

The synthesis of low molecular weight hydroxy-tipped polyethylene and polypropylene by the intermediacy of Ziegler–Natta catalysts

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The use of diethylzinc in conjunction with conventional and supported Ziegler–Natta catalysts permits the synthesis of polypropylene and polyethylene samples with g.p.c. \bar{M}_n values as low as 4000 and 3000 respectively. At high diethylzinc concentrations the number of metal–polymer bonds appears to be 40% for polypropylene and 50% for polyethylene respectively, as measured by a tritium-quench radiotracer method. The metal-bound macromolecules can be efficiently oxidized with molecular oxygen at 60°C, and subsequently hydrolysed to give hydroxy-tipped polymers. The oxidation efficiency appears to be variable and to be lower at high diethylzinc concentrations.

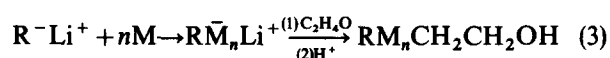
(Keywords: Ziegler–Natta; hydroxy-tipped; polyethylene; polypropylene; diethylzinc; radiotracer)

INTRODUCTION

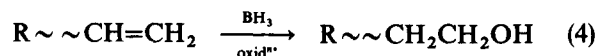
There is a continuing interest in the preparation of functionally terminated polymers as precursors for the synthesis of block or graft copolymers. Hydroxy functionalized macromolecules represent an important class of such materials, and these can undergo a variety of coupling or crosslinking reactions. The hydroxy group may be introduced by a variety of techniques which include: initiation by hydrogen peroxide¹ or a hydroxy-functionalized initiator², e.g.:



termination of an anionic polymerization system with ethylene oxide³, viz.:



or, oxidation of terminally unsaturated polymers⁴, e.g.:

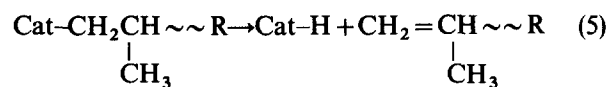


The particular methods are however restricted to certain monomer or polymer types, and are characterized by varying efficiencies and molecular weight distributions.

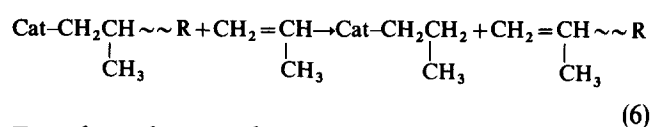
Recently we wished to synthesize low molecular weight ($\approx \bar{M}_n = 10^4$) hydroxy-tipped polymers of ethylene and propylene for use in natural rubber grafting studies⁵. These polymers cannot readily be synthesized by any of the methods outlined above, and indeed polypropylene can only be derived from processes based on transition metal catalysts. Polyolefins prepared by conventional

Ziegler–Natta catalysts are generally of high molecular weight⁶ and are characterized by end-groups determined by the mode of termination or, chain-transfer. Typical molecular weight limiting steps include the following:

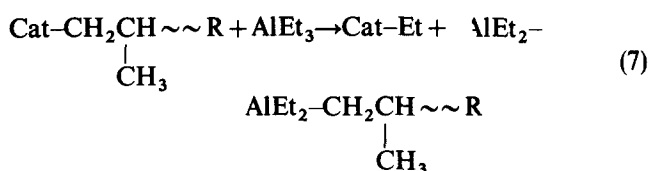
Spontaneous termination



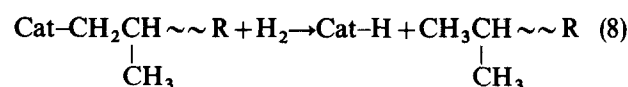
Transfer with monomer



Transfer with co-catalyst



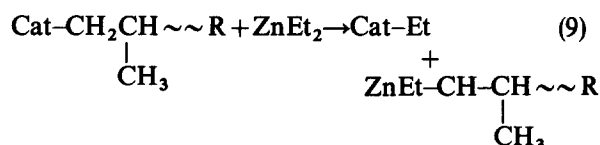
Transfer with hydrogen



which lead to unsaturated (equations (5) and (6)), metal-bound (equation (7)), or saturated (equation (8)) polymer end-groups respectively. The compositional balance of end-groups depends on the reaction conditions, particularly: temperature, monomer and co-catalyst concentrations, and hydrogen pressure. At moderate temperatures in the absence of hydrogen only the monomer

