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Synthesis of Chain-End Functionalized PP and Applications in Exfoliated PP/Clay Nanocomposites

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Summary: This paper summarizes our research to the preparation of chain-end functionalized isotactic polypropylene (i-PP) having a terminal functional group, such as an OH and an NH_2. The chemistry involves metallocene-mediated propylene polymerization using the rac-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO complex in the presence of styrene derivatives (St-f) and hydrogen, which serve as the chain transfer agents. The molecular weight of the resulting i-PP polymers with terminal OH or NH_2 groups (i.e., PP-t-OH and PP-t-NH_2) are inversely proportional to the molar ratio of [St-f]/[propylene]. Despite the extremely low concentration of functional groups, the high molecular weight NH_3^+-terminated PP (PP-t-NH_3^+) exhibits a distinctive advantage over other functional PP polymers containing side chain functional groups or long functional blocks. The terminal hydrophilic NH_3^+ cation, with good mobility and reactivity, effectively ion-exchanges the cations (Li^+, Na^+, etc.) located between the clay interlayers, and anchors the PP chain to the clay surfaces. On the other hand, the remaining rest of the unperturbed, end-tethered, high molecular weight PP tail exfoliates the clay layers. This exfoliated structure is maintained even after further mixing of the PP-bearing platelets with pure, neat PP polymers.

Keywords: functionalization; metallocene; nanocomposite; polypropylene; PP/clay composite

Introduction

A hydrocarbon polymer with a terminal functional group[1] is a very attractive material that possesses an unperturbed polymer chain structure and desirable physical properties (such as melting temperature, crystallinity, glass transition temperature, melt flow, etc.) that are almost the same as those of the pure polymer. Nevertheless, the terminal reactive group at the polymer chain end has good mobility and can provide a reactive site for many applications, such as adhesion to substrates[2] and reactive blending[3], to improve the compatibility of two dissimilar polymer blends. This chain-end functionalized polymer structure is particularly useful in polyolefins (PE, PP, EP, s-PS, etc.), whose lack of

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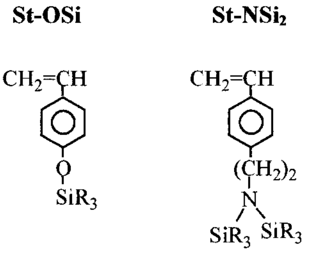
functionality and poor compatibility with other materials has imposed limitations on its applications.[4]

The method of preparation of chain-end functionalized polymers has been largely limited to living polymerization with the use of an initiator bearing a functional group[5] or a control termination (functionalization) reaction[6] of the living polymer chain-end. Unfortunately, there are only a few transition metal coordination catalysts that exhibit living polymerization behavior, and most of them are limited to the preparation of polyethylene and poly(1-hexene) cases[7]. Furthermore, living polymerization only produces one polymer chain per initiator, which presents a relatively low rate of catalyst activity in typical polyolefin preparation.

