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A novel synthesis of PP-b-PMMA copolymers via metallocene catalysis and borane chemistry

T. C. Chung*, H. L. Lu and W. Janvikul
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
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This paper describes a novel route to prepare polypropylene diblock copolymers, such as PP-b-PMMA, which comprise a polypropylene and free radical polymerized polymer segment. The chemistry involves a transformation process from metallocene catalysis to borane chemistry. Firstly, polypropylene with chain end unsaturation was prepared by metallocene catalysts, such as Et(Ind)$_2$ZrCl$_2$/MAO. Secondly, the olefinic chain end was hydroborated by 9-BBN to produce borane terminated PP. Thirdly, the borane group at the chain end was selectively oxidized and interconverted to polymeric radical which then initiated radical polymerization to produce diblock copolymers. Despite the heterogeneous reaction conditions, the overall yield and structure of diblock copolymers are quite satisfactory. In addition, the chain extension process, showing no significant broading in molecular weight distribution, implies a 'stable' radical polymerization. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

Although useful in many commercial applications, polypropylene suffers a major deficiency, i.e. poor interaction with other materials. The inert nature of polypropylene significantly limits its end uses, particularly, those in which adhesion, dyeability, paintability, printability or compatibility with other functional polymers is paramount. The poor compatibility of polypropylene is further evidenced in polypropylene blends. Attempts to blend polypropylene with other polymers have been unsuccessful for much the same reasons, i.e. the incompatibility of two polymers.

An established technique for improving the interfacial interaction between polymers is the use of block and graft copolymers as compatibilizers[1–3]. The diblock copolymer structure is known to be the most effective compatibilizer. Usually, the incompatible polymer blends can be improved by adding a small quantity (as low as 1%) of suitable diblock copolymer, which alters the morphology of these blends as well as the interfacial adhesion between domains. It is especially desirable to prepare polypropylene diblock copolymers containing functional polymers, such as PMMA, PVA, which can dramatically increase the interaction of polypropylene with a broad range of polymers containing functional groups and substrates, such as glass fibre and metals, with polar surfaces.

Most block copolymers have been produced by sequential living polymerization processes, namely anionic[4–6], cationic[7,8], group transfer[9] and recently metathesis[10,11] living polymerizations. However, the extension of sequential living polymerization to Ziegler–Natta and metallocene polymerizations, for the preparation of polypropylene diblock copolymers, has been very limited. Only a few cases[12–14] have been reported using

very low polymerization temperature conditions and vanadium catalysts. The other methods to prepare polypropylene diblock copolymers involved a transformation reaction, from anionic to Ziegler–Natta polymerization[15], from Ziegler–Natta to free radical vinyl polymerization[16,17] and coupling reaction[18]. In general, the product is most likely an intimate mixture of homopolymers with perhaps some block copolymer. Based on measured lifetimes of the growing chains and the efficiency of the coupling reaction, the yields of polypropylene diblock copolymers are estimated to be well below 20%.

In our previous papers, we have systematically investigated borane-containing polyolefins[19–21] and their functionalized derivatives[22–25]. Both direct and post-polymerization processes have been developed to prepare borane-containing polyolefins which have several borane groups located in the side chains of polyolefin. The borane group not only can be converted to various functional groups but also can be selectively oxidized to the free radical initiator for the subsequent grafting reactions. Several polyolefin graft copolymers, such as PP-g-PMMA[26], EP-g-PMMA[27] and PIB-g-PMMA[28], were reported. They proved to be effective compatibilizers for polyolefin blends, by forming small and uniform domain sizes and increasing the interaction between domains.

Experimental

Instrumental and materials. All room and high temperature ^{1}H n.m.r. were recorded on a Bruker AM-300 spectrometer with DISNMR software. Usually, the polypropylene copolymer was dissolved in *o*-xylene-*d*$_8$ at 110°C. Differential scanning calorimetry (d.s.c.) was measured on a Perkin Elmer DSC-7 instrument controller. The d.s.c.s were measured from 30 to 180°C with a heating rate of 20°C min^{-1}. The molecular weight was determined using a Waters 150C which was operated at

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* To whom correspondence should be addressed

135°C. The columns used were μStyragel HT of 10^6, 10^5, 10^4 and 10^3 Å. A flow rate of 0.7 ml min^{-1} was used and the mobile phase was trichlorobenzene. Narrow molecular weight polyethylene samples were used as standards.

Ethylene bis(indenyl)zirconium dichloride (Et(Ind)$_2$ ZrCl$_2$) was prepared as described in the literature[29]. 9-Borabicyclononane (Aldrich), MAO (Ethyl) and high purity grade propylene (MG Industries) were used as received. H.p.l.c. grade tetrahydrofuran and toluene were deoxygenated by argon sparge before refluxing for 48 h and then distilled from their respective deep blue or purple sodium anthracenide solution under argon. Methyl methacrylate, ethyl methacrylate, vinyl acrylate, butyl acrylate and styrene were dried with CaH$_2$ and distilled under N$_2$.

