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Functionalization and Applications of Telechelic Oligopropylenes: Preparation of α,ω-Dihydroxy- and Diaminooligopropylenes

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ABSTRACT: Difunctional propylene oligomers which may be used for preparing novel block copolymers were synthesized from telechelic oligomers containing two terminal vinylidene double bonds (PP-TVDs). The PP-TVDs were converted to α,ω-dihydroxyoligopropylenes (PP-OHs) in good yield by hydroboration with BH_3·THF or 9-BBN, followed by oxidation. Multiple NMR signals from the α-methylene protons and the β-methyl carbons were ascribed to epimers formed during the hydroboration. α,ω-Diaminooligopropylene ($PP-NH_2$) was prepared from PP-OH via tosylate and azide. Copolymerizations of $PP-NH_2$ with terephthalic acid were carried out, and copolymers with molecular weights larger than that of the parent polymer were obtained.

Introduction

In the field of functional polymer synthesis, α,ω-difunctional polymers have been a subject of investigation for several decades. These difunctional polymers or oligomers can be used for preparing novel block copolymers (diblock, triblock, and so on) and interesting materials such as amphiphilic oligomers and supramolecules.[1] For these purposes, poly(alkylene glycol)s and terminal-functionalized oligomers from condensation polymers, e.g., polyamides or polyesters, may be used.[2]

α,ω-Difunctional oligomers or polymers from polyolefins have received much attention as materials for recyclable polymers.[3] However, it is not easy to prepare the difunctional polyolefins.[4] The preparation of polypropylene containing two terminal double bonds has seldom been reported. Murata and co-workers achieved this using living polymerization catalyzed by a $V(acac)_3$/$AlEt_2Cl$/diene system.[5] Copolymerization with 1,3-butadiene followed by metathesis degradation was reported by Ishihara and Shiono.[6]

In an earlier study we found that telechelic propylene oligomers with two terminal vinylidene double bonds (α,ω-bis(2-propenyl)oligopropylene, PP-TVDs) were obtained briefly by controlled thermal degradation from polypropylenes (PPs).[7] In this paper, we report the preparation of telechelic propylene oligomers with a hydroxyl or amino group at both ends and copolymerization of the difunctional oligomers directed toward the novel recyclable polyolefins.

Results and Discussion

1. Hydroxylation of α,ω-Bis(2-propenyl)oligopropylene. Generally, transformations of alkenes to alcohols are achieved by hydroboration followed by oxidation. This method may also be used for hydroxylation of the vinylidene group at one end of a PP chain[4a] and so was considered applicable to PP-TVD. Three varieties of PP-TVD—iPP-TVD, sPP-TVD, and aPP-TVD—were prepared by controlled thermal degradation from isotactic, syndiotactic, and atactic polypropylene, respectively. Characteristics of the PP-TVDs are shown in Table 1. The value f_{TVD} is a measure of functionality and is defined as the average number of terminal vinylidene double bonds (TVDs) per molecule. The number of TVDs and saturated termini is determined by quantitative ^{13}C NMR spectroscopy.[7] Low molecular weight PP-TVD ($M_n \leq 1000$) was also obtained by controlling the degradation conditions, but a slight decrease in f_{TVD} value was observed. This lower microtacticity was due to disorder in the stereoregularity of terminals during degradation.[7]

Table 1. Characteristics of PP-TVDs

PP-TVD	$M_n \times 10^{-3}$	M_w/M_n	microtacticity (mol %) *mm*	*mr*	*rr*	functionality f_{TVD}[a]
iPP-TVD (I)	4.42	1.85	94	4	2	1.84
iPP-TVD (II)	0.90	1.11	78	13	9	1.60
sPP-TVD	5.27	1.78	5	9	86	1.76
aPP-TVD	4.96	1.73	80	12	8	1.66

[a] Determined by quantitative ^{13}C NMR spectroscopy.[7]

Table 2. Hydroxylation of PP-TVDs

run	PP-TVD	boranes (equiv)[a]	end group of the product (mol %)[b] PP-OH	$-CH_2OH$	$=CH_2$	conversion (%)
1	iPP-TVD (I)	9-BBN (16)	iPP-OH (I)	75	14	84
2	iPP-TVD (I)	9-BBN (32)	iPP-OH (II)	84	5	94
3	sPP-TVD	9-BBN (16)	sPP-OH	79	3	96
4	aPP-TVD	9-BBN (16)	aPP-OH	90	3	98
5	iPP-TVD (I)	BH_3·THF (1)	iPP-OH (III)	78	9	90
6	iPP-TVD (III)[c]	BH_3·THF (4)	iPP-OH (IV)	80	0	100

[a] Amount of boranes equivalent to the number of terminal double bonds of PP-TVD. [b] Determined by quantitative ^{13}C NMR spectroscopy.[7] The others (7−20%) are unreactive saturated termini. [c] iPP-TVD (III): $M_n = 0.90 \times 10^3$, $M_w/M_n = 2.2$, $f_{TVD} = 1.75$.

