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Communications to the Editor

Synthesis of Functionalized Polypropylene

Functionalization of polyolefins has been a research subject[1-6] for many decades. Despite commercial applications,[7] polyolefins suffer a major deficiency, i.e., poor interaction with other materials. The inert nature of polyolefins significantly limits their end uses, particularly, those in which adhesion, dyeability, paintability, printability, or compatibility with other functional polymers is paramount. Among the polyolefins, polypropylene is one of the most desirable polymers. Unfortunately, polypropylene is also the most difficult one to be functionalized by the existing processes. Only a Ziegler–Natta polymerization can be used for the preparation of polypropylene. Unfortunately, such catalysts are normally incapable of incorporating functional group containing monomers because of catalyst poisoning.[8] On the other hand, post-polymerization processes suffer other problems, e.g., degradation[9] of the polypropylene backbone. It is clear that there is a fundamental need to develop new chemistry that can address the challenge of preparing functionalized polypropylene.

In the past few years, we have been investigating a new functional polymer approach[10] using the intermediacy of novel borane monomers and transition metal catalysts, including Ziegler–Natta[11,12] and metathesis catalysts.[13] The advantages of this chemistry are (a) the stability of the borane moiety to transition-metal catalyst, (b) the solubility of borane compounds in hydrocarbon solvents (hexane and toluene) used in transition-metal polymerizations, and (c) the versatility of borane groups, which can be transformed to a remarkable variety of functionalities as shown by Professor H. C. Brown.[14] Many new functionalized polyolefins with various molecular architectures have been obtained based on this chemistry.

In this paper, we present another unique molecular structure, one which has a blocky microstructure of isotactic polypropylene and functional polymer. The chemistry involves propylene and borane monomers and Ziegler–Natta catalyst as shown in Scheme I. The polymerization reaction was carried out in the inert-gas atmosphere at ambient temperature, using the catalysts for the preparation of isotactic polypropylene. Typically, two monomers of propylene (3.8 mL, 0.0587 mol) and hexenyl-9-BBN[11] (11.987 g, 0.0587 mol) were dissolved in 150 mL of toluene solution. The polymerization was started by adding 0.168 g (1.113 mmol) of $TiCl_3AA$ and 0.754 g (6.604 mmol) of $Al(Et)_3$, which were premixed and aged for $^1/_2$ h in 30 mL of toluene. Almost immediately precipitate could be seen in the deep purple solution. The copolymer was sampled (30 mL each) during the reaction process and then was terminated by addition of isopropyl alcohol. Excess isopropyl alcohol (50 mL) was used to ensure the complete coagulation of polymer in solution. This borane-containing polypropylene was isolated from solution by simple filtration and then washed repeatedly with isopropyl alcohol before being dried in the vacuum chamber overnight. The resulting polymer was completely insoluble in common organic solvents at room temperature, including THF, which is a good solvent for poly(hexenyl-9-BBN) homopolymer.

