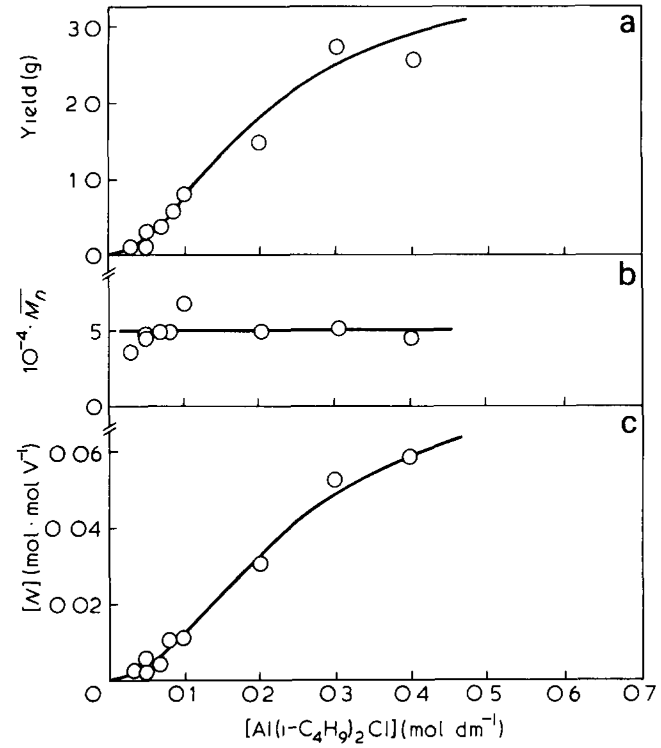


Figure 2 Influences of concentration of Al(i–$C_4H_9)_2$Cl on polymer yield, on number-average molecular weight $\bar{M}_n$, and on the number of polymer chains produced per vanadium atom [*N*] at −78°C. Polymerization conditions are given in *Table 1* (Run no. 7 and 12–19)

Figure 3a shows the relation between the polymer yield and the concentration of propene monomer. The polymer yield was not simple first order in the monomer concentration, but approached a constant value with increasing monomer concentration. The analogous dependence of polymer yield on the monomer concentration has been found in the low-temperature polymerization of propene with the other soluble vanadium-based catalysts[6,10,12]. Conversely, the number of polymer chains [*N*] did not vary with the monomer concentration (see *Figure 3b*), confirming that the chain transfer reaction with propene monomer is not present. The yield of polymers, *Y*, produced at a given polymerization time, *t*, could be expressed by

$$Y=k_p\left(\frac{K_M[M]}{1+K_M[M]}\right)[N]t \tag{2}$$

where [M] denotes the concentration of propene monomer. The values of constants k_p and K_M are given in *Table 2*, together with the values determined in the polymerization of propene with the other soluble vanadium-based catalyst systems at −78°C for comparison. Equation (2) can be interpreted in terms of the mechanism that the polymerization of propene proceeds by a sequence of two successive reactions, represented by a propene monomer coordination to the active vanadium and a subsequent insertion of the coordination monomer into a living polymer chain attached to the metal, V*–P_n.

$$V^*-P_n+C_3H_6 \overset{K_M}{\rightleftharpoons} \overset{C_3H_6}{\underset{}{V^*}}-P_n \xrightarrow{k_p} V^*-P_{n+1} \tag{3}$$

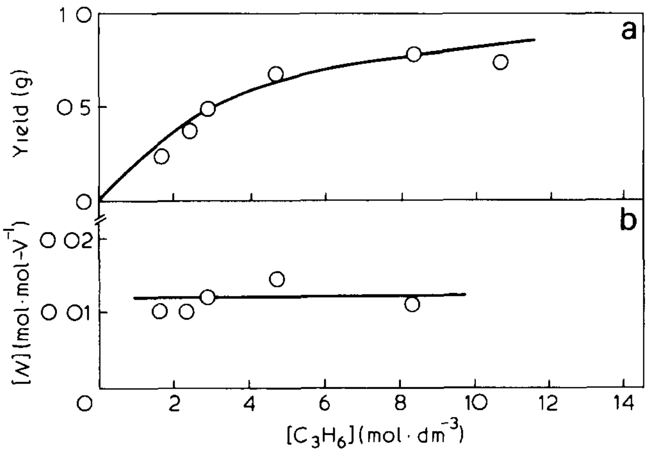


Figure 3 Effects of concentration of propene monomer on polymer yield and on the number of polymer chains produced per vanadium atom [*N*] at −78°C. For polymerization conditions see *Table 1* (Run No. 7 and 20–24)

Table 2 Rate constants K_M and k_p of elementary reactions in the polymerization of propene with various soluble vanadium-based catalyst systems at −78°C