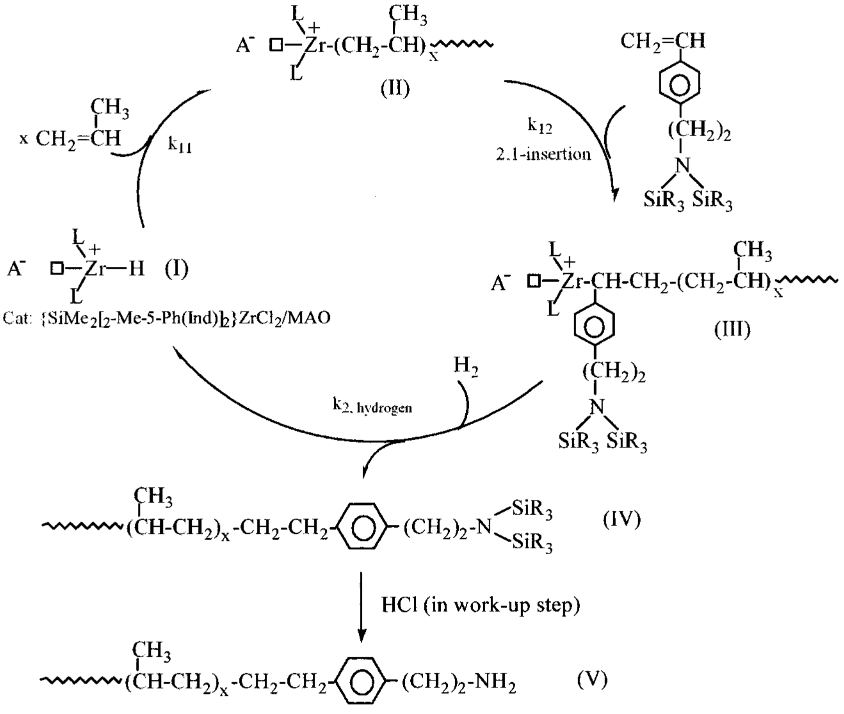
In our previous papers[8], we have reported a new chemical route by which to prepare polyolefins (including PE, PP, s-PS, etc.) with a terminal reactive group and obtain high catalyst activity. The chemistry is based on a chain transfer reaction involving a reactive chain transfer agent, including dialkylborane ($H-BR_2$)[9] and p-methylstyrene/hydrogen (p-MS/H_2)[10], during metallocene-mediated olefin polymerization. All polymers formed contained a terminal borane or p-MS group and had a relatively narrow molecular weight distribution (Mw/Mn~2). The polymer molecular weight (from a few thousand to a hundred thousand) was basically controlled by the mole ratio of [chain transfer agent]/[olefin]. Both the terminal borane and p-MS groups are very versatile, and can serve as the reactive sites for subsequent functionalization reactions or convertion to living initiators for chain extension reactions.

Synthesis of PP-t-OH and PP-t-NH_2

It is very desirable to extend this chemical route to directly prepare polyolefins with a desirable terminal functional groups, such as OH, and NH_2. In other words, the ideal reaction is a one-pot *in situ* polymerization process[11], and no chain-end functionalization would be needed after the polymerization reaction. The basic idea in the direct preparation of the chain-functionalized PP was to use a functionalized styrenic chain transfer agent (St-f) as the chain transfer agent that could engage in similar metallocene-mediated propylene polymerization/chain transfer reaction under certain reaction conditions. Two St-f molecules were investigated, including silane-protected p-vinylphenol (St-OSi) and silane-protected p-ethylaminostyrene (St-NSi_2), as illustrated in Scheme 1. The silane groups provide effective protection for both the OH and NH_2 functional groups during the metallocene catalysis, and they can be completely deprotected by aqueous HCl solution during the sample work-up procedure.



Scheme 1



Equation 1

Equation 1 illustrates the general reaction scheme. During the course of propylene 1,2-insertion, the propagating M$^+$-C site (II) eventually reacts with a St-NSi$_2$ unit (k_{12}) (via 2,1-insertion) to form a St-NSi$_2$ capped propagating site (III) with an adjacent phenyl group interacting with metal cation. The new propagating site (III) is incapable of continuing the insertion of St-NSi$_2$ (k_{22}) or propylene (k_{21}) due to the steric jamming. However, it can react with hydrogen to complete the chain transfer reaction. This consecutive reaction with St-NSi$_2$ and hydrogen results in a PP-t-St-NSi$_2$ polymer chain (IV), and a regenerated Zr-H species (I) reinitiates the polymerization of propylene and continues the polymerization cycles. After completion of the polymerization, the desirable NH$_2$ terminal group in PP-t-NH$_2$ (V) can be easily recovered during the sample work-up step using an HCl aqueous solution. Theoretically, the PP-t- NH$_2$ molecular weight should be linearly proportional to the molar ratio of [propylene]/[St-NSi$_2$].

Table 1. A summary of PP-t-St-OH and PP-t-St-NH$_2$ polymers.[a]

Run	St-f[b] (mol/l)	H_2 (psi)	Yield (g)	Cat. Activity[c]	OH or NH_2 in PP (mol %)	M_n ($\times 10^{-3}$)	PDI (M_w/M_n)	Tm (°C)
A-1	0.198	0	~ 0	~ 0	-	-	-	-
A-2	0.198	6	0.36	1,165	0.09	52.1	2.3	159.1
A-3	0.198	12	2.36	7,637	0.08	53.4	2.4	158.4
A-4	0.198	20	8.34	26,995	0.10	52.5	2.2	158.2
B-1	0.396	0	~ 0	~ 0	-	-	-	-
B-2	0.396	6	~ 0	~ 0	-	-	-	-
B-3	0.396	12	0.63	2,039	0.18	23.4	2.5	157.4
B-4	0.396	20	2.57	8,318	0.20	22.0	2.0	156.3
C-1	0.125	0	~ 0	~ 0	-	-	-	-
C-2	0.125	6	0.41	1,327	0.07	56.3	2.1	159.1
C-3	0.125	12	2.62	8,480	0.06	55.4	2.5	158.4
C-4	0.125	20	9.78	31,655	0.08	58.9	2.3	158.2
D-1	0.250	0	~ 0	~ 0	-	-	-	-
D-2	0.250	12	0.81	2,622	0.18	25.3	2.2	156.3
D-3	0.250	20	3.11	10,066	0.19	24.2	2.3	155.9

