Molecular weight distribution and stereoregularity of polypropylenes obtained with $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3$ catalyst system

Yoshiharu Doi, Yoshio Nishimura, and Tominaga Keii
Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, *Japan*
(*Received* 3 *June* 1980; *revised* 8 *September* 1980)

The effects of temperature and catalyst homogeneity on the molecular weight distribution (*MWD*) and stereochemical regulation of polypropylenes produced by $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3$ system have been investigated. The *MWD* of polymers obtained at temperatures below 21°C were unimodal and narrow ($\bar{M}_w/\bar{M}_n \leqslant 2.0$), whereas those obtained at temperatures higher than 31°C were bimodal with one narrow distribution and the other broad one ($\bar{M}_w/\bar{M}_n = 18$) at higher molecular weights. The existence of two different types of catalyst, one soluble with homogeneous catalytic centres and the other insoluble with heterogeneous catalytic centres was found in the polymerization at 41°C. At temperatures below 21°C only soluble catalyst was present and produced isotactic polypropylenes with $[m] = 0.65$. The isospecific nature of soluble titanium-based catalyst is greatly contrasted to the syndiospecific nature of soluble vanadium-based catalyst.

INTRODUCTION

Gel permeation chromatography (g.p.c.) has been employed successfully for the characterization of propagation centres in various polymerizations[1-6], since the molecular weight distribution (*MWD*) curves of polymers produced are sensitive for changes in the nature of propagation centres. In the polymerization of propene with $VCl_4/Al(C_2H_5)_2Cl$ catalyst system, the effect of polymerization temperature on the *MWD* curves of polymers was investigated[1]. The *MWD* of polymers obtained at temperatures below −40°C were found to be unimodal and narrow ($\bar{M}_w/\bar{M}_n \leqslant 2$), while those obtained at temperatures higher than −21°C were bimodal with one narrow distribution and the other broad one ($\bar{M}_w/\bar{M}_n \approx 15$), explained by the existence of two different types of centres, one homogeneous and the other heterogeneous. Recently, we have investigated the *MWD* curves and stereoregularities of polypropylenes produced with different vanadium-based catalyst systems, and found the generality that apparently soluble vanadium-based catalysts always give syndiotactic forms of polypropylene with a narrow *MWD* ($\bar{M}_w/\bar{M}_n \leqslant 2$), whereas apparently insoluble vanadium-based catalysts give isotactic forms of polypropylenes with a broad *MWD* ($14 \leqslant \bar{M}_w/\bar{M}_n \leqslant 19$)[2]. The generality was understood by the difference in the steric environment of active vanadium centre: the syndiotactic propagation is controlled by the asymmetry of the last propylene unit in the growing chain attached to the vanadium atom, whereas the isotactic propagation occurs because of the dominant asymmetric structure of the catalytic centre.

In the present study we will discuss the general feature of propagating centres in a titanium-based catalyst system, $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3$, examining the *MWD* curves and the stereochemical structures of polypropylenes produced. The $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3$ system is selected as a representative example among many titanium-based catalyst systems, since both types of catalyst, soluble and insoluble, are formed from the reaction of $Ti(OC_4H_9)_4$ with $Al_2(C_2H_5)_3Cl_3$ depending on the polymerization conditions.

EXPERIMENTAL

Operations

Polymerization of propene was carried out at temperatures between −20 and 54°C under a constant pressure of 1013 N dm^{-2} in a 500 cm^3 glass reactor with a magnetic stirrer. 200 cm^3 of heptane was used as a solvent. After propene was introduced, prescribed amounts of $Ti(OC_4H_9)_4$ and $Al_2(C_2H_5)_3Cl_3$ were charged at polymerization temperature. Polymerization was timed from the addition of $Al_2(C_2H_5)_3Cl_3$, and quenched at a given time by introducing 100 cm^3 of a dilute ethanol solution of hydrochloric acid. The polymerization rate was determined from the rate of propene absorption, as measured by means of a hot-wire flowmeter with a recorder or a wet gas meter. The polymers obtained were washed several times with 200 cm^3 of ethanol and dried *in vacuo* at 50°C.