Catalyst system	K_M ($dm^3 \cdot mol^{-1}$)	k_p (h^{-1})	Reference
V(acac)$_3$–Al(i–$C_4H_9)_2$Cl	0.27 ± 0.03	320 ± 40	This work
V(acac)$_3$–Al($C_2H_5)_2$Cl	0.37 ± 0.01	190 ± 70	Doi *et al.*[6]
V(acac)$_3$–$Al_2(C_2H_5)_3Cl_3$	0.16 ± 0.01	5700 ± 1400	Ueki[11]
VCl_4–Al($C_2H_5)_2$Cl	0.26 ± 0.03	4300 ± 1000	Doi *et al.*[10]
VCl_4–Al($C_2H_5)_3$	0.04 ± 0.01	53000 ± 6000	Doi *et al.*[10]

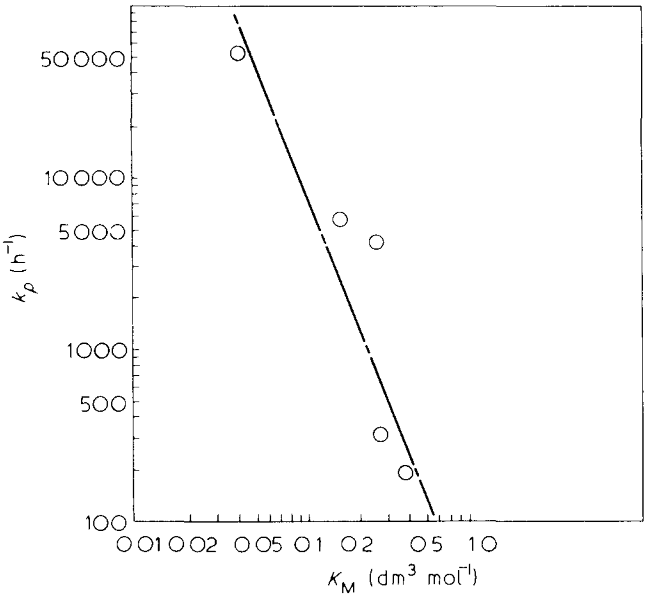
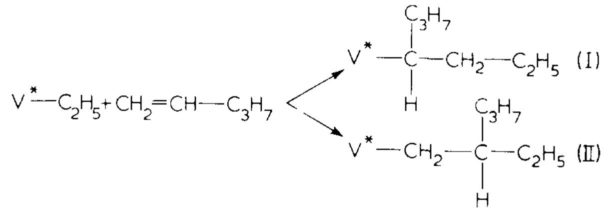


Figure 4 Plots of k_p *versus* K_M

Here, the constants K_M and k_p represent the equilibrium constant for a propene monomer coordination to the active vanadium and the rate constant for a subsequent insertion of the coordinated monomer into a living polymer chain, respectively. *Figure 4* shows the relation between the constants K_M and k_p listed in *Table 2*. The values of K_M and k_p depend on both the vanadium and the aluminium components, and the VCl_4-$Al(C_2H_5)_3$ system gives the highest value of k_p. It can be concluded from *Figure 4* that too strong an interaction between vanadium and propene is unfavourable for the insertion of the coordinated propene into a living polymer chain.

Initiation reaction

In order to elucidate the initiation reaction in the living polymerization, the reaction of pentene-1 with the $V(acac)_3$-$Al(C_2H_5)_2Cl$ system was examined. In this experiment $Al(C_2H_5)_2Cl$ was used in place of Al(i-$C_4H_9)_2Cl$ for convenience on gas-liquid chromatography analysis of the reaction products, and 0.1 mmol cyclopentane was admitted into the reactor as an internal calibrant. After pentene-1 was reacted with the $V(acac)_3$–$Al(C_2H_5)_2Cl$ system at −78°C, the reaction mixture was taken out by means of a syringe at different periods and hydrolysed with cold water. The produces obtained by hydrolysis were then analysed by gas-liquid chromatography (Hitachi 163 FID) with a 2.0 m column filled with squalane. As shown in *Table 3*, heptane and 3-methylhexane were detected after the hydrolysis of the reaction mixture, and their amounts remained unchanged during the course of reaction from 1 to 300 min, indicating that the reaction of pentene-1 with the $V(acac)_3$–$Al(C_2H_5)_2Cl$ system was complete within 1 min. The total amount (0.034 ± 0.002 mol/mol of V) of both C_7-alkanes produced per vanadium atom was almost consistent with the number of polymer chains $[N]$ (0.04 ± 0.01 mol/mol of V) produced per vanadium atom in the living polymerization of propene with the $V(acac)_3$–$Al(C_2H_5)_2Cl$ system[6]. In a control test we confirmed that the hydrolysis of the catalyst mixture itself of $V(acac)_3$ with $Al(C_2H_5)_2Cl$ did not give any C_7 alkanes. These results can be explained in terms of the following mechanism[13] that a pentene-1 molecule adds to an active vanadium–ethyl bond formed by the reaction of $V(acac)_3$ with $Al(C_2H_5)_2Cl$, as



(4)

The resulting vanadium-alkyls, I and II, seems to be stable for long time periods and to be inactive for the subsequent insertion of penetene-1.