Synthesis of chain-end unsaturated PP. A 100 ml quantity of toluene and 0.5 g (2.5 mmol in Al) methylaluminoxane (MAO) (30 wt% in toluene) were charged to a Parr reactor in an argon filled dry-box. The sealed reactor was then moved out of the dry box and purged with propylene gas. At 30°C, the catalyst solution of 2.09 mg (5 μmol) of Et(Ind)$_2$ZrCl$_2$ in 2 ml of toluene was added under propylene pressure to initiate the polymerization. Additional propylene was fed continuously into the reactor to maintain a constant pressure of 10 psi during the course of the polymerization. After 60 min, the reaction was terminated by addition of 100 ml of dilute HCl solution in MeOH, the polymer was isolated by filtering and washed completely with MeOH and dried under vacuum at 50°C for 8 h. About 33.7 g of PP fine powder (mp = 138.7°C; $M_n = 25\,700\,\mathrm{g\,mol^{-1}}$; $M_w/M_n = 1.70$; mm = 92.8%) was obtained. The chain end unsaturation was observed by i.r., ^{1}H and ^{13}C n.m.r. measurements.

Hydroboration and oxidation reactions of chain-end unsaturated PP. To a 250 ml glass flask with magnetic stirrer bar, 4.0 g chain-end unsaturated PP was placed in a suspension of 100 ml dry, O$_2$-free THF in an argon filled dry box, the polymer was hydroborated by the addition of 5.0 ml, 0.5 M 9-BBN solution in THF. The polymer slurry was stirred at 55°C for 5 h, then filtered, washed with dry, O$_2$-free IPA and dried *in vacuo*. Chain-end borane containing polypropylene was then obtained.

About 2.0 g of borane terminated PP was placed in a suspension 50 ml dry, O$_2$-free THF in a dry box. The sealed reactor was moved out and purged with nitrogen gas. To the polymer slurry, a solution containing 0.4 g of NaOH in 2 ml H$_2$O and 0.5 ml MeOH purged by N$_2$ was added at room temperature, then 1.6 ml of 30% oxygen-free H$_2$O$_2$ was added dropwise at 0°C. The oxidation was performed at 40°C for 6 h before being poured into 100 ml of MeOH. The polymer solid was filtered, then was refluxed in 100 ml of MeOH for 2 h before distilling off 10 ml MeOH. The hydroxylated PP was then recovered by filtration and was dried in a vacuum oven at 50°C for 8 h. Chain-end OH group in PP was observed by i.r. and ^{1}H n.m.r. measurements.

Synthesis of PP-b-PMMA copolymer. In a typical example, 0.5 g of borane-terminating polypropylene was placed in a suspension of 5 g dry uninhibited MMA with 5 ml THF in a sealed, opaque flask. The reaction was initiated by injecting 0.44 ml dry O$_2$ over a period of 5 h. After stirring the mixture at room temperature for 16 h, the reaction was terminated by addition of 10 ml methanol. The polymer mixtures were isolated by filtration. After drying in a vacuum oven, 1.2 g of white solid was obtained. The polymer mixtures were then fractionated by acetone and heptane extractions in a Soxhlet apparatus under N$_2$ for 24 h, respectively. After solvent removal by vacuum, 0.25 g of acetone-soluble PMMA homopolymer and 0.18 g of heptane-soluble PP homopolymer were obtained. The acetone and heptane insoluble fraction (but soluble in xylene at elevated temperatures) yielded 0.72 g of PP-b-PMMA diblock copolymer with a 67/33 mol ratio between PP and PMMA by ^{1}H n.m.r. measurement.
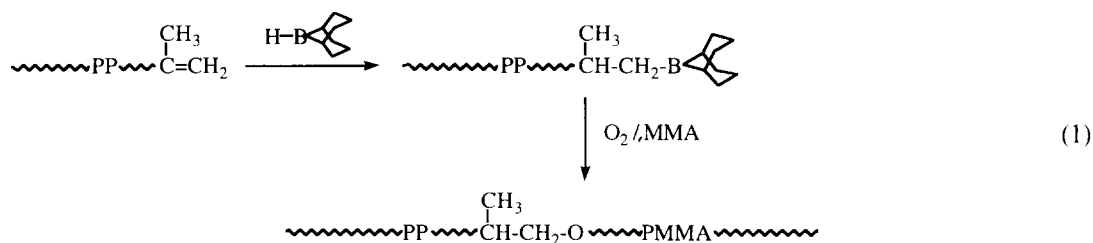
Results and discussion

In this paper, our major goal is to develop a facile method for the preparation of polypropylene diblock polymers, that would permit access to different PP polymers in diblock form. Equation (1) illustrates the reaction scheme which includes three steps, (i) the preparation of polypropylene with chain end unsaturation, (ii) the hydroboration by borane reagent and (iii) oxidation and subsequent free radical chain extension.
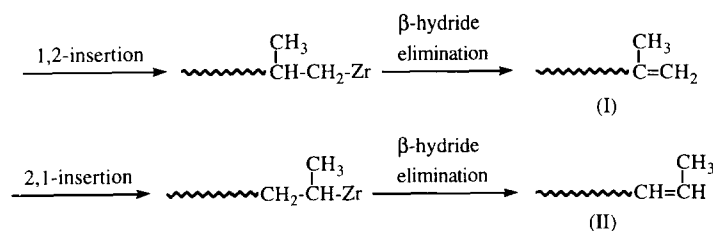
The chemistry involves only one borane group per polymer chain, which provides an ultimate test for examining the efficiency of borane reagent in the chain extension process. In addition, the molecular structure of diblock copolymer will offer valuable information about the reaction mechanism of this new radical polymerization.

