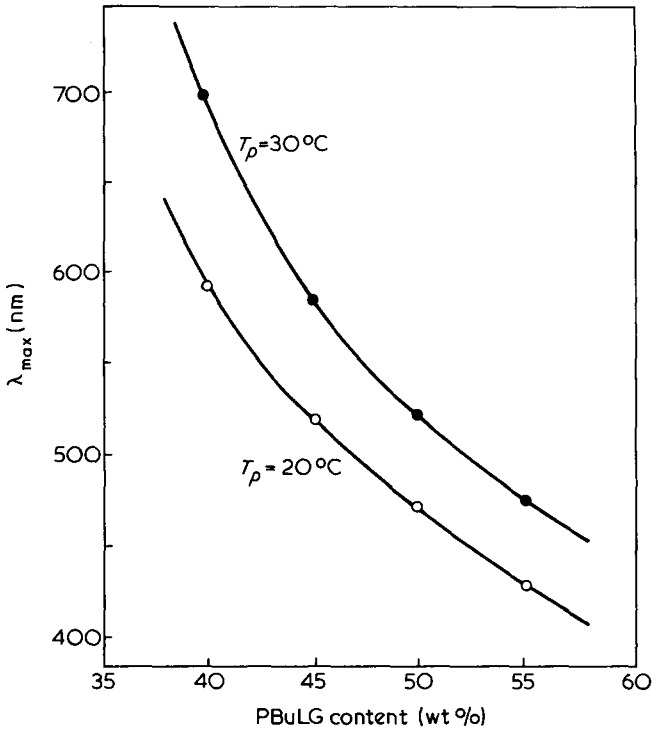

Figure 2 Peak wavelength of selective reflection plotted against the PBuLG content. T_p designates the temperature of polymerization

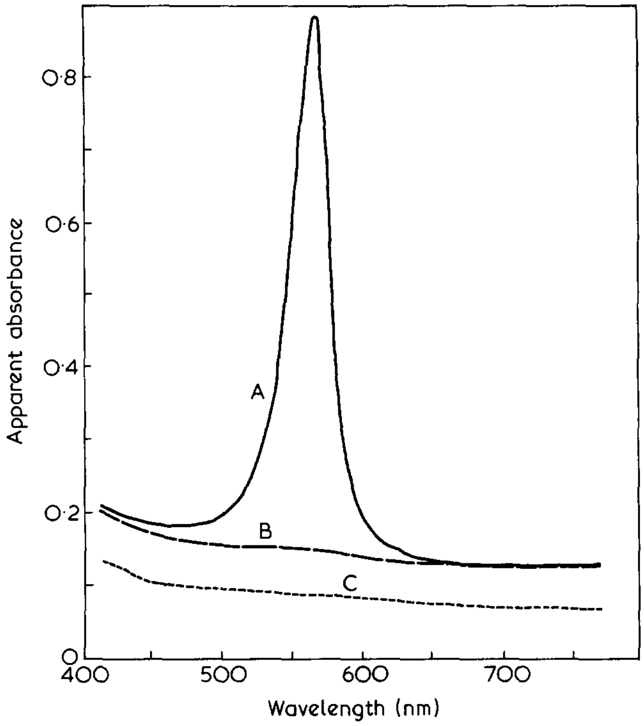

Figure 3 Transmission spectra of the PBuLG/TGDM 50/50 composite films polymerized at 40°C: A, incident light was right circularly polarized; B, incident light was left circularly polarized; C, shifted zero line due to a circular polarizer

mm for example, can easily be prepared. Polymer composites of any shape (and not just thin films) can be moulded, if the cells for the polymerization of the PBuLG/TGDM solutions are properly designed. Third, the wavelengths of their selective reflection can be varied continuously through the entire visible spectral region and tuned precisely to requirements. Finally, the method of preparation is extremly simple: it only requires homogeneous mixing of the two components followed by photo-irradiation.