Scheme I

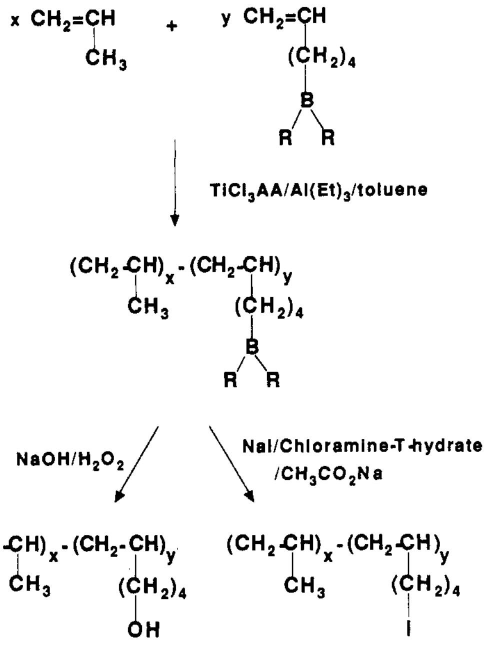

Figure 1 shows the ^{11}B NMR spectra of the copolymers that were sampled during the copolymerization reaction. Each NMR sample was prepared by dissolving 70 mg of polymer in 0.7 g of toluene-*d* solvent, containing an internal standard of triethylborate (7×10^{-5} M), at 110 °C, and was then kept at 70 °C during the measurement. The single chemical shift at 87 ppm, the same as that of monomer, in all samples is corresponding to the trialkylborane groups.[15] This indicates no side reactions in the polymerization and purification processes. The intensity of the trialkylborane peak increases continuously with the reaction time. The boron concentration in polymer can be calculated by comparing the peak intensity of trialkylborane (87 ppm) to the internal reference of triethylborate (17.3 ppm). Due to the significant difference in polymerization reactivity between two comonomers, the initial incorporation of borane monomer in copolymer was very small, only 1.6 mol % in the first 0.1 h, and then increased to 3.5 and 6.3 mol % after 1 and 2 h, respectively. It is obvious that propylene was preferentially polymerized in the initial copolymerization reaction. In fact, the copolymer formed insoluble particle in the early stage of the polymerization process. The crystalline nature of polypropylene may also limit the insertion reaction of bulky borane monomer to active sites that are located in polypropylene. Fortunately, the copolymerization of borane monomer continued in the heterogeneous phase; the concentration of the borane group increased in proportion to the reaction time. The change in the incorporation ratio between two monomers is obviously due to the change in monomer mole ratio during the batch reaction. It is interesting to note that the reactivity of hexenyl-9-BBN in this copolymerization is significantly lower than those of homopolymerization[11] and copolymerization with 1-octene.[12] In both cases, the growing polymer chains are soluble in the reaction mixture.

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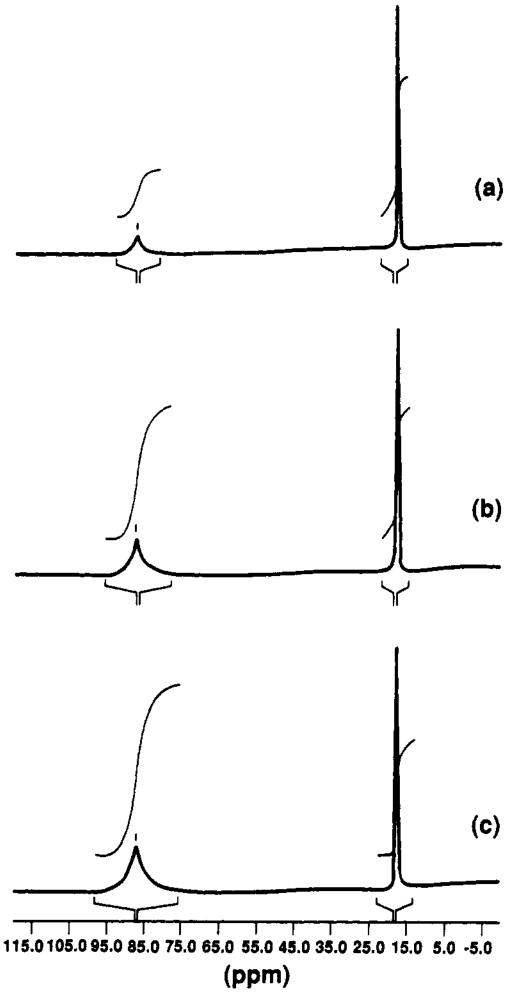

Figure 1. ^{11}B NMR spectra of poly(propylene-*co*-hexenyl-9-BBN) with various borane mole concentrations: (a) 1.5%, (b) 3.5%, (c) 6.3%.