Polypropylene with chain end unsaturation. The polymerization reaction was carried out in a Parr reactor under N$_2$ atmosphere by using a homogeneous Et(Ind)$_2$ZrCl$_2$/ MAO catalyst. Usually, the reaction was initiated by charging catalyst solution into the mixture of propylene and toluene. A constant propylene pressure was maintained throughout the polymerization process. The polymerization was terminated by addition of dilute HCl/CH$_3$OH solution. *Figure 1* shows the ^{1}H n.m.r. spectra of polypropylene produced at various temperatures.

As is well known, the major chain transfer reaction in metallocene polymerization of α-olefins is β-hydride elimination, which creates a double bond at the end of each polyolefin chain, as illustrated in Scheme 1.

The unsaturated region in the ^{1}H n.m.r. spectra

$$\mathrm{\sim\sim\sim PP \sim\sim C{=}CH_2} \overset{\mathrm{H-B}}{\longrightarrow} \mathrm{\sim\sim\sim PP \sim\sim CH{-}CH_2{-}B}$$

$$\downarrow \mathrm{O_2\,/\,MMA} \qquad\qquad (1)$$

$$\mathrm{\sim\sim\sim\sim PP \sim\sim CH{-}CH_2{-}O \sim\sim\sim PMMA \sim\sim\sim\sim}$$

Scheme 1

$$\xrightarrow{\text{1,2-insertion}} \text{wwwwwww}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}CH_2\text{-}Zr \xrightarrow[\text{elimination}]{\beta\text{-hydride}} \text{wwwwwww}\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$$

(I)

$$\xrightarrow{\text{2,1-insertion}} \text{wwwwwwww}CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\text{-}Zr \xrightarrow[\text{elimination}]{\beta\text{-hydride}} \text{wwwwwww}CH=\overset{\overset{\displaystyle CH_3}{|}}{CH}$$

(II)
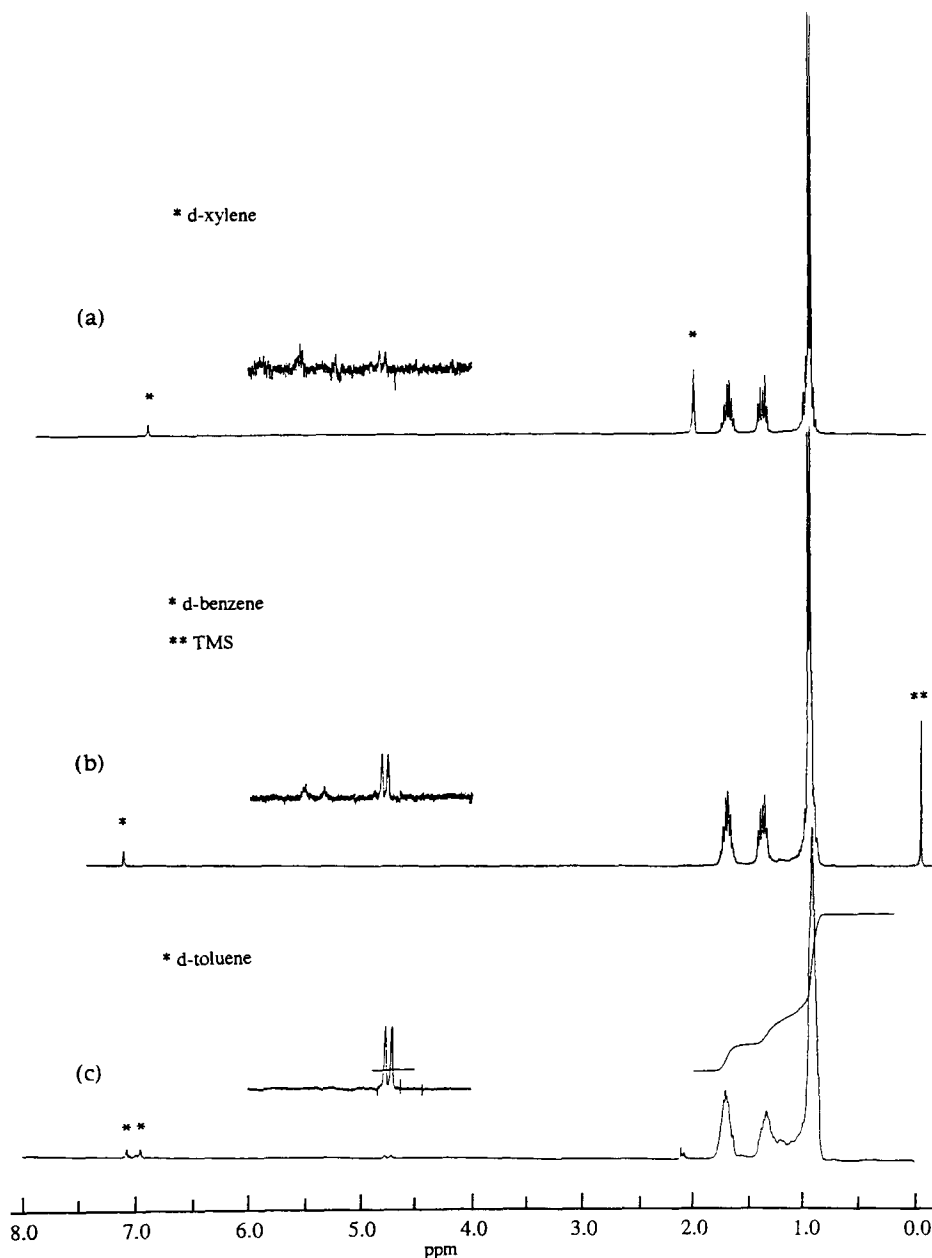
Figure 1 The comparison of ^{1}H n.m.r. spectra of PP polymers prepared by homogeneous $Et(Ind)_2ZrCl_2$/MAO catalyst at (a) 30, (b) 50 and (c) 80°C