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Chain transfer induced by molecular hydrogen in the 'living' polymerization of propene with soluble V(acac)$_3$/Al(C$_2$H$_5$)$_2$Cl

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Introduction

Polymers with a narrow Poisson distribution of chain lengths can be obtained by living polymerization, because propagation of all chains is initiated simultaneously and chain transfer and termination are absent[1,2]. Recently, we found that the low-temperature polymerization of propene initiated by the soluble system, V(acac)$_3$ (acac = acetyl acetonate) with Al(C$_2$H$_5$)$_2$Cl gives a syndiotactic polypropylene having a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.05$–$1.20$)[3,4]. This was the first Ziegler-type catalyst exhibiting 'living' character comparable with that of sodium naphthalene or lithium alkyl in anionic polymerization[2]. Here we report the change in the molecular weight distribution of polypropylenes during living polymerization involving molecular hydrogen as a transfer agent. Hydrogen is known to be an effective transfer agent in the polymerization of α-olefins with Ziegler-type catalysts[5–9]. However, there are few reports[10] on the effect of hydrogen on the molecular weight distribution of polymers.

Experimental

A three-necked glass flask (~300 ml) with a magnetic stirrer was used as a reactor. Propene (0.83 mol) was condensed into toluene in the reactor, and kept at −78°C by a methanol/dry ice bath. The amount of toluene was

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adjusted to give a total volume of 100 ml. Given amounts of $Al(C_2H_5)_2Cl$ and $V(acac)_3$ were then charged for the start of the polymerization. For the experiment in which hydrogen was added to the reaction system, hydrogen was first introduced to a desired pressure and the catalyst components were then transferred into the reactor. The polymerization was quenched by adding 100 ml of an ethanol solution of hydrochloric acid kept at −78°C. The molecular weight distribution of the resulting polymers were measured by gel permeation chromatography (g.p.c.) (Waters Associates, Model 200) using 5 polystyrene gel columns (10^7, 10^6, 10^5, 10^4 and 10^3 Å pore sizes) and *o*-dichlorobenzene as solvent as 135°C. The correction of g.p.c. peak spreading (zone spreading) for the polydispersity parameters ($\bar{M}_w/\bar{M}_n$) was carried out on the basis of the method of Hamielec and Ray[11,12].

Results and discussion

Table 1 shows the yields, molecular weights and polydispersity parameters, $\bar{M}_w/\bar{M}_n$, of polymers produced in the course of the polymerization of propene at −78°C in the absence or presence of hydrogen. All of the polymerizations were carried out to low conversions of propene monomer (up to several percent). The concentration of propene monomer, therefore, may be regarded as a constant during the polymerization. Also, it was found that the partial pressure of hydrogen remained essentially constant, since the hydrogen was almost unconsumed during the polymerization. As shown in *Figure* 1*a*, the yield of polymers, i.e. the polymerization activity, was not affected by the presence of hydrogen and was an almost linear function of time through the origin, which indicates that the formation of propagation centres is complete just after starting polymerization and that subsequent polymerization proceeds without deactivation of the centres in each case. The time dependence of the number-average molecular weight, $\bar{M}_n$, of polymers produced is shown in *Figure* 1*b*, and *Figure* 1*c* shows the relation between polymerization time and the number of polymer chains produced per vanadium atom, [N], calculated from the relation [N] = polymer yield/$\bar{M}_n$. In the absence of hydrogen the number of polymer chains produced per vanadium atom remained almost constant (≈0.04+0.01) during the course of polymerization, indicating that the polymerization proceeds without any

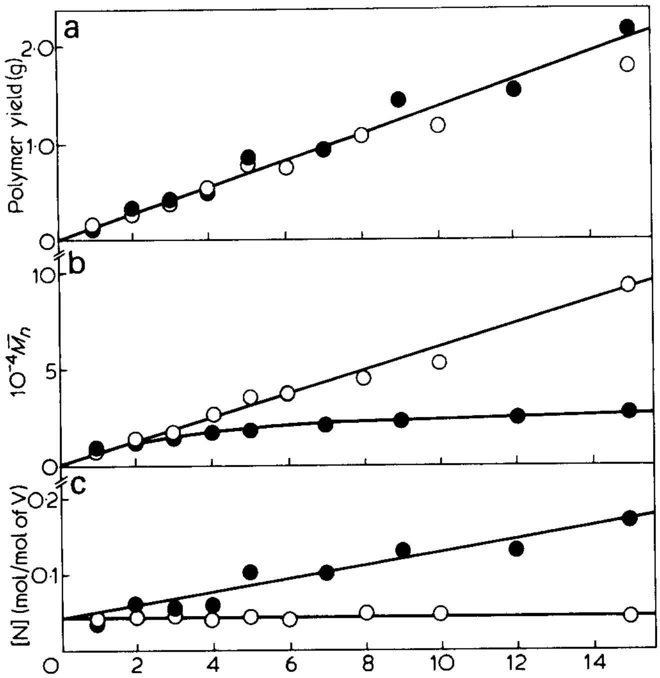

Figure 1 Time dependence of yields and number-average molecular weights $\bar{M}_n$ of the resulting polymers and of the number of polymer chains produced per vanadium atom [N] in polymerization of propene at −78°C with $V(acac)_3/Al(C_2H_5)_2Cl$ in the absence or presence of hydrogen: ○, without hydrogen; ●, under a hydrogen pressure of 0.91 bar. Polymerization conditions are given in *Table 1*