Subsequently, borane groups in propylene copolymer were interconverted to various functional groups under mild conditions. One example is the oxidation reaction. Despite the heterogeneous nature of the reaction, insoluble borane-containing polypropylene suspended in THF at 40 °C for 5 h was reacted with $NaOH/H_2O_2$ reagents and was completely converted to the corresponding hydroxy group containing polypropylene. The resulting polymer was boron free and completely soluble in xylene at high temperature (>120 °C). The IR spectrum in Figure 2a shows the characteristic vibrational bands for O–H (3300 cm^{-1}) and C–O (1050 cm^{-1}). The quantitative hydroxy group concentration in polypropylene was obtained by ^1H NMR measurement, which was carried out at 130 °C in trichlorobenzene. As shown in Figure 2b, the peak intensity of the chemical shift at 3.5 ppm, corresponding to the methylene group of the primary alcohol, indicates 4.2 mol % hydroxy groups in the polymer. This concentration result is quite consistent with that obtained from ^{11}B NMR studies.

Likewise, borane-containing polymer was converted to the corresponding iodine-containing polymer. The conversion of borane to iodine groups is quite complete using the reagent of NaI/chloramine-T hydrate in base condition at room temperature. The Figure 3 compares the IR spectra of homo- and copolymers of polypropylene. The absorption at 725 cm^{-1}, corresponding to the C–I vibration mode, shows the iodo groups in the copolymer. Complete modification of an insoluble polymer by such mild reaction conditions is very unusual. This suggests a high surface area of borane groups available to the reagents. While the thermoplastic segments were crystallized, the borane groups might be expelled out to the surface of the crystalline phase. This morphological picture is also consistent with the results in thermal studies shown later. It is interesting to note that the corresponding hydroxy copolymer is able to cocrystallize with pure isotactic polypropylene. Detailed studies in this area are currently underway.

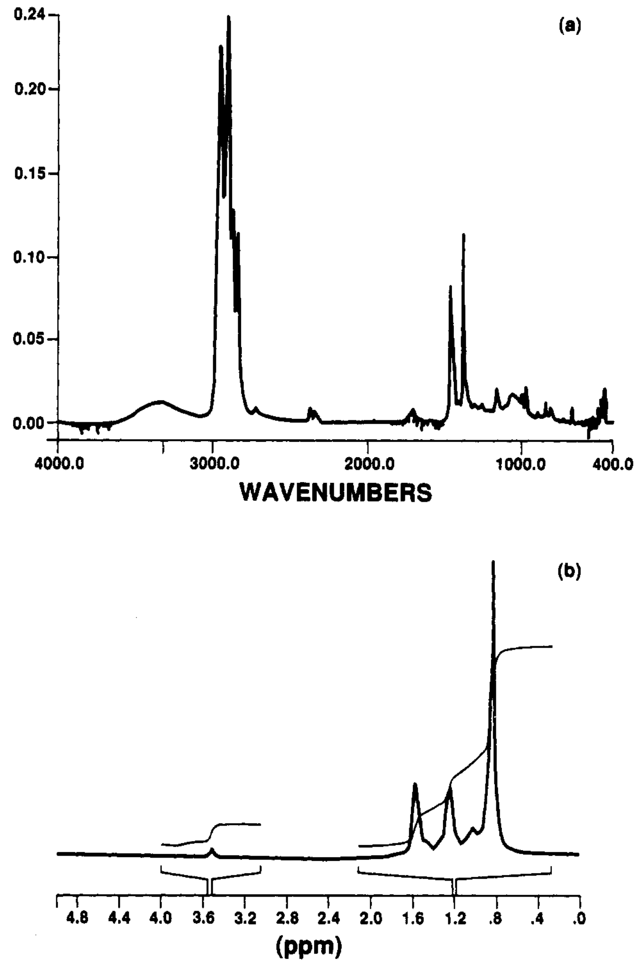

Figure 2. (a) IR and (b) ^1H NMR spectra of poly(propylene-*co*-hexenol) with 4.2 mol % alcohol groups.

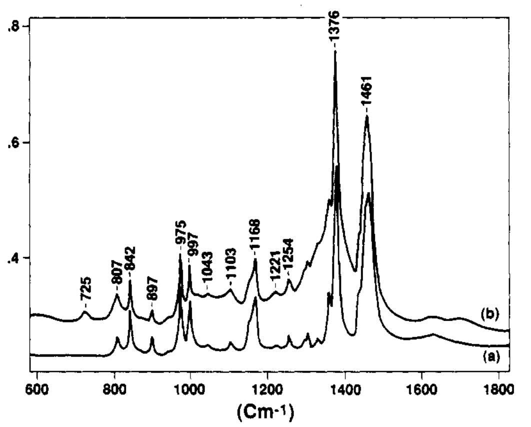

Figure 3. Comparison of IR spectra between (a) polypropylene and (b) iodine-containing polypropylene.