clearly shows two types of double bonds. Two singlets at 4.78 and 4.72 ppm, corresponding to $(CH_2=)$ in the external olefin (I), resulting from β-proton elimination from the 1,2-inserted propagating chain end. The multiplets at 5.51 and 5.18 ppm correspond to $(CH=)$ in the internal double bond (II), which is the product of β-proton elimination of the 2,1-inserted propagating chain end. The higher the reaction temperature becomes the higher the olefin concentration, which also indicates

the lower molecular weight. These results are consistent with g.p.c. measurements (discussed later). It is very interesting to note that the ratio of external and internal olefins is very dependent on the reaction temperature. At elevated temperature (such as 80°C), the external double bond is the major product.

Table 1 summarizes the experimental conditions and results. All reactions were carried out under similar conditions, except reaction temperature. The molecular

Table 1 A summary of polypropylene prepared by Et(Ind)$_2$Cl$_2$/MAO catalyst[a]

Run no.	Reaction temp.(°C)	PP molecular weight GPC	$(M_n \times 10^{-3})$ n.m.r.	mm (%)	T_m (°C)	H (Jg^{-1})
1	30	25.7	29.94	92.8	138.7	68.4
2	50	13.0	14.02	87.8	121.1	50.5
3	80		3.2	55.8	61.7	

[a] Al/Zr ratio = 500, propylene pressure = 10 psi, polymerization time = 1 h

weight was determined by both end group (olefin) analysis and g.p.c. analysis. Assuming each polymer has one olefin, the integrated intensity ratio between the chemical shifts of unsaturated (4.5–5.6 ppm) and saturated (0.8–1.8 ppm) regions in ¹H n.m.r. spectra provides the number average molecular weight of polypropylene. Overall, the molecular weights estimated from ¹H n.m.r. spectra are slightly higher than those obtained from g.p.c. measurements. The discrepancy indicates that some of the polypropylene chains may not have olefinic end groups. The isotacticity of polypropylene was determined by ¹³C n.m.r. spectra (mm, isotactic triad) and d.s.c. curves (melting point, T_m and heat of fusion, ΔH). As expected, a high reaction temperature reduces steric regularity and the crystallinity of the polypropylene.

Borane terminated polypropylene. The chain end unsaturated polypropylene was used as the starting material for the preparation of diblock copolymers.
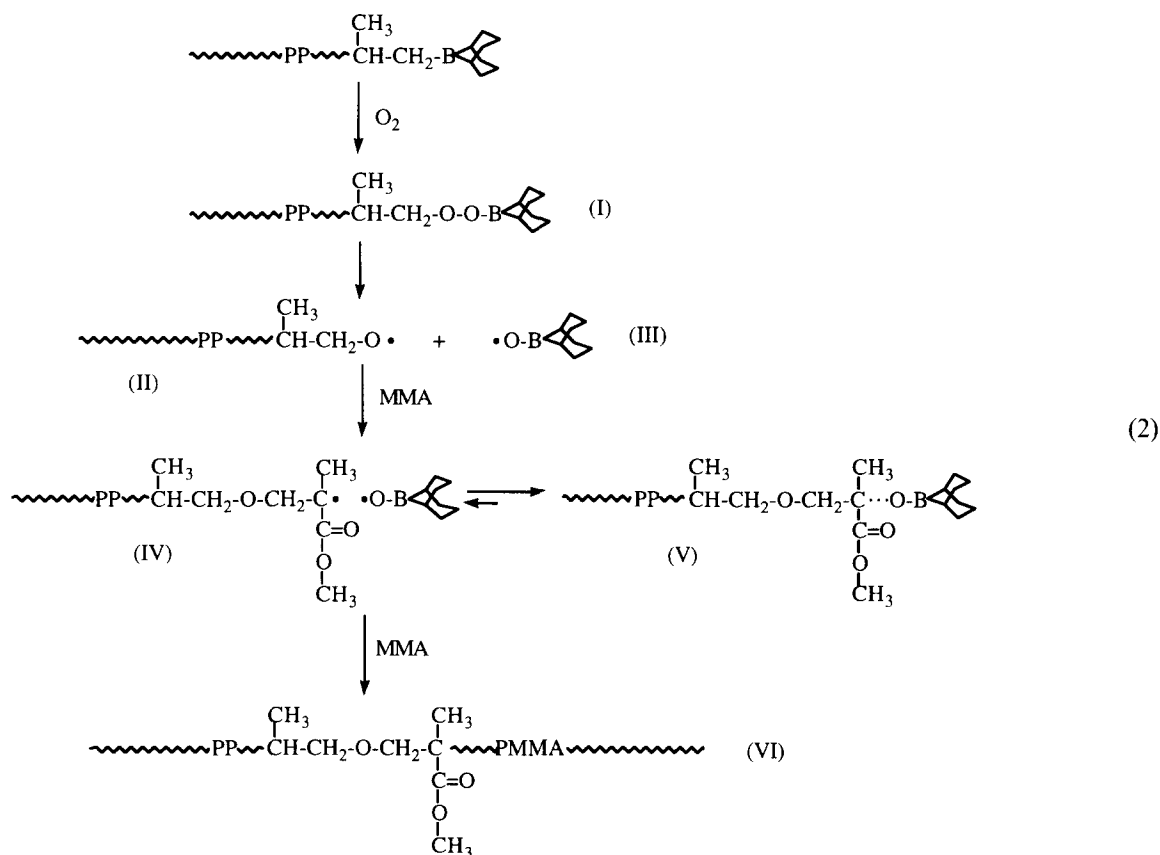
The hydroboration reactions were carried out under heterogeneous reaction conditions by suspending the powder form of polypropylene in THF. A slight excess of 9-borabicyclononane (9-BBN) was used to ensure complete reaction. Usually, the reaction mixture was stirred at 55°C for 5 h before removing the polymer powder from solution by filtration. To examine the efficiency of reaction, some of the hydroborated polymer was oxidized to hydroxylated polymer by using NaOH/H$_2$O$_2$ reagents at 40°C for 6 h. *Figure 2* compares the ¹H n.m.r. spectra of hydroxylated PP and the starting PP (sample 2 in *Table 1*).