a) Reaction conditions: 50 ml toluene, catalyst: *rac*-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/ MAO catalyst, [Zr] = 1.25×10^{-6} moles, [MAO]/[Zr] = 3000, temperature = 30 °C, time = 15 min.

b) St-f: St-OSi for Runs A and B, St-NSi2 for Runs C and D.

c) Catalyst activity = kg of PP/ mol of catalyst.h.

Table 1 summarizes the experimental results involving St-OSi/H_2 and St-NSi$_2$/H_2, respectively, in the rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyzed polymerization of propylene. In all control reactions, a small amount of any styrene derivative (St-f) effectively stops the polymerization of propylene. The introduction of hydrogen gradually restores the catalyst activity. Overall, the PP molecular weight is governed by the chain transfer agent - the higher the concentration of the St-f, the lower the molecular weight of the resulting polymer.

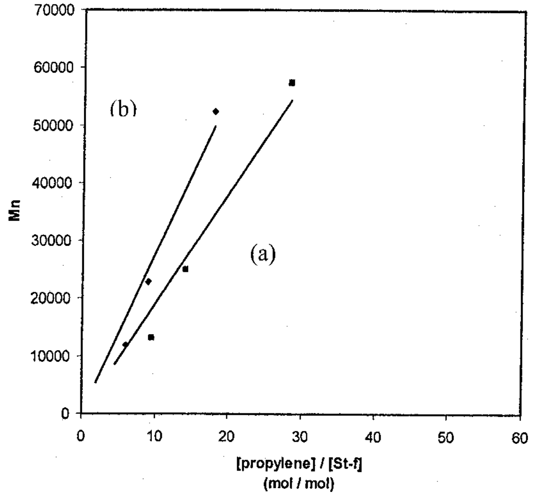


Figure 1. The plots of number average molecular weights (Mn) of PE-t-St-f polymers versus the mole ratio of [propylene]/[St-f] using (a) St-OSi and (b) St-NSi$_2$, respectively.

Figure 1 shows the plot of the polymer molecular weight (Mn) versus the molar ratio of [propylene]/[St-f], including both St-OSi/H$_2$ and St-NSi$_2$/H$_2$ chain transfer agents. In general, the polymer molecular weight and molar ratio of [propylene]/[St-f] are linearly proportional. It is clear that the chain transfer reaction to St-f (with rate constant k_{tr}) is the dominant termination process, and that it competes with the propagating reaction (with rate constant k_p). The degree of polymerization (X_n) follows a simple comparative equation $X_n=k_p[\text{olefin}]/k_{tr}[\text{p-MS}]$ with a chain transfer constant of k_{tr}/k_p of 1/48 for St-OSi/H$_2$, and 1/34 for St-NSi$_2$/H$_2$, respectively. It is intriguing that the k_{tr}/k_p values are significantly lower than those seen in styrene and p-MS cases[11] under similar reaction conditions. The bulky protected functional groups may reduce the frequency of chain transfer reaction. Polymers with very low molecular weights (a few thousand) were obtained, and the molecular weight distributions were quite narrow. This is generally consistent with single site polymerization processes. Some low molecular weight polymers with exceptionally low Mw/Mn < 2 (despite extra efforts to recover all polymers) may be associated with the sensitivity of the GPC analytical technique at very low molecular range.