and co-catalyst transfer reactions are of significance. Thus in the polymerization of 4-methyl-1-pentene by the catalyst system $VCl_3/AlEt_3$ at $30^\circ C$ aluminium bound polymers comprise 60% of the end-groups⁷.

However, earlier work has shown⁸ that diethyl zinc is a particularly effective chain-transfer agent in propylene polymerization. It would thus be anticipated that olefin polymerizations conducted in the presence of diethyl zinc should lead to low molecular weight polymer chains predominantly bound to zinc, through transfer reactions such as:



If this is the case, it should prove possible to transform these low molecular weight zinc terminated polymers to hydroxy functionalized macromolecules by appropriate conversion chemistry (*vide infra*).

The development of such a method for the synthesis of functionalized low molecular weight polyethylene and polypropylene forms the subject matter of this paper.

EXPERIMENTAL

Materials

Solvents for polymerization and acetylation procedures were A.R. grade materials which were purified over a period of 3–4 days by drying with two batches of activated ($300^\circ C$) 4 Å molecular sieves⁹ (10% w/v), followed by sparging (10 min) with dry nitrogen.

Ethylene and propylene were B.O.C., C.P. grade (99.5% and 99% minimum purity respectively) and were dried by passing through a molecular sieve column.

Polymerization catalysts $TiCl_3$ Type 1.1 (Ex. Stauffer Co. USA) and Montedison type $MgCl_2$ -supported $TiCl_3$ were supplied by I.C.I. Plastics Division, courtesy of Dr A. D. Caunt. The former catalyst is a purple solid consisting of $TiCl_3$ co-crystallized with approximately 30% $AlCl_3$, whereas, the latter catalyst is derived from a process whereby $MgCl_2$ is first extensively ballmilled with ethylbenzoate and subsequently treated with $TiCl_4$. This high activity catalyst was a brown solid supplied as a slurry, in a high boiling hydrocarbon solvent (EC180), at a titanium concentration of approximately 0.055 M.

Diethyl zinc was purchased as a 25% w/v solution in hexane (Lancaster synthesis) whereas, tri-isobutylaluminium was provided by I.C.I. Plastics as a 1.5 M solution in EC180.

Tritiated methanol of activity approximately 4 mCi/mol was synthesized by the addition of 1 ml (5 mCi) of T_2O (Ex. Amersham International) to 50 ml of dry AR grade methanol. After overnight exchange excess water was removed by drying¹⁰ the labelled methanol with three sequential batches of activated 3 Å molecular sieves (≈ 15 –20 w/v). The labelled methanol was stored in a conical flask equipped with rubber serum cap in a fume-cupboard.

^{14}C -labelled acetic anhydride of specific activity 590 $\mu Ci/mol$ was prepared by dilution of 250 μCi of labelled anhydride, supplied by Amersham International, with 40 ml (43 g) of inactive AR grade acetic anhydride. The compound was stored at $-20^\circ C$ to minimize decomposition.

Polymerization procedure

The polymerization apparatus shown schematically (Figure 1) was set up in a fume cupboard. The polymerization vessel (100 ml or 500 ml two-neck r.b. flask) was cleaned, dried for at least several hours in an oven ($110^\circ C$) and slowly purged with N_2 for at least 1 h before use.

After the final N_2 purging the two stopcocks on the reaction vessel head adaptor were closed and vessel transferred to the dry-box. (At the same time the monomer gas flow was started so as to purge the drying column and system from nitrogen).