Figure 2b exhibits both primary methylene and secondary methine alcohol peaks, appearing between 3.2 and 3.6 ppm, and olefinic chemical shifts between 4.7 and 5.6 ppm disappear to the limit of n.m.r. sensitivity. Apparently, both hydroboration and oxidation reactions were not inhibited by the insolubility of polypropylene. The efficiency of the reaction must be due to the high surface area of reaction sites. While some of the polypropylene segments are crystallized, the polymer chain ends with high mobility are expelled into the amorphous phase which is swellable by the appropriate solvent during the reaction. In addition, the high reactivities in both hydroboration and oxidation reactions certainly enhance the efficiency of functionalization.

Polypropylene diblock copolymers. Most of 9-BBN terminated polypropylene (PP-9-BBN) was subjected to

* d-benzene

** TMS
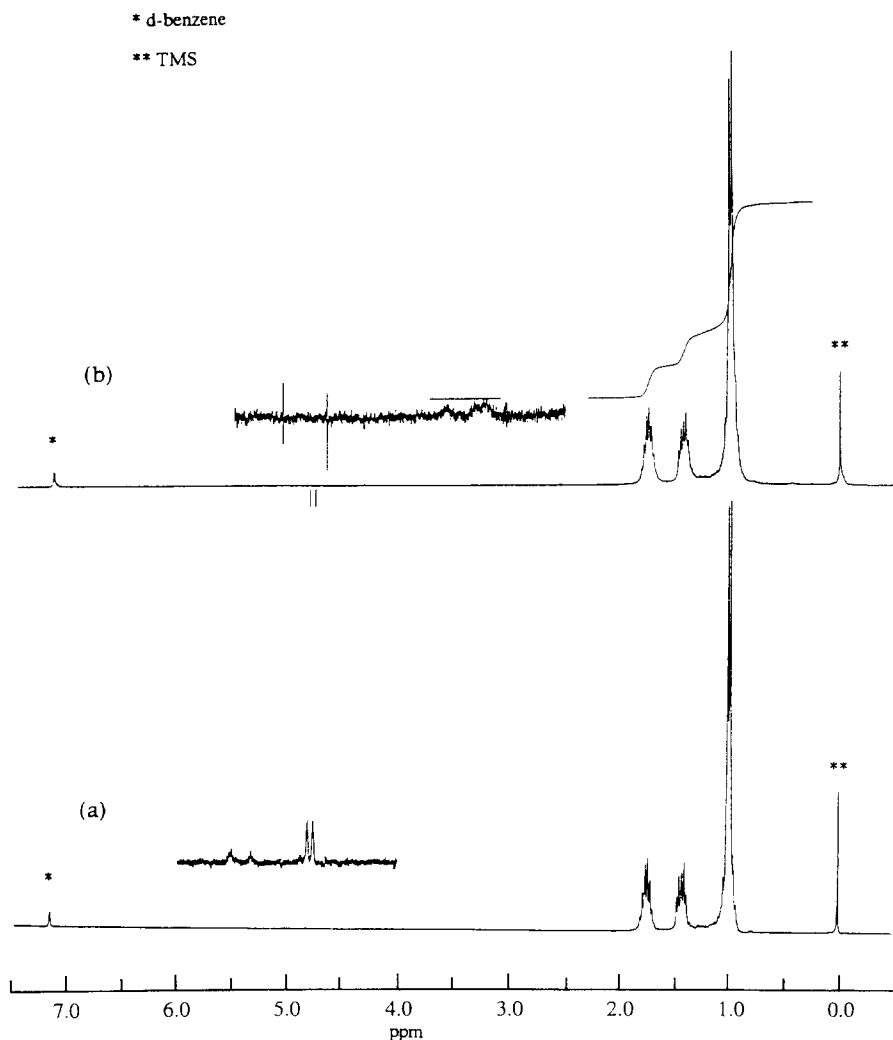
Figure 2 ¹H n.m.r. spectra of (a) the chain end unsaturated PP and (b) the corresponding hydroxy terminated PP