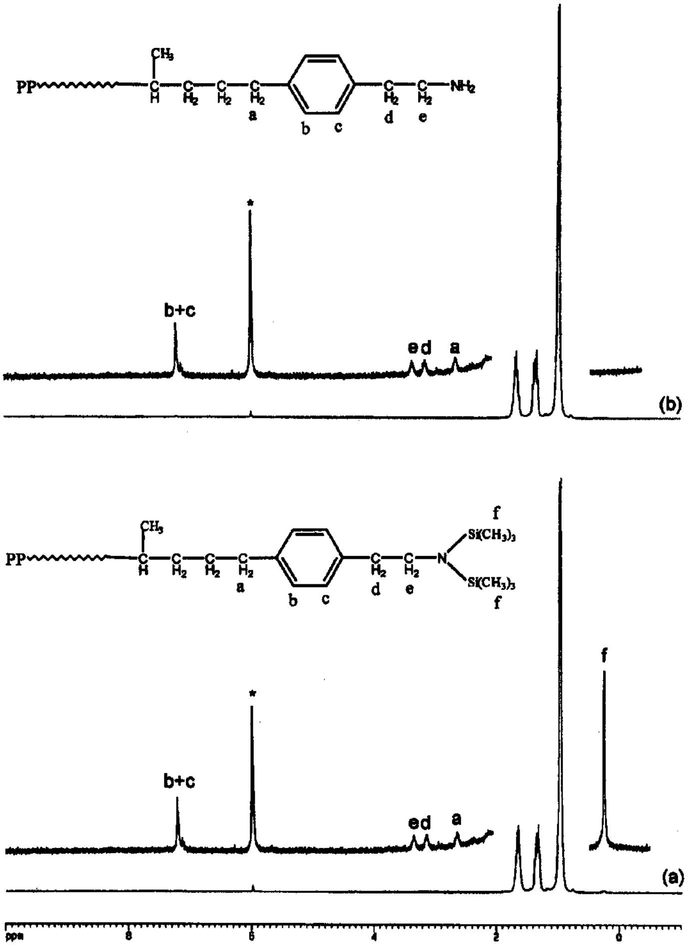


Figure 2. ^{1}H NMR spectra of (a) a PP-t-St-NSi$_2$ polymer and (b) its corresponding PP-t-St-NH$_2$ (Mn= 24,200 g/mol, Mw/Mn= 2.3). (solvent: $C_2D_2Cl_4$; temp.: 110° C.)

Figure 2 compares the ^{1}H NMR spectra of the PP-t-St-NSi$_2$ polymer (Mn= 24.2 x 10^3; Mw/Mn= 2.3) and the corresponding PP-t-St-NH$_2$ polymer. In addition to the chemical shifts for the PP polymer, Figure 2(a) shows all of the chemical shifts associated with the protecting bis(trimethylsily)amino terminal group that is connected to the symmetrical p-dialkylbenzene moiety. In fact, all four phenyl protons merge into a single chemical shift at 7.22 ppm. Figure 2(b) shows an almost identical spectrum, except for the disappearance of the silane protecting group at 0.24 ppm.

Overall, the combined experimental results strongly indicate a clean and effective reaction scheme, as illustrated in Equation 1. The combination of the facile *in situ* chain transfer to St-f/H_2 during the catalytic polymerization of propylene and the subsequent complete deprotection reaction during the sample work-up step affords a very interesting reaction scheme in the preparation of the chain-end functionalized i-PP with a OH, and NH_2, terminal group via a one-pot reaction process.

PP/Clay Nanocomposites

The availability of a broad range of well-defined functionalized PP polymers provides us with a great advantage in evaluating their applications in PP/clay nanocomposites[12]. The most desirable ammonium group terminated i-PP (PP-t-$NH_3^+Cl^-$) polymers were prepared by simple mixing between PP-t-NH_2 and HCl. Both pristine Na^+-montmorillonite clay (Na^+-mmt), with an ion-exchange capacity of ca. 0.95 meq/g, and a dioctadecylammonium-modified montmorillonite organophilic clay (2C18-mmt) were obtained from Southern Clay Products. Static melt intercalation was employed to prepare all PP/clay nanocomposites.