Functional polypropylene prepared by this route has many interesting physical properties. The polymer not only contains functional groups but also preserves some original physical properties of pure isotactic polypropy-

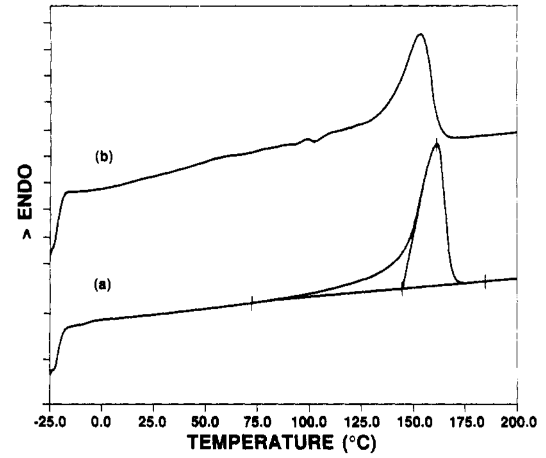

Figure 4. Comparison of DSC curves between (a) isotactic polypropylene and (b) poly(propylene-*co*-hexenol) with 4.2 mol % alcohol groups.

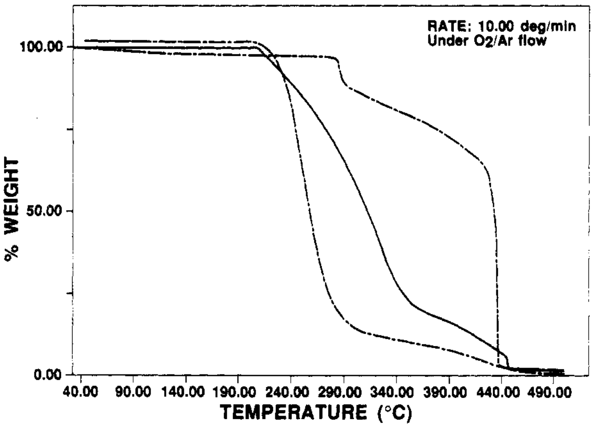

Figure 5. TGA curves of (a) isotactic polypropylene, (b) poly(propylene-*co*-hexenol) with 4.2 mol % alcohol groups, and (c) polyhexenol.

lene. Figure 4 compares the DSC curves between isotactic polypropylene and a 4.3% hydroxy group containing polypropylene. Both samples have approximately the same melting point (~160 °C); the actual depression in the melting point caused by functional groups is less than 5 °C. Preservation of crystallinity in the propylene copolymer apparently due to its blocky microstructure offers enough consecutive sequences of propylene units in the polymer backbone to form a crystalline phase. In addition, the thermal stability of functionalized polypropylene is also very similar to that of pure isotactic polypropylene. As shown in Figure 5, the decomposition temperature of hydroxy polypropylene in air is about 205 °C. A slightly better resistance in the decomposition process may be contributed from the relatively high thermal stability of polyhexenol. It is interesting to note that primary hydroxy groups are essential if we wish to maintain the thermal stability of polypropylene. The thermal stability of a primary alcohol is better than that of a secondary alcohol, as in poly(vinyl alcohol),[16] which decomposes below 150 °C under the same conditions.

In this paper, we have shown a new method that not only achieves the functionalization of polypropylene but also preserves most of useful physical properties in the isotactic homopolymer. The combination of blocky molecular microstructure and crystallization of polypropylene results a unique morphological arrangement, in which the functional groups are located on the surface of the thermoplastic crystalline phases. This polymer has been demonstrated as a very effective interfacial modifier to improve the adhesion between pure polypropylene and substrates, such as aluminum and glass. Detailed studies will be reported in the near future.

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