Table 1 Results of propene polymerization at −78°C with the $V(acac)_3/Al(C_2H_5)_2Cl$ system in the absence or presence of hydrogen: [propene] = 8.3 mol dm^{-3}, [$V(acac)_3$] = 0.005 mol dm^{-3}, [$Al(C_2H_5)_2Cl$] = 0.05 mol dm^{-3} and toluene solution = 0.1 dm^3

Run	P_{H_2} (bar)	Time (h)	Yield (g)	Molecular Weight		$[N]^b$ (mol/mol of V)
				$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n{}^a$	
1	0	1.0	0.11	0.604	1.11	0.036
2	0	2.0	0.27	1.20	1.13	0.045
3	0	3.0	0.35	1.60	1.14	0.044
4	0	4.0	0.51	2.50	1.17	0.041
5	0	5.0	0.75	3.52	1.12	0.043
6	0	6.0	0.75	3.75	1.12	0.040
7	0	8.0	1.07	4.42	1.14	0.048
8	0	10.0	1.18	5.16	1.16	0.046
9	0	15.0	1.76	9.13	1.18	0.039
10	0.91	1.0	0.11	0.671	1.17	0.033
11	0.91	2.0	0.33	1.06	1.25	0.062
12	0.91	3.0	0.40	1.42	1.38	0.056
13	0.91	4.0	0.50	1.61	1.49	0.062
14	0.91	5.0	0.86	1.71	1.51	0.100
15	0.91	7.0	0.96	1.96	1.62	0.098
16	0.91	9.0	1.41	2.21	1.61	0.128
17	0.91	12.0	1.55	2.40	1.69	0.129
18	0.91	15.0	2.17	2.66	1.68	0.163

[a] Corrected for g.p.c. peak spreading; [b] number of polymer chains produced per vanadium atom

chain transfer reaction. The polydispersity parameters ($\bar{M}_w/\bar{M}_n$) of the resulting polymers were as narrow as 1.14 ± 0.04. However, under a hydrogen pressure of 0.91 bar the number of polymer chains increased with polymerization time, indicating that hydrogen acts as a chain transfer agent in the living polymerization initiated by the soluble $V(acac)_3/Al(C_2H_5)_2Cl$ system. The polydispersity parameters of polymers increased during the polymerization and approached 2.0, corresponding to a most probable chain length distribution.

The effects of hydrogen pressure on the yield and the molecular weight of polymers produced in 5 h are given in *Table* 2. The polymer yield remained constant while the number-average molecular weight, $\bar{M}_n$, decreased with the hydrogen pressure, indicating the instantaneous rebirth of propagation centres following chain transfer by hydrogen. As shown in *Figure* 2, the number of polymer chains increased with the hydrogen pressure. As a result, the number of polymer chains, [N], produced per vanadium atom at time, *t*, could be expressed by:

$$[N]=[N^*]+k_t[H_2][N^*]t \qquad (1)$$

where [N*] is the number of propagation centres per vanadium atom and k_t is the rate constant for chain transfer by molecular hydrogen, H_2. The chain propagation, the chain transfer by molecular hydrogen and the subsequent reinitiation may be written schematically as:

$$\text{Propagation: } V-P_i^*+M\xrightarrow{k_p}V-P_{i+1}^* \qquad (2)$$

$$\text{Transfer: } V-P_i^*+H_2\xrightarrow{k_t}V-H+P_i \qquad (3)$$

$$\text{Reinitiation: } V-H+M\xrightarrow{k_i}V-P_1^* \qquad (4)$$

Here, $V-P_i^*$, P_i and M denote the living *i*-mer chain attached to the active vanadium atom, the dead *i*-mer chain and propene monomer, respectively, and k_p and k_i represent the rate constants for propagation and reinitiation.