The reaction vessel was then charged with the requisite amounts of solvent, co-catalyst, transfer agent and catalyst in that order. (The Stauffer $TiCl_3$ catalyst was preweighed into a small double closure weighing bottle, whereas, the $MgCl_2$ catalyst slurry was vigorously shaken and added by syringe).

After addition of catalyst, the reaction vessel was immediately and swiftly removed from the dry-box and coupled to the polymerization line. (Note: it is essential to avoid excessive delays as the catalyst decays rapidly in the absence of monomer.) On reconnection of the reaction vessel both stopcocks were opened, rapid magnetic stirring commenced, and the gas flow adjusted so that a positive monomer pressure was maintained without excessive wastage of material. When necessary the reaction vessel was surrounded by an oil-bath so as to moderate or elevate the temperature as required.

After 1 h polymerization (or, as otherwise specified) the monomer flow was stopped and replaced by a stream of nitrogen. The reaction mixture was then either quenched with tritiated methanol or oxidized with molecular oxygen. In the former case an appropriate excess of tritiated methanol ($\approx 50\%$ molar excess on all hydrolysable metal bonds) was added dropwise (over a 20–25 min period) by syringe through the serum cap. (This slow addition obviates the necessity for correction of the isotope effect¹³). The reaction mixture was then left for a further 30 min before pouring into excess ($\times 8$) acidified methanol (1% v/v conc. HCl).

Oxidation procedure

The polymerization mixture, under nitrogen, was first heated by means of an oil-bath to approximately $60^\circ C$, whereupon a slow stream of oxygen was passed through the rapidly stirred mixture. This was continued for 1 h (for small scale reactions) or $1\frac{1}{2}$ h (for larger scale) with the temperature maintained between 60° – $65^\circ C$. At the end of this period no white fumes were visible in the reaction pot, and the catalyst was hydrolysed by the addition of a 50/50 mixture of methanol/concentrated HCl (1 ml/mmol

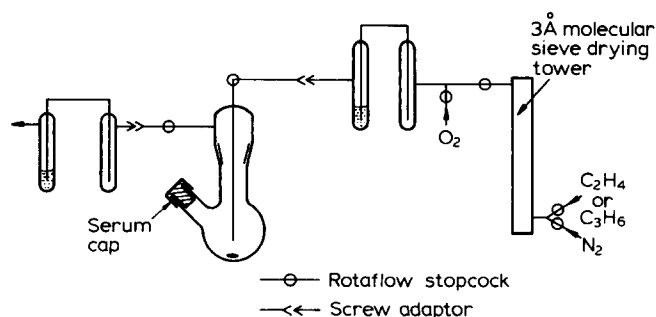


Figure 1 Schematic diagram of polymerization and oxidation apparatus

ZnEt₂). (Caution: vigorous effervescence may accompany the addition of acid at high zinc concentrations probably due to the evolution of hydrogen on reaction of acid with precipitated metallic zinc.) After 10–15 min, during which time the reaction mixture was decolorized, the polymer was precipitated by pouring into a large excess ($\times 6$) of methanol.

Polymer purification

Poly(olefins) were filtered on a glass sinter, sucked dry, and subsequently dried overnight under high vacuum at 60°C. Polymers were purified by reprecipitation from toluene. (Dissolution was effected by stirring whilst heating under nitrogen in an oil-bath at 120°C.)

Polymer acetylation

The hydroxy content of oxidized polymers was assayed by acetylation with ¹⁴C-labelled acetic anhydride¹¹. In a typical procedure 50 mg of dimethylaminopyridine (DMPA), 0.5 ml pyridine and 400 mg of sample were stirred together in 10 ml of dry toluene. After addition of 0.15 ml labelled acetic anhydride the mixture was refluxed with stirring in an oil-bath set at 120–130°C. The reaction mixture was maintained for 1 h under a positive pressure of nitrogen after which the polymer was precipitated into a large excess ($\times 15$) of acidified methanol. The labelled polymer was dried at the pump (≈ 30 min) and subsequently reprecipitated twice from hot toluene before final vacuum drying at 60°C overnight. (Control experiments showed that this procedure was adequate for removal of radioactive by-products.)