The *MWD* of polymers were measured by g.p.c. (Waters Associates, Model 200) with 5 polystyrene gel columns (10^7, 10^6, 10^5, 10^4 and 10^3 pore sizes) at 135°C. The solvent was *o*-dichlorobenzene and the flow rate was 1.0 cm^3 min^{-1}. A *MW* calibration curve was obtained on the basis of the universal calibration[7,8], with 10 standard samples of monodisperse polystyrene of *MW* between 2 100 and 2 610 000. From g.p.c. curves, the number-average and weight-average molecular weights ($\bar{M}_n$, $\bar{M}_w$) were obtained by standard procedures using data at 1/2 count (2.5 cm^3 elution volume).

^{13}C n.m.r. spectra of polypropylenes were recorded at 140°C using a JEOL PS-100 Fourier transform system operating at 25.14 MHz. Solutions were made up in *o*-

0032-3861/81/040469-04$02.00

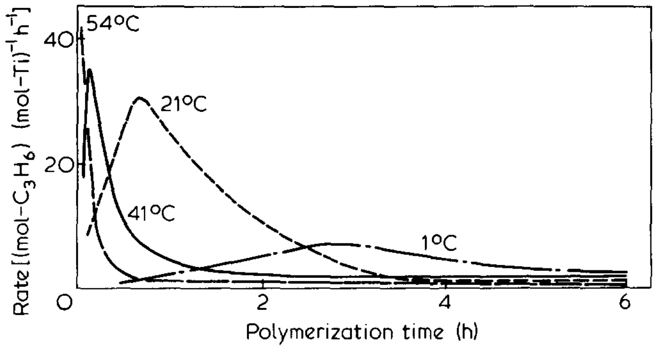

Figure 1 Polymerization rate–time curves at different temperatures (1, 21, 41 and 54°C) with $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3$ catalyst system. Polymerization conditions: $Ti(OC_4H_9)_4$ = 1.2 mmol, $Al_2(C_2H_5)_3Cl_3$ = 12 mmol, heptane volume = 200 cm^3, propene pressure = 1013 N dm^{-2}

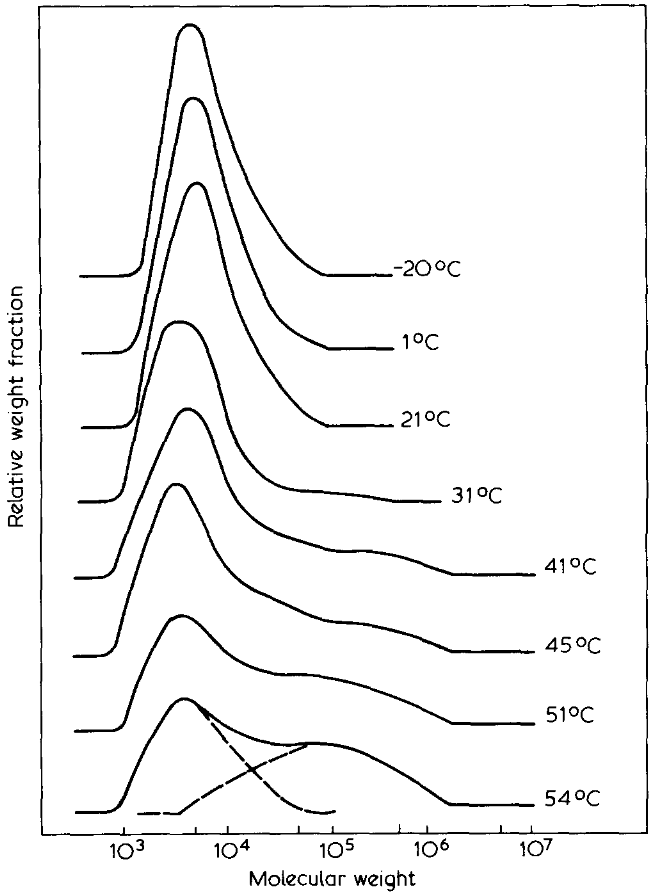

Figure 2 *MWD* curves of polypropylenes obtained in 3 h at different polymerization temperatures. Polymerization conditions are given in *Table 1*

dichlorobenzene to 0.2–0.3 g per 1.0 cm^3 solvent. Instrument conditions were: $\pi/4$ pulse of 13 μs, 4.0 s repetition rate and 4000 Hz sweep width. The number of transients accumulated was 1000. The chemical shift was presented in ppm down field from TMS as internal standard.