If we make the following assumptions: (a) an instantaneous formation of propagation centres at $t=0$; (b) an instantaneous reinitiation after the transfer reaction, i.e. $k_i[M]\rightarrow\infty$; and (c) both concentrations of propene monomer and hydrogen remaining constant during the polymerization, then the number-average and weight-average degrees of polymerization at time *t* are given by[13]:

$$\bar{P}_n=\frac{\sum\limits_i i(P_i^*+P_i)}{\sum\limits_i (P_i^*+P_i)}=\frac{1+(\alpha+\beta)t}{1+\beta t} \qquad (5)$$

$$\bar{P}_w=\frac{\sum\limits_i i^2(P_i^*+P_i)}{\sum\limits_i i(P_i^*+P_i)}=\frac{1+(\alpha+\beta)(1+2\frac{\alpha}{\beta})t-2(\frac{\alpha}{\beta})^2(1-e^{-\beta t})}{1+(\alpha+\beta)t} \qquad (6)$$

with $\alpha=k_p[M]$ and $\beta=k_t[H_2]$. Combining equations (5) and (6), we calculated the polydispersity parameter ($\bar{M}_w/\bar{M}_n$) of polymers during polymerization under a hydrogen pressure of 0.91 bar, using the mean values of $\alpha(=150\ h^{-1})$ and $\beta(=0.18\ h^{-1})$ determined from *Figure* 1. The result is shown in *Figure* 3 by a full line. For comparison, experimental data in *Table* 1 are plotted in *Figure* 3. The theoretical and experimental polydispersity parameters are in agreement.

Table 2 Polymerization results obtained at −78°C under different pressures of hydrogen: polymerization time = 5 h, [propene] = 8.3 mol dm^{-3}, [V(acac)$_3$] = 0.005 mol dm^{-3}, [Al(C$_2$H$_5$)$_2$Cl] = 0.05 mol dm^{-3} and toluene solution = 0.1 dm^3

Run	P_{H_2} (bar)	Yield (g)	Molecular weight $10^{-4}\bar{M}_n$	Molecular weight $\bar{M}_w/\bar{M}_n$ [a]	[N] [b] (mol/mol of V)
5	0	0.75	3.52	1.12	0.043
19	0.21	0.81	2.83	1.24	0.057
20	0.51	0.85	2.45	1.36	0.069
21	0.71	0.91	2.03	1.48	0.089
14	0.91	0.86	1.71	1.51	0.100

[a] Corrected for g.p.c. peak spreading; [b] number of polymer chains produced per vanadium atom

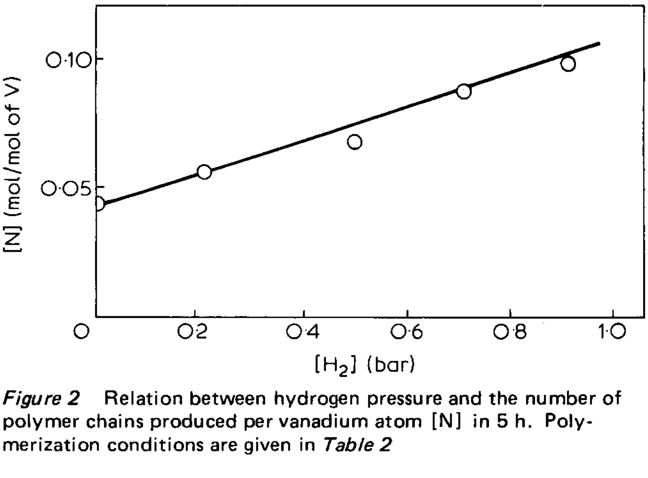

Figure 2 Relation between hydrogen pressure and the number of polymer chains produced per vanadium atom [N] in 5 h. Polymerization conditions are given in *Table 2*

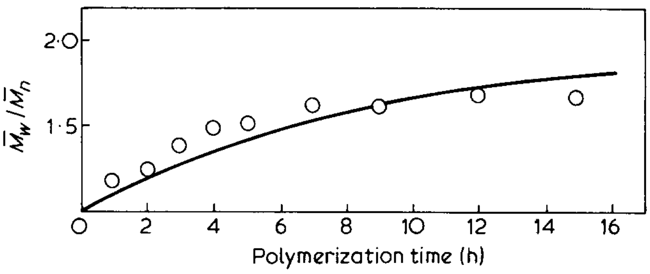

Figure 3 Change in the polydispersity parameter ($\bar{M}_w/\bar{M}_n$) of polymers during the polymerization at −78°C under the hydrogen pressure of 0.91 bar: ○, experimental data in *Table 1*; ———, theoretical curve calculated from equations (5) and (6) with α = 150 h^{-1} and β = 0.18 h^{-1}

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Hypersonic loss processes in poly(dimethyl siloxane) and the effects of crosslinking

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In an earlier paper we reported Brillouin scattering measurements of the hypersonic sound speed and damping of longitudinal acoustic phonons in a series of poly(dimethyl siloxane) (PDMS) rubbers[1]. It was proposed that the observed dependence of the sound speed (V_s) and loss tangent ($\alpha\lambda_s$) on crosslink density might be accounted for by movement of the α loss peak in a manner analagous to the well-known dependence of the glass transition temperature on the degree of crosslinking.