Radiochemical purity of acetic anhydride

The radiochemical purity was determined by derivative analysis through acetylation of high purity n-octadecanol. (BDH minimum purity 99%.) The acetylation was carried out under the procedure described above but using 11.40 mg of n-octadecanol weighed precisely with a micro-balance. After 1 h the reaction mixture was cooled to room temperature and 0.2116 g of octadecylacetate was added. After thorough mixing the toluene solution was washed twice with 2N HCl (2 \times 20 ml) and twice with water (2 \times 20 ml). The toluene solution was dried overnight with molecular sieves (10% w/v) and evaporated to dryness on a rotary evaporator. The white residue was then dissolved in the minimum amount of benzene and freeze dried overnight.

Comparison of the specific activities of the initial acetic anhydride and the derived octadecyl acetate showed a radiochemical purity of 92.6%.

[Note: The efficiency of acetylation at temperatures of 110°C is markedly dependent on the molar excess of acetic anhydride. Thus for a small scale acetylation using only a 3 molar excess the efficiency is only 29%. For polymer acetylations approximately a 40 molar excess was used, as in the above determination of radiochemical purity.]

Radioassay of labelled compounds

Labelled polymers and precursors were assayed in a toluene based scintillation cocktail containing 6 g/l of butyl-PBD. Polymers were assayed as gels prepared by heating approximately 100 mg of sample in 10 ml of the above cocktail in an oilbath at 120°C. Solution was normally complete in 10–30 min.

Acetic anhydride (¹⁴C) and tritiated methanol were assayed by a dilution analysis in toluene.

Samples were counted to a 0.5% counting error with a Beckmann Liquid Scintillation Spectrometer.

Radioactivities of polymers and reagents were determined by a ratio method which precludes the necessity of determination of absolute counting efficiency. The method is described in detail elsewhere¹².

Molecular weight assay

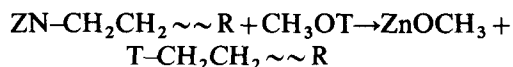
The polyolefin samples were characterized by g.p.c. analysis utilizing the commercial service offered by RA-PRA, UK. Measurements were made in 1,2-dichlorobenzene, stabilized with 2,6-di-tertbutyl-*p*-cresol, at 150°C using P.L. gel columns of dimensions 1 \times 10⁶ Å, 1 \times 10⁴ Å, 1 \times 500 Å. Molecular weights were calculated by applying the 'Universal Calibration' procedure.

Samples were analysed in three separate batches over a period of several months. A standard polypropylene sample was, however, run in each batch and showed the following series of values: $\bar{M}_n = 9000$, $D = 37.6$; $\bar{M}_n = 9300$, $D = 30.3$; $\bar{M}_n = 7800$, $D = 28.1$.

RESULTS AND DISCUSSION

Synthesis of metal-bound polypropylene

Initial experiments centred on the use of a TiCl₃.AA/Al(*i*Bu)₃ catalyst system for propylene polymerization with diethyl zinc as transfer agent. The formation of metal-bound chains was monitored by quenching the polymerization mixture with methanol labelled with tritium in the hydroxyl position⁷:



Only chains bound to zinc or aluminium are labelled with tritium, and under these conditions contamination by extraneous tritium exchange¹³ is negligible. The tritium content of the polymer is most meaningfully expressed by calculation of the equivalent number average molecular weight (\bar{M}_{n_T}) assuming one bound tritium per chain. This quantity is readily calculated from the expression:

$$\bar{M}_{n_T} = \frac{\text{specific activity of methanol (dpm/mol)}}{\text{specific activity of labelled polymer (dpm/g)}}$$

The results (Figure 2) summarize the effect of diethyl-zinc concentration on the polymer yield and \bar{M}_{n_T} . It is apparent that increasing [ZnEt₂] progressively decreases the tritium average molecular weight. The results are closely similar (Figure 2) with the much earlier work of Firsov *et al.*⁸ who determined molecular weight by viscometry. However, in contrast to earlier kinetic studies¹⁴ the polymer yield only falls slowly at increased [ZnEt₂]. This is probably due to the lower polymerization temperatures employed in the present work which minimizes the tendency for over-reduction of the catalyst. This interpretation is corroborated by the reduced yields obtained on polymerizing at 50°C (Figure 2).