Figure 3 compares the X-Ray Diffraction (XRD) patterns before and after static annealing of a physical mixture (90/10 weight ratio) of an ammonium terminated i-PP (PP-t-NH_3^+ Cl^-; M_n= 58,900 and M_w= 135,500 g/mol; T_m= 158.2° C) and a pristine Na^+-mmt clay. Namely, simple mixing of dried PP-t-$NH_3^+Cl^-$ powder and Na^+-mmt, ground together by mortar and pestle at ambient temperature, creates the XRD pattern in Figure 3(a), with a (001) peak at $2\theta \cong 7^\circ$, corresponding to the characteristic Na^+-mmt d-spacing of *ca.* 1.26 nm. The mixed powder was then heated, and annealed under static conditions at 190°C for 2 hours under vacuum. The resulting PP-t-NH_3^+/mmt hybrid shows a featureless XRD pattern as in Figure 3(b), indicating the formation of an exfoliated clay structure, which corresponds to the thermodynamically stable state, as the ammonium-terminated PP exchanges the alkali (Na^+) cations at the mmt surfaces.

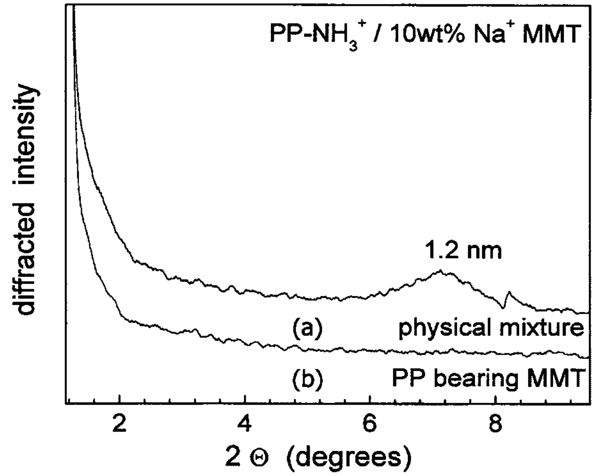


Figure 3. X-ray diffraction patterns of PP-t-$NH_3^+Cl^-/Na^+$-mmt (90/10 weight ratio) (a) physical mixture by simple powder mixing at ambient temperature and (b) the same mixture after static melt-intercalation (PP-t-NH_3^+/mmt hybrid).

Similar results were also observed in the PP-t-$NH_3^+Cl^-/2C_{18}H_{37}$-$2CH_3$-N^+-mmt nanocomposite case, suggesting that the dioctadecylammonium cations in organophilic clay may also be ion-exchanged by PP-t-NH_3^+ to form a similar PP-t-NH_3^+/mmt structure. It is clear that an organic surfactant is not needed to promote compatibility between PP-t-$NH_3^+Cl^-$ and pristine Na^+-mmt clay. Beyond any economic benefits, such an elimination of the mmt's organic surfactant also offers some significant materials advantages; for example, it eliminates two major concerns relating to the thermal stability of the surfactant during high temperature melt processing and to the long term stability of the small organic surfactant in the polymer/clay nanocomposite under various application conditions.

The binary PP-t-NH_3^+/mmt hybrid was subsequently further mixed/blended (at a 50/50 weight ratio) with a neat –unfunctionalized– i-PP (Mn= 110,000 and Mw= 250,000 g/mol). Figure 4 shows the XRD patterns of (a) the physical mixture and (b) the melt blending, of the exfoliated PP-t-NH_3^+/mmt structures with neat i-PP. The exfoliated structure is maintained after further mixing with i-PP, which is compatible (co-crystallizable) with the backbone of the largely-isotactic PP-t-NH_3^+ polymer, as also directly observed in the TEM. Apparently, the i-PP polymer chains largely serve as diluents in the ternary PP-t-NH_3^+/mmt/i-PP system, with the thermodynamic stable PP-t-NH_3^+/mmt exfoliated structure dispersed in the i-PP matrix.[13]