$$\begin{array}{c}
\overset{\displaystyle CH_3}{\underset{}{\text{~~~PP~~CH-CH}_2\text{-B}}} \\[2mm]
\Big\downarrow\ O_2 \\[2mm]
\overset{\displaystyle CH_3}{\underset{}{\text{~~~~~PP~~CH-CH}_2\text{-O-O-B}}}\quad (I) \\[2mm]
\Big\downarrow \\[2mm]
\overset{\displaystyle CH_3}{\underset{(II)}{\text{~~~~~~PP~~CH-CH}_2\text{-O}\,\bullet}}\ +\ \bullet\text{O-B}\quad (III) \\[2mm]
\Big\downarrow\ MMA \\[2mm]
(IV)\quad\longrightarrow\quad(V) \\[2mm]
\Big\downarrow\ MMA \\[2mm]
(VI)
\end{array}$$

$$(2)$$

(IV): ~~~PP~~CH-CH$_2$-O-CH$_2$-C$\bullet$ $\bullet$O-B, with CH$_3$ substituents and C=O, O, CH$_3$ group

(V): ~~~PP~~CH-CH$_2$-O-CH$_2$-C$\cdots$O-B, with CH$_3$ substituents and C=O, O, CH$_3$ group

(VI): ~~~~~~~PP~~CH-CH$_2$-O-CH$_2$-C~~~PMMA~~~, with CH$_3$ substituents and C=O, O, CH$_3$ group

the oxidation reaction by oxygen in the presence of free radical polymerizable monomers, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acetate (VA), butyl acrylate (BA) and styrene. The reaction was usually conducted by slowly adding oxygen to the suspension, containing polypropylene, monomer and solvent, at ambient temperature. Due to the unfavourable ring strain increase by inserting oxygen into the C–B bonds in the bicyclic ring of 9-BBN, which destroys the stable double chair-form structure, the oxidation reaction selectively takes place at the C–B bond[27,28] in the linear alkyl group to produce peroxyborane (C–O–O–B) (I) as shown in equation (2).

The peroxyborane (I) behaves very differently from regular benzoyl peroxides and consequently decomposes by itself even at ambient temperature. The decomposition reaction may follow the homolytical cleavage of peroxide to generate an alkoxy radical (C–O∗) (II) and a borinate radical (B–O∗) (III), which shall be relatively stable due to the back-donating of electron density to the empty *p*-orbital of boron. The alkoxyl radical (II), produced by the homolytical cleave of peroxyborane, shall be very reactive and can then be used for the initiation of radical polymerization[30]. On the other hand, the borinate radical (III) stabilized by the empty *p*-orbital of boron through back-donating electron density, may be too stable to initiate polymerization. However, the borinate radical (III) may form a weak and reversible bond with the growing chain end (VI) during the polymerization reaction. Upon the dissociation of electron pair in the resting state (V), the growing chain end (VI) can then react with monomers to extend the polymer chain. This chain extension mechanism is consistent with a control oxidation study* of ethyl-9-BBN

which was exposed to oxygen under various oxidation conditions, such as concentration of oxygen, reaction temperature and with and without the presence of MMA monomers. The oxidative adducts were analysed by [11]B n.m.r. spectroscopy; the detailed results will be discussed in a future publication.

The radical polymerization was terminated by precipitating the polymer mixture into MeOH. The product, isolated by filtration and washed with MeOH, was then subjected to the fractionation. In the PP-b-PMMA case, the sample was extracted with refluxing acetone and heptane in a Soxhlet apparatus for 24 h, respectively. *Figure 3* compares the ^{1}H n.m.r. spectra of three fractions.

The heptane-soluble fraction shown in *Figure 3a* is basically pure PP, which has three multiple peaks around 1.09, 1.39 and 1.75 ppm, corresponding to CH$_3$, CH$_2$ and CH protons, respectively. It is interesting to note that there is no detectable chemical shift between 2.5 and 6.5 ppm, corresponding to olefin protons, methylene and methine alcohols. On the other hand, the acetone-soluble fraction shown in *Figure 3b* contains only PMMA. The peak at 3.58 ppm corresponds to methoxyl groups (CH$_3$O) in PMMA. The PMMA hompolymer may be due to the non-selective oxidation reaction (~10%) which produces a radical in the bicyclic ring, instead of a