The results show that poly(propylene) with \bar{M}_{n_T} values of 15–25 $\times 10^3$ may be readily produced at moderate concentrations of transfer agent. The lower molecular weight limit at very high [ZnEt₂] would appear to be about 8 $\times 10^3$.

The fraction of chains bound to zinc or aluminium (x_{Me})

may be estimated by comparison of the value of \bar{M}_{nT} with the number average molecular weight as measured independently by g.p.c. ($\bar{M}_{ng.p.c.}$) (Table 1). In the absence of transfer agent approximately 16% of the chains appear to be bound to aluminium and this apparently increases to about 40% in the presence of $ZnEt_2$. The latter value appears much too low bearing in mind that the presence of $ZnEt_2$ increases the chain transfer rate by a factor of about 13–24 times. It seems possible that the accuracy of the g.p.c. measurement may be poor at these low molecular weights especially as the molecular weight distribution is exceedingly broad (see Experimental section).

Two further experiments were conducted using a high activity magnesium chloride supported catalyst. These appear to give slightly higher \bar{M}_{nT} values but are characterized by much narrower MWD (Table 1), and show somewhat lower metal end-group composition.

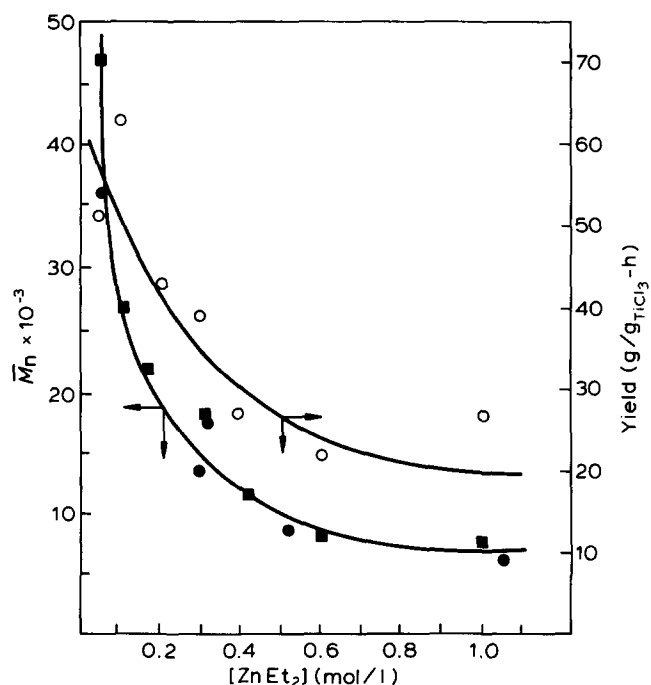


Figure 2 Dependence of molecular weight and polymer yield on diethylzinc concentration. ■ M_{nT} data (this study); ● M_n data from Firsov *et al.*⁸; ○ yield data (this study); catalyst = $TiCl_3 \cdot AA/Al(iBu)_3$; solvent = toluene; temperature = 15°–40°C

Synthesis of metal-bound polyethylene

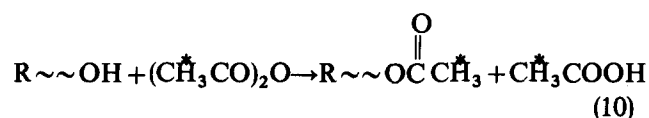
Several analogous exploratory experiments were conducted employing ethylene as monomer, and the results of these for both catalyst types are summarized in Table 1. It is apparent that the catalysts are somewhat more active for ethylene polymerization and the polymers are of lower molecular weight than the propylene counterparts. At modest levels of transfer agent \bar{M}_{nT} values of around 6000 are readily obtainable. Depending on the validity of the g.p.c. \bar{M}_n values a functionality of about 52% appears to be achieved.