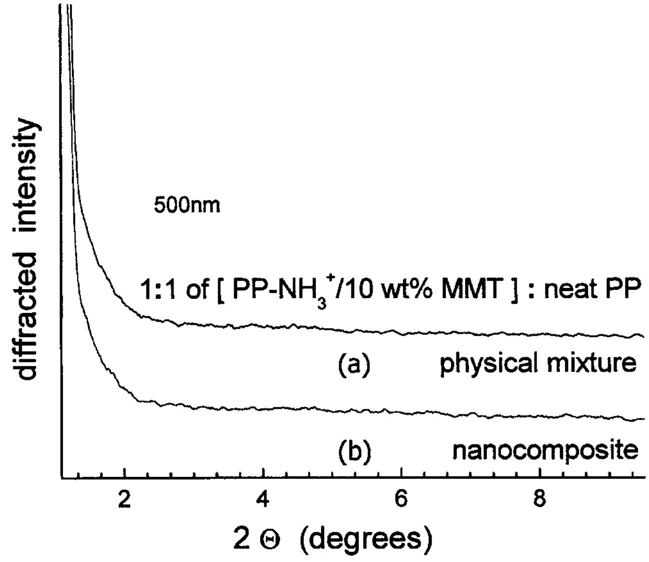


Figure 4. X-ray diffraction patterns of the 50/50 mixture by weight of exfoliated PP-t-NH_3^+/ mmt structure (90/10 weight ratio) and neat –unfunctionalized– i-PP. The XRD traces shown correspond to (a) the physical mixture of PP-t-NH_3^+/mmt and i-PP, and (b) the same mixture after static melt-intercalation.

For comparison, several functionalized PP polymers, containing randomly distributed functional groups in the side chains or lumped together in a block-copolymer microstructure, were also evaluated in PP/montmorillonite nanocomposites. Similar static melt-intercalation procedures were followed, except for employing alkylammonium-modified montmorillonites (2C18-mmt for all random copolymers, and C18-mmt for the block copolymer). XRD patterns of four nanocomposites made with 6 wt. % of 2C18-mmt clay and 94 wt. % of three side-chain functionalized PPs (M_n= 95,000 and M_w = 210,000 g/mole) containing (a) 1 mole % p-methylstyrene, (b) 0.5 mole % maleic anhydride, and (c) 0.5 mole % hydroxy side groups, respectively, and the original 2C18-mmt clay. All the functionalized PPs were derived from the same random PP copolymer synthesized by metallocene catalysis, which contained 1 mole % p-methylstyrene (p-MS) comonomer.

Subsequently, the p-MSs were selectively functionalized towards hydroxy (OH) and maleic anhydride, respectively, without changing the PP backbone. In addition, we also compared the XRD pattern of PP-*b*-PMMA block copolymer/6 wt % C18-mmt, which contained a 5 mole % methyl-methacrylate block. These XRD patterns clearly show that there is a definite intercalated structure for all the side-chain functionalized PP cases, manifesting itself through an interlayer d-spacing increase of about 1 nm compared to that of the parent alkyl-ammonium-mmt. TEM was also employed to examine the degree of exfoliated (disordered) structure. The quantitative image analysis indicates only between 20 and 40% exfoliated layers in all four systems.[14]

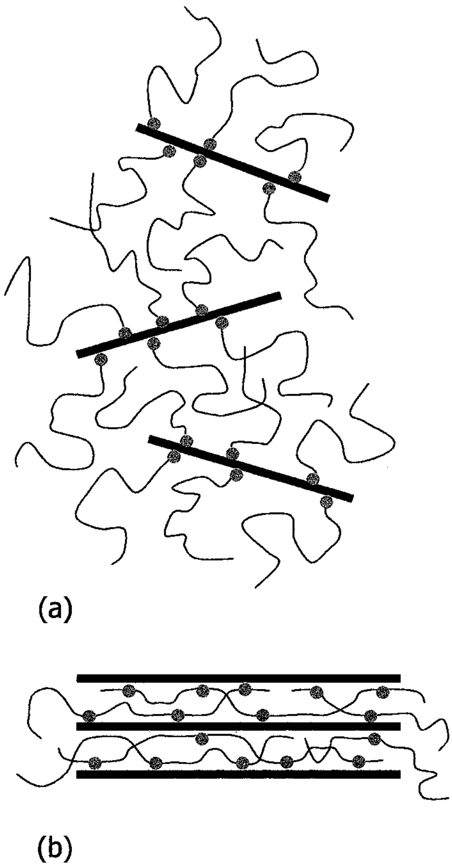


Figure 5. Illustration of the molecular structures of (a) chain-end functionalized and (b) side-chain functionalized polyolefin located between clay interlayers.

The experimental results clearly demonstrate the advantage of chain-end-functionalized PP (PP-t-NH_3^+), that seems to adopt a unique molecular structure atop of the clay surfaces, and results in an exfoliated montmorillonite structure (Figure 5(a)). The terminal hydrophilic NH_3^+ functional group anchors the PP chains (via ion-exchange) on the inorganic surfaces, and the hydrophobic high molecular weight and semicrystalline PP "tail" effectively exfoliates the clay platelets an exfoliated structure which is maintained even after further mixing with neat PP. In contrast, side-chain functionalized or block copolymer PPs form multiple contacts with each of the clay surfaces, as illustrated in Figure 5(b), which not only results in aligning the polymer chains parallel to the clay surfaces, but can also bridge consecutive clay platelets promoting intercalated structures, especially for the higher lateral size montmorillonites.