Materials

$Ti(OC_4H_9)_4$ (from Wako Pure Chemicals) and $Al_2(C_2H_5)_3Cl_3$ (from 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 passing through columns of sodium hydroxide, phosphorus pentoxide and activated 13X molecular sieve to remove the trace of water. Heptane (pure grade, from Wako Pure Chemicals) was dried by refluxing over sodium metal under a nitrogen atmosphere prior to use.

RESULTS AND DISCUSSION

Molecular weight distribution

Figure 1 shows typical kinetic (polymerization rate *versus* time) curves observed at different temperatures in the polymerization of propene with 1.2 mmol of $Ti(OC_4H_9)_4$ combined with 12 mmol of $Al_2(C_2H_5)_3Cl_3$. The polymerization rate increased during the initial period of polymerization and attained a maximum value. After that, the polymerization rate decreased gradually toward a very low value.

Figure 2 shows the *MWD* curves of polymers obtained in 3 h at different polymerization temperatures. The number-average and weight-average molecular weights ($\bar{M}_n$, $\bar{M}_w$) and the polydispersities ($\bar{M}_w/\bar{M}_n$) calculated from these curves are given in *Table 1*. The *MWD* curves of polymers obtained at temperatures below 21°C are unimodal and narrow ($\bar{M}_w/\bar{M}_n \leq 2.0$). *Figure 3* shows the dependence of polymerization time on the *MWD* curve of polymers obtained at 21°C. The polydispersities were in the range of $\bar{M}_w/\bar{M}_n = 1.8 \pm 0.2$ during the course of polymerization, and are in close agreement with the theoretical value ($\bar{M}_w/\bar{M}_n \leq 2.0$)[9] of polymerization involving chain transfer reactions in which only one type of catalytic centres is operative. However, the *MWD* curve of polymers obtained at 31°C appears to be skewed toward higher molecular weights, as seen from *Figure 2*. This change in the curve can be recognized in the curves of polymers obtained at temperatures higher than 41°C, which are bimodal with one narrow distribution at lower molecular weights and another broad distribution at higher molecular weights. The effect of polymerization temperature on the *MWD* curves may be interpreted in terms of the existence of two different types of catalyst, one homogeneous (soluble) and the other heterogeneous (insoluble), as proposed in $VCl_4/Al(C_2H_5)_2Cl$ catalyst system[1]. It appears that only homogeneous catalyst is present at temperatures below 21°C, while a heterogeneous catalyst participates in the polymerization tog-

Table 1 Molecular weights $\bar{M}_n$ and $\bar{M}_w$ and polydispersities $\bar{M}_w/\bar{M}_n$ of polypropylenes obtained at different polymerization temperatures

Sample	Temp. (°C)	Time (h)	Yield (g)	$\bar{M}_n$ (x10^{-3})	$\bar{M}_w$ (x10^{-3})	$\bar{M}_w/\bar{M}_n$
1	−20	3.0	0.08	3.73	6.75	1.8
2	1	3.0	0.70	3.78	6.05	1.6
3	21	0.25	0.09	4.62	7.83	1.7
4	21	0.5	0.44	4.38	7.27	1.7
5	21	1.0	1.1	3.92	6.91	1.8
6	21	1.5	1.6	3.65	6.81	1.9
7	21	3.0	1.7	4.00	6.56	1.6
8	21	6.0	2.2	3.37	6.77	2.0
9	31	3.0	1.3	2.42	10.8	4.5
10	41	3.0	0.74	5.23	61.3	12
11	45	3.0	0.72	3.20	46.2	14
12	51	3.0	0.46	4.01	106	26
13	54	3.0	0.43	3.90	66.3	17

Polymerization conditions: $Ti(OC_4H_9)_4$ = 1.2 mmol, $Al_2(C_2H_5)_3Cl_3$ = 12 mmol, heptane volume = 200 cm^3, propene pressure = 1013 N·dm^{-2}