As with propylene, the supported catalyst gives very similar \bar{M}_{nT} values to the conventional Stauffer catalyst.

Synthesis of hydroxy-tipped polymers

Determination of hydroxy functionality. A prerequisite for evaluation of hydroxy-tipped polymers is a suitable procedure for measurement of the end-group concentration. Traditionally such analyses have been effected by chemical methods involving acetylation and analysis of unreacted acetic anhydride, but of late spectroscopic methods have been proposed. Thus details of methods based on i.r. measurements of polymer solutions have recently been published^{15,16} and the advantages of this approach discussed.

However, the insolubility of crystalline polyolefins at ambient temperatures precludes the application of solution i.r. studies for this class of polymers, and we decided to employ a sensitive radiotracer earlier used for assay of the hydroxy-content of poly(vinylalcohol) samples¹¹. The method involves acetylation using ¹⁴C-labelled acetic anhydride followed by assay of the tagged polymer:



The method was initially evaluated with samples of hydroxyl-tipped polystyrene³. The efficiency of a variety of catalysts in enhancing the rate of acetylation is summarized in Table 2 for polystyrene samples reacted at 70°C. Acetylation in the presence of an acidic catalyst or a pyridine/DMAP mixture was shown to be superior to pyridine alone. The DMAP-system was chosen as this is a

Table 1 Comparative molecular weight data for polypropylene and polyethylene samples as deduced from g.p.c. and radiotracer measurements

Run No.	Catalyst	[ZnEt ₂] mmol/l	Yield g/gTiCl ₃ -h	\bar{M}_{nT} × 10 ⁻⁴	$\bar{M}_{ng.p.c.}$ × 10 ⁻⁴	D^a	x_{Me}^b
Polypropylene							
5	TiCl ₃ ·AA	0	51	30.2	4.9	22	0.16
10	"	150	—	2.31	0.9	38	0.39
11	"	400	27	1.26	0.42	24	0.33
20	TiCl ₄ /MgCl ₂	0	3795	72.2	2.6	8.8	0.04
19	"	100	966	3.03	0.74	9.9	0.30
Polyethylene							
E4	TiCl ₃ ·AA	0	—	5.05	1.3	31.5	0.26
E1	"	100	97.8	0.58	0.30	30.0	0.52
E6	TiCl ₄ /MgCl ₂	100	3705	0.65	0.27	32.7	0.42

Solvent = toluene; Temperature ≈ 15°–40°C; [Al(iBu)₃] = 30 mmol/l

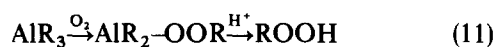
^a Molecular Weight Distribution from g.p.c. \bar{M}_w/\bar{M}_n

^b $x_{Me} = \frac{\bar{M}_{ng.p.c.}}{\bar{M}_{nT}}$

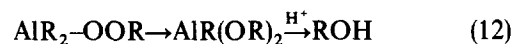
proven mild catalyst¹⁷ with less likelihood of unwanted side reactions. The apparent efficiency of the assay under these conditions is approximately 80%. The absolute efficiency is, however, dependent on the accuracy of the hydroxyl content of the polystyrene sample which was based on a combined g.p.c. and t.l.c. analysis¹⁸.

For subsequent polyolefin analysis the assay was carried out at higher temperatures and one hour reaction time using highly pure n-octadecanol as the standard. Under these conditions the efficiency is anticipated to be high.

Oxidation of metal-polymer bonds. Oxidation reactions of Group II and III metal alkyls have been widely studied, particularly compounds of zinc and aluminium, and these results have been reviewed¹⁹. At low temperatures in the presence of excess oxygen the principal product is a metal peroxide which can be cleaved to yield an alkylhydroperoxide, e.g.:



whereas, at higher temperatures and maintaining low oxygen concentrations the intermediate peroxide is converted to alkoxide and subsequently to an alcohol on acidification:



or,



These processes are moderately efficient and patents claim up to 50% yields²⁰ of alkylhydroperoxide from oxidation of dialkylzincs at -10°C and up to 98% yields²¹ of octanol on oxidizing tri-octylaluminium at 50°C .