We first attempted a hydroboration reaction of iPP-TVD with equimolar amounts of 9-borabicyclo[3.3.1]-nonane (9-BBN) in THF, but IR spectroscopy revealed only a low conversion rate of iPP-TVD. The reason for

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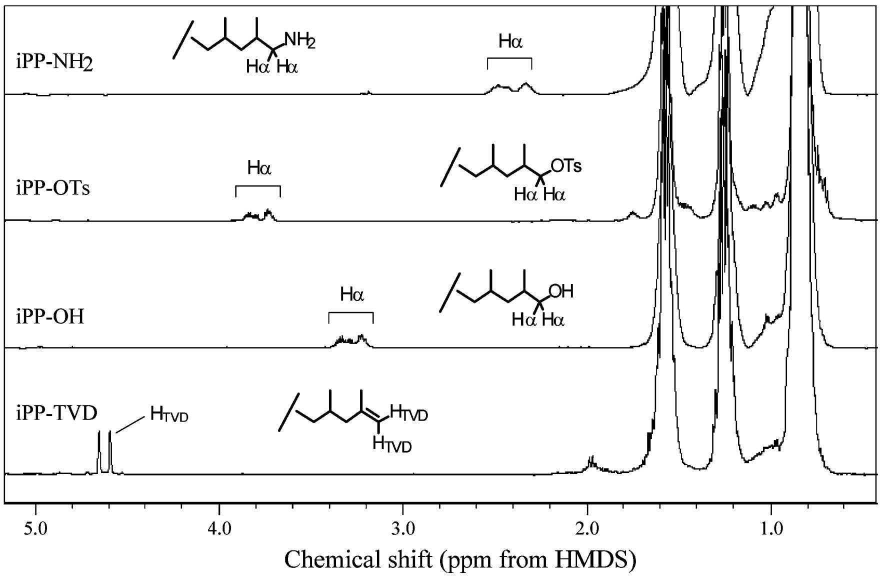


Figure 1. ^{1}H NMR spectra of iPP-TVD and α,ω-difunctional iPPs (α-methylene proton region).