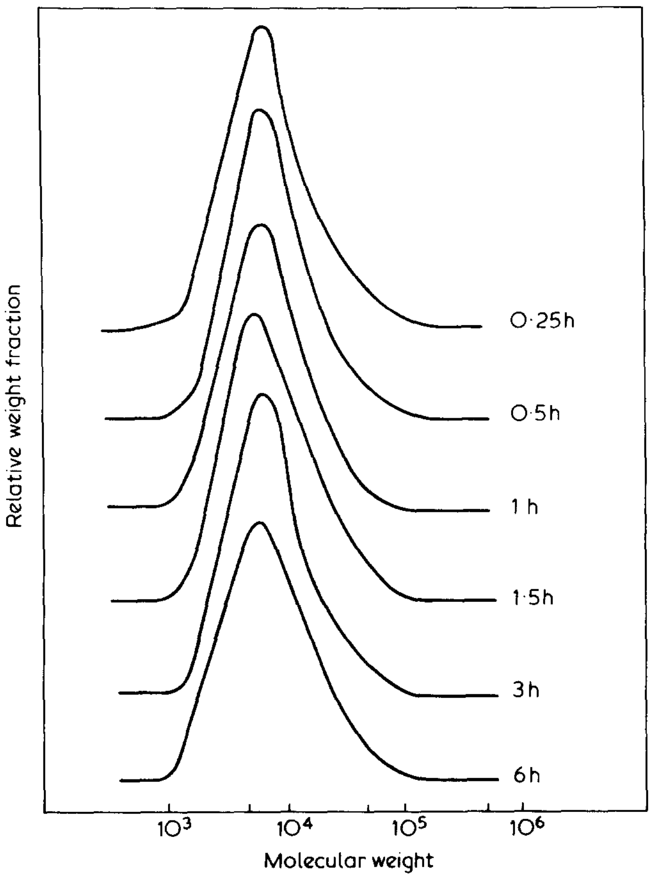

Figure 3 *MWD* curves of polypropylenes obtained in different polymerization times at 21°C

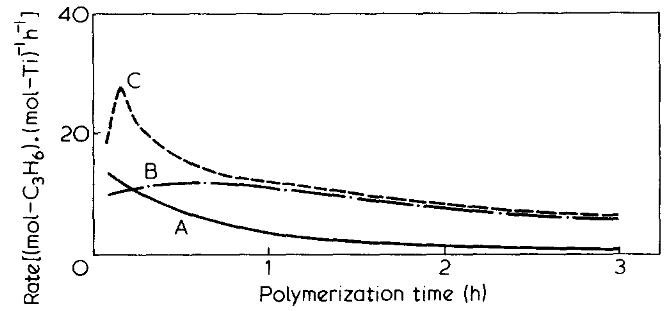

Figure 4 Polymerization rate–time curves at 41°C with the soluble and insoluble catalysts from the reaction of $Ti(OC_4H_9)_4$ (1.2 mmol) with $Al_2(C_2H_5)_3Cl_3$ (4.0 mmol). Polymerization conditions and procedures are referred to in the text. Curve A (——): with soluble catalyst, Curve B (— · —): with insoluble catalyst, Curve C (— — — —): with both catalysts

ether with the homogeneous one at temperatures higher than 31°C. This account may be supported by the observation that the initial catalyst system is apparently soluble at temperatures below 21°C, while fine brown solids appear rapidly when the catalyst components are mixed at temperatures above 41°C.

The following experiment has been made to prove the coexistence of both types of catalyst during the course of polymerization at 41°C. After the polymerization of propene was carried out for 6 min at 41°C with 1.2 mmol of $Ti(OC_4H_9)_4$ and 4.0 mmol of $Al_2(C_2H_5)_3Cl_3$ in 200 cm^3 of heptane, the propene in a reactor was pumped out and nitrogen was admitted. The polymerization solution stood for 5 min to precipitate insoluble catalyst. To fractionate the solution into two portions, a brown solution *A*(ca. 170 cm^3) without any precipitates was transferred into another reactor by means of syringe. The residual solution *B*(ca. 30 cm^3) contained dark brown precipitates. The gas phases in both reactors were changed to propene at the same time and the polymerizations were started again. The results are shown in *Figure 4*. The rate of polymerization with the soluble catalyst decreased rapidly toward a very low value within a few hours of polymerization time (see curve A in *Figure 4*). In contrast, the insoluble catalyst exhibited relatively stable activity during the course of polymerization (see curve B). *Figure 5* shows the *MWD* curves of polymer samples *A* and *B* obtained in 3 h in the respective portions of solution *A* and *B*. The sample *A* has a narrow *MWD* ($\bar{M}_w/\bar{M}_n = 1.8$), whereas the sample *B* a broad *MWD* ($\bar{M}_w/\bar{M}_n = 18$), indicating that the two types of catalyst, one soluble with homogeneous centres and the other insoluble with heterogeneous ones, coexist and function independently in the $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3$ catalyst system at the present experimental conditions.