It was argued that crosslinking the gum extended the minimum size of the region which must simultaneously undergo rearrangement in order to permit mobility — essentially an application of the cooperaitve model of Adam and Gibbs[2]. However, a simple model based on this notion, and assuming the 240K loss peak to be the main α process[3], failed to account quantitatively for the frequency dependence of the loss data. It is the purpose of this communication to report measurements of hypersonic loss in a highly crosslinked PDMS rubber taken over a wide temperature range (200–400K). These measurements were made in order to discover the effect of crosslinking on the 240K loss peak, and in the Figure we display the hypersonic loss tangent ($\alpha\lambda_s$) measured as a function of temperature for a network of shear modulus 6.4×10^5 N m^{-2} (○), and an uncrosslinked fluid of weight-average molecular weight 7.7×10^4 (ICI S273-11-3) (x). Both sets of data were obtained at an internal scattering angle of 124° corresponding to phonon frequencies of ~5 GHz. Experimental technique and sample preparation are discussed elsewhere (see ref 1 and refs therein).

One difference is the method by which our samples are mounted in the light scattering cryostat. It was necessary to freeze the polymer in liquid nitrogen because the smallest traces of vapour prevented the necessary sealing of the small glass vial in which they were held. This difficulty prevented us from obtaining the data presented here at the time of our original work: we found a large and irreversible increase in $\alpha\lambda_s$ in networks handled this way[1]. In this work the samples were held in unsealed cells, and measurements made at the relatively low ambient pressure of the cryostat (~0.1 torr). However, the effects of reducing ambient pressure are not detectable in the Brillouin spectra at room temperature, and we assume any effect to be small over the entire range of temperatures. The fluid data is identical to the 5 GHz data reported elsewhere[4]. Clearly the 240K loss peak is little affected by crosslinking, though the loss maximum may be raised by a few degrees.

A similar small effect is seen on the glass transition temperature in differential scanning calorimetry data[1]. However, the relaxation at ~315K is clearly more sensitive to crosslinking. There is a marked increase in relaxation strength, though experimental uncertainty masks any movement of this loss maximum. We must reject the proposal that the crosslink dependence of the 240K process may account for the observed hypersonic properties of these networks. However, these data do indicate that the 318K process is a main chain relaxation of some sort. Our original assignment of the 240K maximum to the α relaxation was based on an extrapolation of a limited amount of dielectric and microwave data on a transition map[4] and the dominance of this process in determining hypersonic loss in series of PDMS oligomers[3]. However, it may be that both these maxima

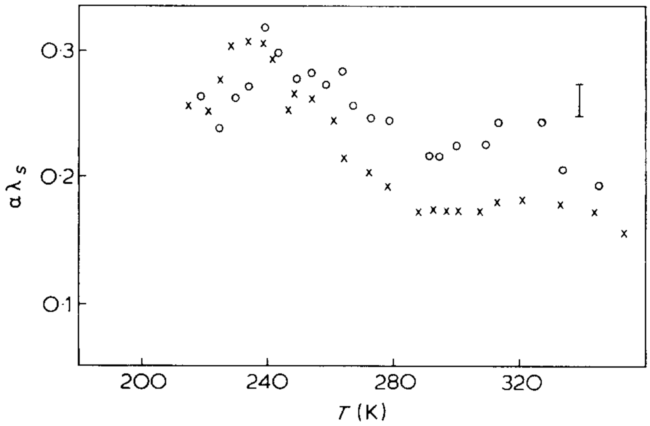

Figure 1 Hypersonic loss tangent ($\alpha\lambda_s$) plotted against temperature for ~5 GHz longitudinal phonons in a PDMS fluid sample (x) and a rubber network of shear modulus 6.4×10^5 N m^{-2} (○). For clarity only one representative error bar is shown

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