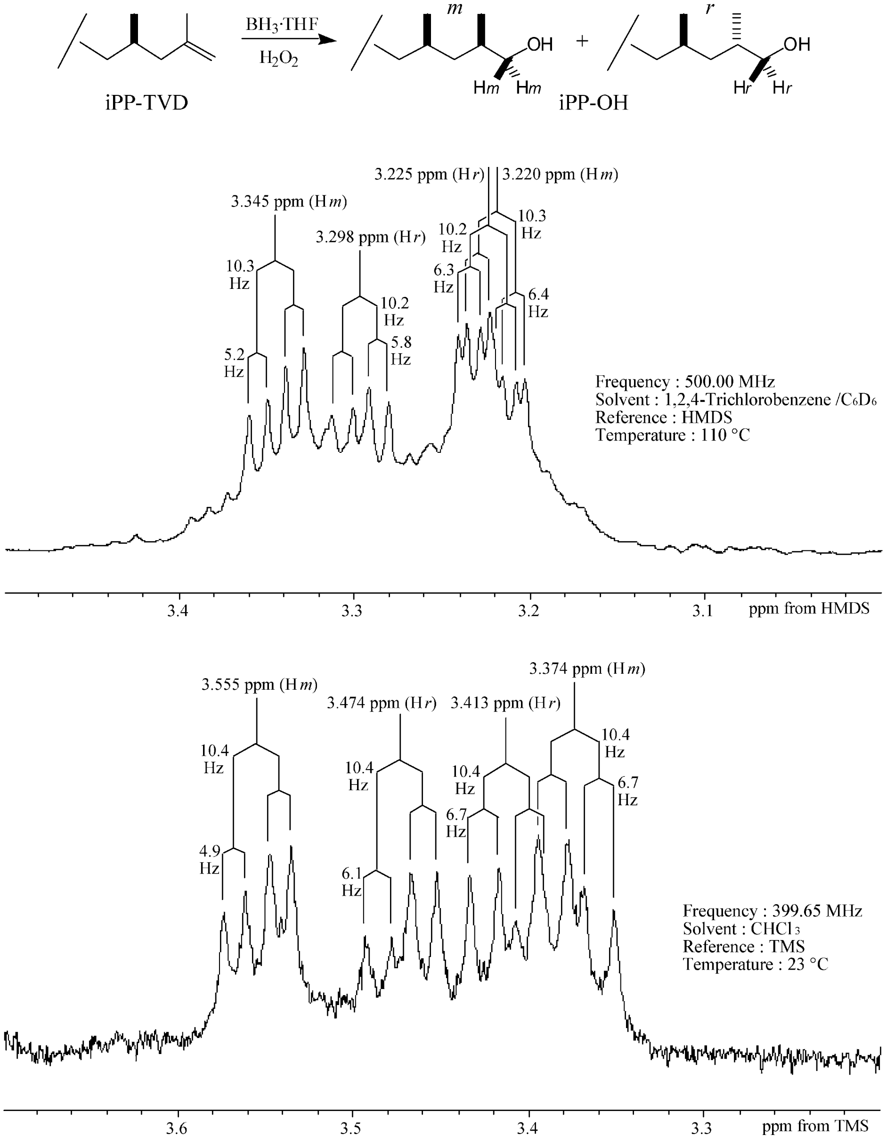


Figure 2. ^{1}H NMR assignment of α-methylene protons of iPP-OH.

this low reactivity seemed to be the insoluble character of iPP-TVD. The reaction mixture was heterogeneous, and the hydroboration did not proceed effectively. By using a large excess of 9-BBN, however, the desired α,ω-dihydroxyoligopropylenes (PP-OHs) were obtained in good yield. The results are shown in Table 2. For sPP-

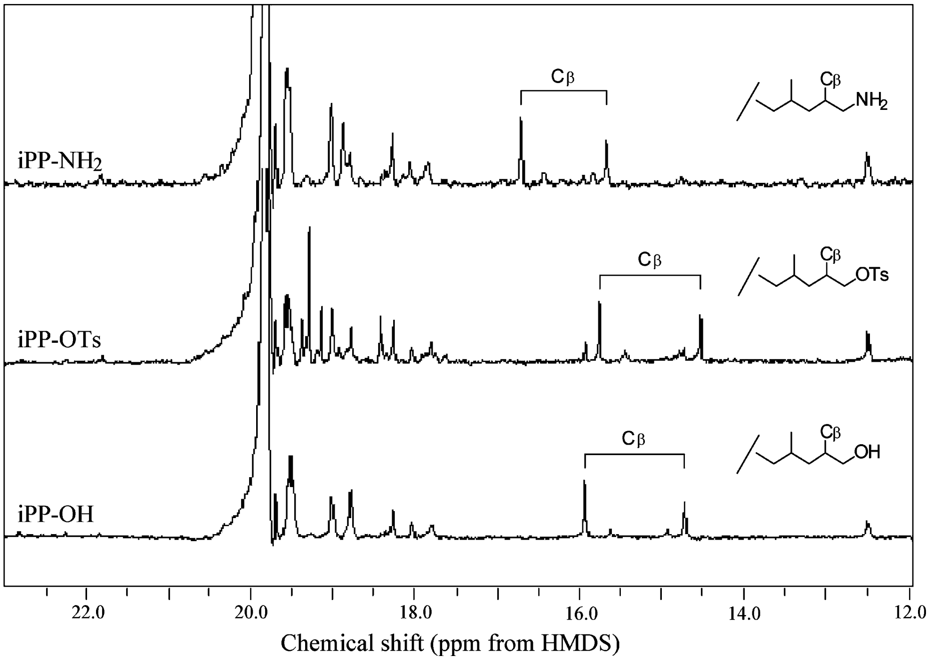


Figure 3. ^{13}C NMR spectra of α,ω-difunctional iPPs (β-methyl carbon region).

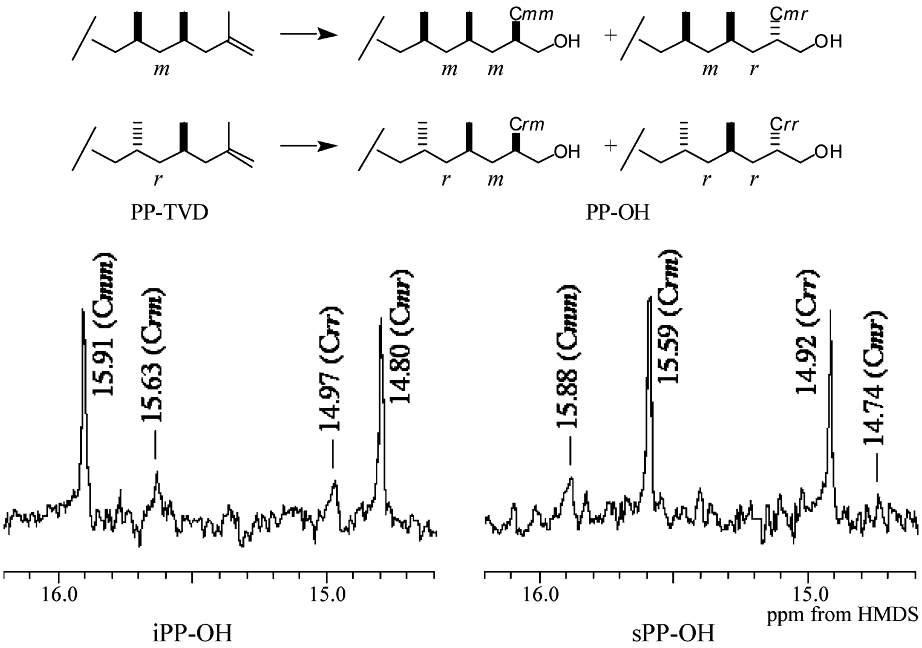


Figure 4. ^{13}C NMR assignment of β-methyl carbons of PP-OH.