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* In the oxidation reaction ethyl-9-BBN with the presence of MMA monomers, the major (> 80%) oxidized species shown in the [11]B n.m.r. spectrum is borinate radical (III). The MMA monomers may serve as the radical traps to react with the alkoxyl radical (II) formed right after the oxidation reaction as illustrated in equation (2). On the other hand, in the oxidation reaction of alkyl-9-BBN without MMA monomers the formed alkoxyl radical (II) further reacts with borane species to produce a complicated oxidized borane mixture
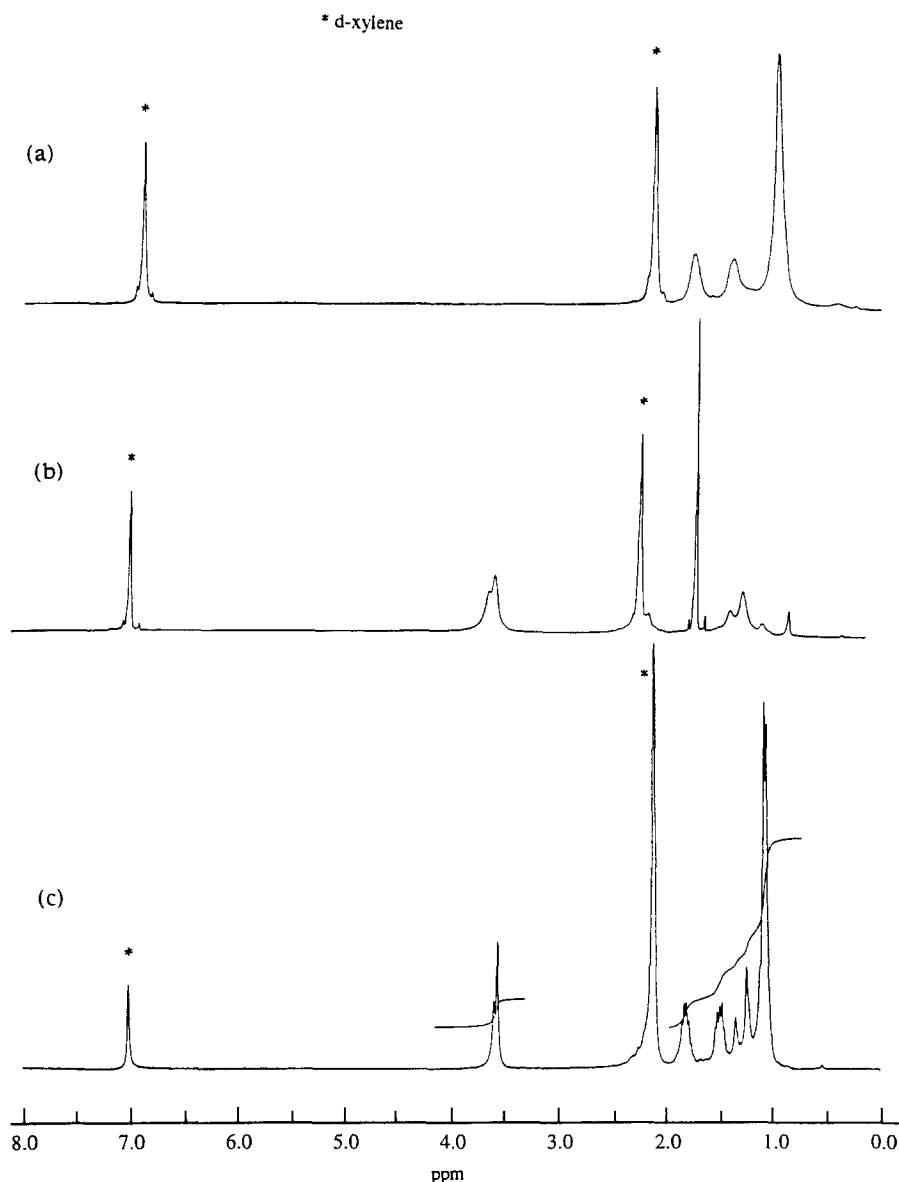
Figure 3 ^{1}H n.m.r. spectra of three fractionation products, (a) heptane soluble fraction, (b) acetone soluble fraction and (c) both solvent insoluble fraction

polymeric radical. The major fraction, insoluble in heptane and acetone but soluble in toluene at elevated temperature, is PP-b-PMMA diblock copolymer. The ^{1}H n.m.r. spectrum of PP-b-PMMA in *Figure 3c* shows 45 mol% of PMMA. *Figure 4* compares the g.p.c. curves between the starting PP homopolymer and the resulting PP-b-PMMA diblock copolymer.

The product molecular weight increases more than double from $M_n = 13\,000$ to $29\,000\,\mathrm{gmol}^{-1}$ and molecular weight distribution (MWD) slightly increases from 1.48

to 1.69. The g.p.c. results are consistent with the ^{1}H n.m.r. measurement, which show about a 1/1 mole ratio between PP and PMMA in copolymer. During the propagation step, the resting state (V) of growing chain end forming a weak bond with the borinate radical (III) may minimize the undesirable chain transfer and termination reactions, namely, radical coupling and disproportional reactions between two growing chain ends. In fact, these results are consistent with the control reactions using alkyl-9-BBN as the radical initiator,