As shown in *Figure 2c*, only a small mol % of the vanadium species are active for the living polymerization and the other vanadium species remain inactive. We tentatively propose the following initiation reactions involving alkylation and complexing of $V(acac)_3$ with AlR_2Cl.

$$V(acac)_3 + Al_2R_4Cl_2 \xrightarrow{k_1} \underset{[S_1]}{V(acac)Cl_2\ (AlR_2(acac))_2} \tag{5}$$

$$[S_1] + 2Al_2R_4Cl_2 \xrightarrow{k_2} \underset{[\text{Active complex}]}{RV(acac)Cl\cdot Al_2R_4Cl_2} + 2AlR_2(acac) + Al_2R_3Cl_3 \tag{6}$$

$$[S_1] \xrightarrow{k_3} \text{Inactive complex} \tag{7}$$

$$V(acac)_3\cdot\cdot Al_2R_4Cl_2 \xrightarrow{k_4} [S_2] \longrightarrow \text{Inactive complex} \tag{8}$$

where R, S_1 and S_2 denote an alkyl and different reaction intermediates. Alkylaluminium chloride is known to exist in a dimer form at low temperatures[14]. The inactive complexes may be given *via* reactions (7) and (8) in parallel with the formation of an active complex. Assuming the above schemes, the amount of active vanadium species, [V] active, is given by

$$[V]\ \text{active} = \left(\frac{k_1}{k_1 + k_4}\right)\left(\frac{k_2[A]^2}{k_3 + k_2[A]^2}\right)[V]\ \text{total}$$

$$= \alpha\left(\frac{K_A[A]^2}{1 + K_A[A]^2}\right)[V]\ \text{total} \tag{9}$$

Table 3 Reaction of pentene-1 with $V(acac)_3$–$Al(C_2H_5)_2Cl$ system at −78°C[a]

Time (min)	Products[b] (mmol)		
	Heptane	3-Methylhexane	C_7-Alkene
1	0.023	0.010	0
5	0.022	0.013	0
15	0.023	0.010	0
30	0.024	0.010	0
45	0.023	0.013	0
60	0.024	0.008	0
185	0.024	0.009	0
300	0.022	0.010	0

[a] Reaction conditions: $V(acac)_3$ = 1.0 mmol, $Al(C_2H_5)_2Cl$ = 3.0 mmol, pentene-1 = 9.2 mmol, cyclohexane = 0.1 mmol and toluene = 10 cm^3

[b] The products obtained by hydrolysis of reaction mixture were analysed by gas liquid chromatography

with $\alpha = k_1/(k_1 + k_4)$ and $K_A = k_2/k_3$. Equation 9 is consistent with the experimental formula, equation 1, using the relation that $[N] = [V]$ active/$[V]$ total.

REFERENCES

1 Szwarc, M. *Nature (London)* 1956, **178**, 1169; Szwarc, M., Levy, M and Milkovich, R. *J. Am Chem. Soc.* 1956, **78**, 2656

2 Hostalka, H., Figuni, R. V. and Schulz, G. V. *Makromol. Chem.* 1964, **71**, 198

3 Szwarc, M. 'Carbanions, Living Polymers and Electron Transfer Processes', Interscience, New York (1968)

4 Boor, Jr. J. 'Ziegler-Natta Catalysis and Polymerizations', Academic Press, New York (1979), pp 611–613

5 Doi, Y., Ueki, S. and Keii, T. *Makromol. Chem.* 1979, **180**, 1359

6 Doi, Y., Ueki, S and Keii, T. *Macromolecules* 1979, **12**, 814

7 Grubisic, Z., Rempp, P. and Benoit, H. *J. Polym. Sci. B* 1967, **5**, 753

8 Ogawa, T., Tanaka, S. and Hoshino, S. *Kobunshi Kagaku* 1972, **29**, 6

9 Hamielec, A. E. and Ray, W. H. *J. Appl. Polym. Sci.* 1969, **13**, 1319; Hamielec, A. E. *J. Appl. Polym. Sci* 1970, **14**, 1519

10 Doi, Y., Takada, M. and Keii, T. *Bull. Chem. Soc. Jpn.* 1979, **52**, 1802

11 Ueki, S. *M. Eng. Thesis*, Tokyo Institute of Technology (1979)

12 Zambelli, A., Pasquon, I., Signorini, R. and Natta, G. *Makromol. Chem.* 1968, **112**, 160

13 Takegami, Y. and Suzuki, T. *Bull. Chem. Soc. Jpn.* 1969, **42**, 848; Suzuki, T. and Takegami, Y. *Bull. Chem. Soc. Jpn.* 1970, **43**, 1484

14 Dewar, M. J. S., Patterson, D. B. and Sympson, W. I. *J. Am. Chem. Soc.* 1971, **93**, 1030