In view of the above claims, and the process conditions revealed in the patents it was decided to attempt oxidation of the polymer-metal bonds by treating the polymerization mixture *in situ* with oxygen at a reaction temperature of approximately 60°C . Admission of oxygen into the reaction flask was accompanied by the formation of white fumes presumably due to a gas-phase reaction between oxygen and diethylzinc. For small scale reactions the white fumes were absent after about 20–30 min oxidation and this may be an indicator of complete diethylzinc consumption.

In an initial experiment the reaction mixture was quenched with tritiated methanol after 1 h oxidation. Radioassay of the resultant polymer revealed only 5% incorporation compared with a control. This strongly suggests that oxidation of the metal polymer bonds is essentially complete under the conditions employed. In subsequent experiments the oxidation mixture was hydrolysed in order to generate the functionalized polymer. The results of these experiments (Table 3) indicate that the oxidation efficiency varies considerably but overall the process is surprisingly efficient. Efficiencies in excess of 100% may represent cumulative errors in the analyses, and the fact that the \overline{M}_{nT} value is determined from a separate polymer sample prepared under similar but not identical conditions.

The oxidation efficiency appears to decrease with increasing diethylzinc concentration (compare runs 3, 13, 15 and 8) and this may be indicative of incomplete oxidation at higher levels of transfer agent.

Generally the oxidation efficiency for polyethylene is somewhat lower but whether this can be ascribed to differences in the reactivity of the metal-polymer bond or to differences in the morphology of the nascent polymer is not clear.

CONCLUSION

Low molecular weight hydroxy-tipped polyethylene and

Table 2 Acetylation of hydroxy-tipped poly(styrene)

Catalyst system	$\overline{M}_{n\text{ACET}} \times 10^{-4}$		
	1 h	4 h	
pyridine (0.5 ml)	18 900	13 100	—
p-toluene sulphonic acid hydrate (30 mg)	12 400	12 000	—
pyridine (0.5 ml)	12 200	11 800	
DMAP (50 mg)			
HClO ₄ (μ l)	12 200	11 200	Coloured product

Experimental conditions: Toluene = 7 ml; ¹⁴C-acetic anhydride = 0.15 ml; Temperature = 70°C ; Hydroxy-poly(styrene) = 200 mg

(Calculated $\overline{M}_{n\text{ACET}} = 9 500$); $\overline{M}_{n\text{ACET}} = \frac{1}{2} \times \text{Specific activity acetic anhydride (dpm/mol)} / \text{Specific activity of polymer (dpm/g)}$

Table 3 Oxidation efficiency of metal-polymer bonds

Run No.	[ZnEt ₂] mmol/l	[Catalyst] g/l	[Polymer] g/l	Reaction time (min)	Oxidation Time (min) ^a	$\overline{M}_{nT}^b \times 10^{-4}$	$\overline{M}_{n\text{ACET}} \times 10^{-4}$	Oxidation efficiency (%)
Polypropylene								
3	100	1.34	154	60	60	2.7	2.0	135
13	300	2.18	111	60	60	1.9	1.6	118
15	300	5.96	372	80	70	1.9	2.4	79
8	600	3.31	133	120	60	0.91	1.8	50
Polyethylene								
E2	100	1.91	160	60	60	0.58	0.90	64
E7	100	—	73	60	60	0.65	0.89	73

^a Temperature of oxidation 60° – 65°C

^b Value deduced from Figure 2 or from analogous but separate polymerization

polypropylene can be prepared by the intermediacy of Ziegler-Natta catalyst. The molecular weight distribution of samples prepared with conventional catalysts are, however, extremely broad and this hinders the accurate characterization of the product.

ACKNOWLEDGEMENTS

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