Table 2 A summary of PP-b-PMMA diblock copolymers

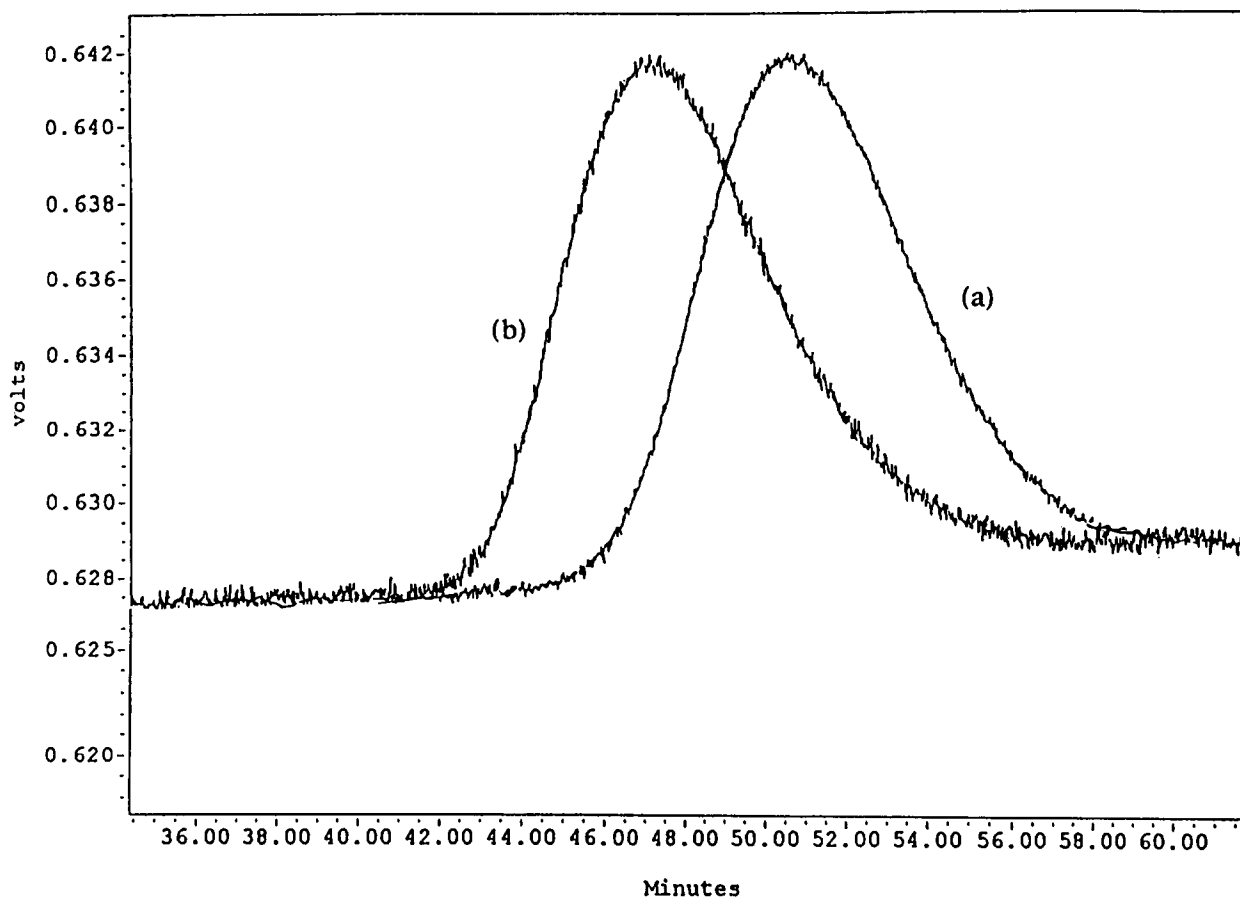| Reaction conditions				Fractionation product			Mol% MMA in diblock copolymer
PP (g)	MMA (g)	Solvent (ml)	Oxygen (ml)	Acetone (g)	Heptane (g)	Insoluble (g)	
0.5	5	THF/5	0.44	0.25	0.18	0.72	33
0.5	5	benzene/5	0.44	0.16	0.08	0.90	28
13.3	80	THF/80	10.8	^{a}	^{a}	22.5	45

^{a} Undetermined

Figure 4 G.p.c. curves of (a) PP and (b) the corresponding PP-b-PMMA copolymer

which showed 'stable' radical polymerization[30] of MMA under similar reaction conditions.

The detailed experimental conditions and results are summarized in *Table 2*. All reactions were started from the same PP sample with $M_n = 13\,000$ and $M_w/M_n = 1.48$. The reactions were conducted at ambient temperature for 16 h.

The overall conversion of diblock copolymer from PP homopolymer is usually between 80 and 50%, which is very encouraging since (up to 20%) of the polymer chains are without a borane group. All three reactions, including hydroboration, oxidation and radical polymerization, must be very effective despite the heterogeneous conditions. Slightly better results, with less homopolymers, using benzene solvent may be due to the slow diffusion of oxygen in reaction media, which offers better selectivity in the oxidation of PP-9-BBN.

Conclusions

It is both a scientific challenge and an industrial wish to develop a facile method to prepare polyolefin diblock copolymers, especially, containing functional groups and having relatively well defined molecular structures. The unique combination of metallocene (single-site) catalysis and borane chemistry provides a valuable and effective route to prepare polyolefin diblock copolymers. In this paper, the preparation of PP-b-PMMA is discussed. The same radical chain extension can be extended to other free radical polymerizable monomers, such as ethyl methacrylate (EMA), vinyl acetate (VAc), butyl acrylate (BA) and styrene. These are currently under investigation.

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