Stereochemical structure

Figure 6 shows the ^{13}C *NMR* spectra of two samples (*A* and *B* in *Figure 5*) of polypropylenes obtained at 41°C with the soluble and insoluble catalysts arising from the reaction of $Ti(OC_4H_9)_4$ with $Al_2(C_2H_5)_3Cl_3$. The chemical shift assignment and nomenclature for each ^{13}C resonance are the same as those reported by us[10-12]. Each tertiary carbon is denoted as *T* with two Greek subscripts indicating its position relative to the nearest tertiary carbons in both directions along the polymer chain, as suggested by Carman and Wilkes[13]. Each primary carbon is designated by *P* with same Greek subscripts as those for the attached tertiary carbon. Each secondary carbon is designated by *S* with four Greek subscripts, which indicate its position from the nearest and the next neighbour tertiary carbons in both directions along the polymer chain. Some small peaks, other than the major three peaks $S_{\gamma\alpha\alpha\gamma}$, $T_{\beta\beta}$ and $P_{\beta\beta}$, in the spectra arise from the irregular linkage of propylene units in the

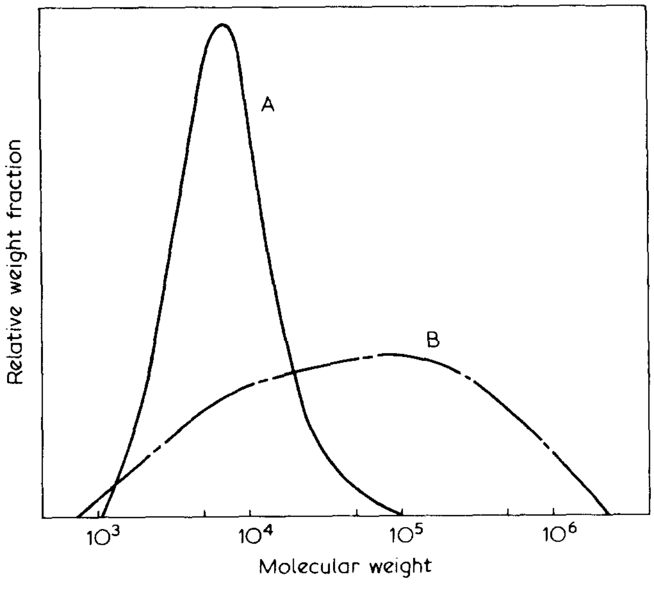

Figure 5 *MWD* curves of polymer samples, *A* and *B*. Samples *A* and *B* were obtained at 41°C in 3 h with the soluble and insoluble catalysts, respectively

Table 2 The stereoregularities and the mol fractions of chemical inversion of polypropylene samples, 2, 7, *A* and *B*

		Stereoregularity (mol %)							
		triad			diads^a	$\frac{2[rr]}{[mr]}$	$\frac{4[mm][rr]}{[mr]^2}$	Chemical inversion	*MWD*
Sample	Temp. (°C)	[*mm*]	[*mr*]	[*rr*]	[*m*]			in mol %	$\bar{M}_w/\bar{M}_n$
2	1	0.51	0.31	0.18	0.66	1.2	3.8	6.9	1.6
7	21	0.49	0.31	0.20	0.65	1.3	4.1	5.6	1.6
A	41	0.48	0.33	0.19	0.65	1.2	3.3	9.5	1.8
B	41	0.60	0.24	0.16	0.72	1.3	(6.7)	5.3	18