Experimental Section

All manipulations were carried out under inert atmosphere or by using the standard Schlenk technique. ^1H NMR spectra were recorded on a Bruker AM-300 or WM-360 spectrometer with DISNMR software. The measurements were usually taken at 120°C, using d_2-1,1,2,2-tetrachloroethane as solvent. The molecular weight and molecular weight distribution of the polymers were determined by Gel Permeation Chromatography (GPC) using a Waters 150 C with a refractive index (RI) detector. The measurements were taken at 140°C, using 1,2,4-trichlorobenzene (TCB) as solvent and a mobile phase of 0.7 ml/min flow rate. Broad molecular weight PE samples were used as standards for calibration. Differential scanning calorimetry (DSC) was measured on a Perkin Elmer DSC-7 instrument controller. The DSC curves were recorded during the second heating cycle from 30° to 180°C using a heating rate of 20°C/min. XRD data were collected on a diffractometer using Cu Kα radiation (λ = 0.1506 nm). Bragg's law ($\lambda = 2d \sin\theta$) was used to calculate the spacing. Direct observation of the PP/clay nanocomposite structure was realized by bright field TEM of nanocomposite films under strain in a JEOL – 1200EX, operating at 120kV. Ultrathin sections of the PP/clay with a thickness of approximately 50 nm were prepared at room temperature using an ultramicrotome equipped with a diamond knife. The sections were transferred dry to carbon-coated Cu grids of 200 mesh.

Me_2Si(2-methyl-4-phenyl-indenyl)$_2$ $ZrCl_2$ (Boulder Scientific Co.) was used as received. MAO (Albemarle) in 30 wt % solution in toluene was isolated by vacuum removal of toluene and re-compounded to 2.5 M toluene solution prior to use. CP grade propylene gas (MG Industries) was dried over CaH_2 prior to use. CP grade toluene, hexane, and THF were deoxygenated by argon purge before refluxing for 48 hours and then distilled over sodium benzophenone immediately prior to use.

Synthesis of 4-{2-[*N,N*-Bis(trimethylsilyl)amino]ethyl}styrene (p-NSi_2-St)

A silane-protected chain transfer agent p-NSi_2-St was prepared in two steps. In a 500 ml flask equipped with a magnetic stirring bar, 100 g of lithium bis(trimethylsilyl)amide dissolved in 200 ml of THF was slowly added into a mixture of 50 ml (0.658 mol) of chloromethyl methyl ether and 50 ml of THF at 0° C under a nitrogen atmosphere. After completing the addition, the solution was allowed to warm up to room temperature for 2 hours before evaporating of the excess chloromethyl methyl ether and THF solvent. *N,N*-bis(trimethylsilys)methoxymethylamine (80% yield) was isolated by distillation. In the second step, p-NSi_2-St was prepared by treating 4-vinylbenzylmagnesium chloride with *N,N*-bis(trimethylsilys)methoxymethylamine. In a 500 ml flask equipped with a magnetic stirring bar and a condenser, 15.2 g of magnesium was suspended in 50 ml dry ether, and 80 ml of 4-vinylbenzyl chloride diluted with 50 ml dry ether was then introduced dropwise through the condenser. The solution was refluxed for 4 hours before the addition of 117 g of *N,N*-bis(trimethylsilys)methoxymethylamine over a period of 2 hours. The reaction was allowed to proceed at room temperature for another 2 hours before adding 100 ml of aqueous NaOH solution (30%). The organic layer was separated and dried, and the residual was then distilled over CaH_2 to obtain p-NSi_2-St in a 70% yield.

Synthesis of NH_2 group terminated PP (PP-t-NH_2)

The p-NSi_2-St terminated PP polymers (PP-t-St-NSi_2) were prepared by using in a combination of rac-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst and p-$NSi_2$-St and H_2 as the chain transfer agents. A systematic study was conducted to evaluate the effects of p-NSi_2-St and H_2 concentrations on the catalyst activity and polymer molecular weight. The PP-t-NH_2 polymers were then prepared from PP-t-St-NSi_2 polymers by treating them with hydrogen chloride. Alternatively, the isolated PP-t-St-NSi_2 (2 g) was suspended in 50 ml of THF at 50° C before the dropwise addition of 2 N methanolic hydrogen chloride solution. The mixture was stirred for 4 hours at 50° C, and then poured into 1 N methanolic NaOH solution. The PP-t-NH_2 polymer was collected by filtration and washed with 1 M aqueous ammonia and water under a nitrogen atmosphere. The polymer was dried overnight at 50° C under vacuum. The PP-t-NH_2 polymer yield was quantitative. Overall, the PP-t-NH_2 molecular weight is governed by the chain transfer agent - the higher the concentration of the p-NSi_2-St, the lower the molecular weight of the resulting polymer. It is clear that the chain transfer reaction to p-NSi_2-St (with rate constant k_{tr}) is the dominant termination process, and that it competes with the propagating reaction (with rate constant k_p). The degree of polymerization (X_n) follows a simple comparative equation $X_n=k_p[\text{olefin}]/k_{tr}[\text{St-NSi}_2]$ with a chain transfer constant of $k_{tr}/k_p=1/34$. ^1H NMR spectra of PP-t-St-NSi_2 polymer and the corresponding PP-t-St-NH_2 show a clean deprotection reaction with the complete disappearance of the silane protecting group at 0.24 ppm.

Preparation of PP/PP-t-$NH_3^+Cl^-$/ Na^+-montmorillonite clay nanocomposite

Na^+-montmorillonite clay (Na^+-mmt) with an ion-exchange capacity of about 95 mequiv/100g (WM) was obtained from Southern Clay Product. PP-t-$NH_3^+Cl^-$ (T_m = 158.2°C; M_n = 58,900 and M_w = 135,500 g/mole) was prepared using excess HCl reagent. Static melt intercalation was employed to prepare the PP-t-$NH_3^+Cl^-$/ Na^+-montmorillonite nanocomposite. PP-t-$NH_3^+Cl^-$ dried powder and Na^+-mmt with 90/10 weight ratio were first mixed and ground together in a mortar and pestle at ambient temperature. The XRD pattern of this simple mixture shows a (001) peak at 2θ ~7, corresponding to a Na^+-mmt interlayer structure with a d-spacing of 1.45 nm. The mixed powder was then heated at 190° C for 2 hours under nitrogen. The resulting PP-t-$NH_3^+Cl^-$/Na^+-mmt nanocomposite shows a featureless XRD pattern, indicating the formation of an exfoliated clay structure.

The binary PP-t-$NH_3^+Cl^-$/Na-mmt exfoliated nanocomposite was further melt mixed (50/50 weight ratio) with commercial, neat i-PP (Mn= 110,000 and Mw= 250,000 g/mol). First, the PP-t-$NH_3^+Cl^-$/Na-mmt exfoliated nanocomposite and neat i-PP with 50/50 weight ratio were ground together in a mortar and pestle at ambient temperature. This simple mixture shows a featureless XRD pattern. The mixed powder was then heated at 190° C for 2 hours under nitrogen. The resulting ternary PP/PP-t-$NH_3^+Cl^-$/ Na^+-mmt nanocomposite also shows a featureless XRD pattern, indicating that the stable exfoliated structure in the binary PP-t-$NH_3^+Cl^-$/Na-mmt exfoliated nanocomposite is clearly maintained after further mixing with PP, and that it is compatible with the backbone of PP-t-$NH_3^+Cl^-$.

Conclusion

We have shown a one-pot process by which to prepare chain-end functionalized PP polymers, involving a metallocene-mediated propylene polymerization/chain transfer reaction. With the proper choice of reaction conditions, chain transfer agents, and catalyst system, it is very convenient and efficient (with high catalyst activity) to prepare i-PP with a terminal styrenic unit containing either an OH, or NH_2 group. This reaction scheme is especially useful in the preparation of chain-end functionalized PP with high molecular weight. Almost the same reaction procedures used in regular PP polymerization can be directly applied, except for the addition of a small amount of chain transfer agent. In turn, the PP polymer with a reactive functional group is a useful interfacial material that can be used as polymeric surfactant to prepare the exfoliated PP/clay nanocomposites.

Acknowledgment

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