^{a} Calculated from triad fractions

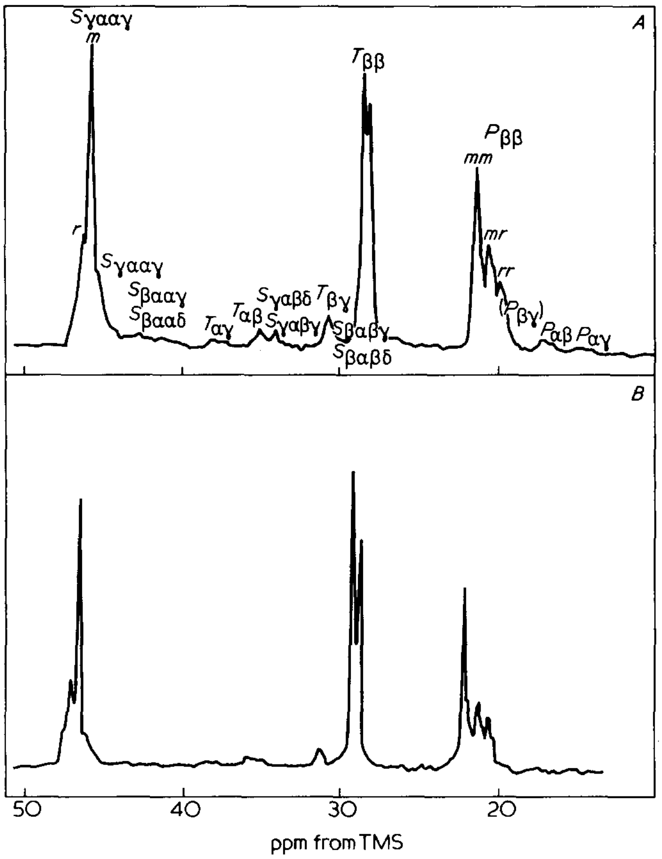

Figure 6 ^{13}C n.m.r. spectra of polypropylene samples *A* and *B* at 140°C in *o*-dichlorobenzene

polymer chain such as a head-to-head unit $\{CH_2-CH(CH_3)-CH(CH_3)-CH_2\}$ and a tail-to-tail unit $\{CH(CH_3)-CH_2-CH_2-CH(CH_3)\}$. The mol fractions of the chemical inversion of the propylene units were determined from the peak areas of tertiary carbon resonances ($T_{\beta\beta}$, $T_{\beta\gamma}$, $T_{\alpha\beta}$ and $T_{\alpha\gamma}$) by the same method used in a previous paper[11]. The results are given in *Table 2*, together with those of polypropylenes (samples 2 and 7 in *Table 1*) obtained at 1 and 21°C. The mol fractions of the steric triads, [*mm*], [*mr*] and [*rr*], were determined from the triad peaks of primary carbon resonance $P_{\beta\beta}$ and listed in *Table 2*. The polypropylene sample *A* obtained at 41°C with soluble catalyst has predominantly isotactic form with $[m]=0.65$. The mol fraction of isotactic dyad, [*m*], is consistent with those of samples 2 and 7 with narrow *MWD* ($\bar{M}_w/\bar{M}_n=1.6$) obtained at 1 and 21°C. Conversely, the insoluble catalyst gives a slightly higher level of isotacticity of $[m]=0.72$ (see sample *B*).

The stereospecific nature of soluble titanium-based catalyst is a great contrast to that of the soluble vanadium-based catalyst which affords syndiotactic form of polypropylene with a narrow *MWD* ($\bar{M}_w/\bar{M}_n=1.1-2.0$). At this time we are not able to present a reliable interpretation concerning the cause of difference in the stereospecific nature of the two soluble catalysts. This problem is the focus of further investigation.

REFERENCES

1 Doi, Y., Kinoshita, J., Morinaga, A. and Keii, T. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 2491
2 Doi, Y., Takada, M. and Keii, T. *Makromol. Chem.* 1979, **180**, 57
3 Soga, K., Izumi, K., Ikeda, S. and Keii, T. *Makromol. Chem.* 1977, **178**, 337
4 Higashimura, T. and Kishiro, O. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 967
5 Pepper, D. C. *J. Polym. Sci., Symp.* 1975, **50**, 51
6 Wada, T., Watanabe, T., Takehisa, M. and Machi, S. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 1585
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 Doi, Y., Takada, M. and Keii, T. *Bull. Chem. Soc. Japan* 1979, **52**, 1802
10 Asakura, T., Ando, I., Nishioka, A., Doi, Y. and Keii, T. *Makromol. Chem.* 1977, **178**, 791
11 Doi, Y. *Macromolecules* 1979, **12**, 248
12 Doi, Y. *Makromol. Chem.* 1979, **180**, 2447
13 Carman, C. J. and Wilkes, C. E. *Rubber Chem. Technol.* 1971, **44**, 781