TVD and aPP-TVD, 16 equiv of 9-BBN was used, but 32 equiv was required for iPP-TVD, which has lower solubility (runs 1−4). However, because of its high reactivity, the use of an equimolar amount or a small excess of BH_3·THF gave the desired iPP-OH in high yield (runs 5, 6).

In the ^{1}H NMR spectra of the precursor and products (Figure 1), the signals assigned to the vinylidene protons of iPP-TVD (4.59 and 4.66 ppm) almost disappear, and signals corresponding to the α-methylene protons of iPP−OH (3.20−3.37 ppm) appear. The multiple signals of the α-methylene protons can be explained as representing two sets of double-doublets for each of the epimers (two sets for *m* and two set for *r*) formed on the sp^2 vinylidene carbon during hydroboration, as shown in Figure 2. Conversion of the vinylidene group to a hydroxymethyl group is observed in the ^{13}C NMR spectra (Figure 3). In the region of the β-methyl carbon, two major signals (14.80 and 15.91 ppm) and two minor signals (14.97 and 15.63 ppm) are seen. The major signals are due to epimers from the isotactic terminals (*mr* and *mm*, respectively), and the minor signals result from the disordered terminals (*rr* and *rm*). In contrast, the spectrum of sPP-OH from syndiotactic PP shows β-methyl carbon signals for *rr* and *rm* which are larger than those of *mr* and *mm* (Figure 4). This indicates that the disorder in the stereoregularity of the terminals is the result of thermal degradation, as described in our previous paper.[7] In the IR spectra, the disappearance of a band at 887 cm^{-1} in the spectrum of iPP-TVD (C=CH_2, out-of-plane bending) and the appearance of a band at 3350 cm^{-1} in the spectrum of iPP-OH (O−H, stretching) are observed (Figure 5).

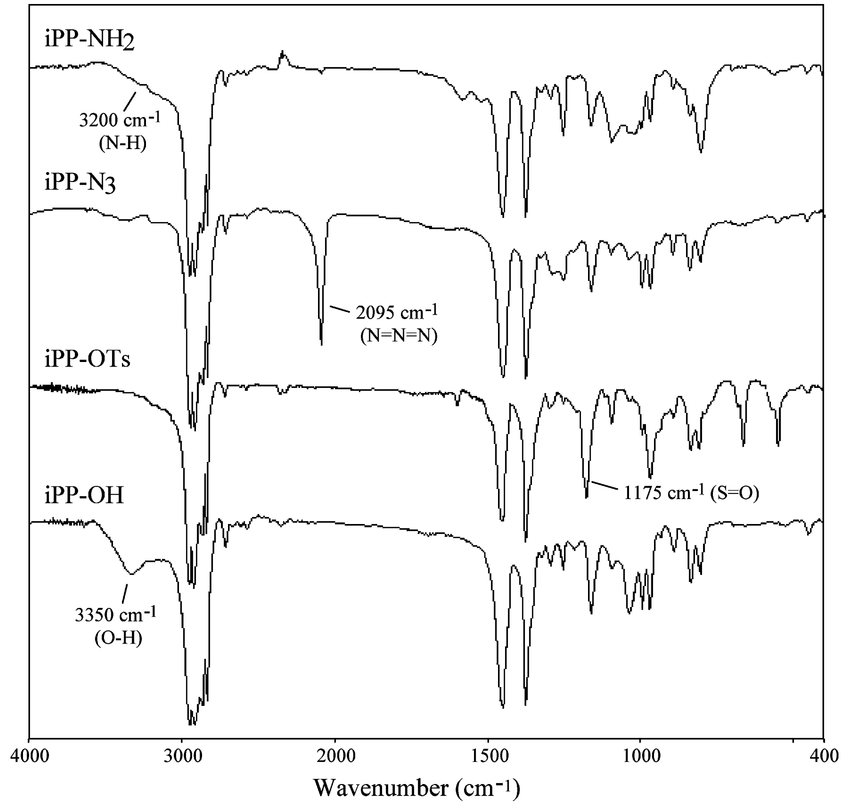


Figure 5. IR spectra of α,ω-difunctional iPPs.

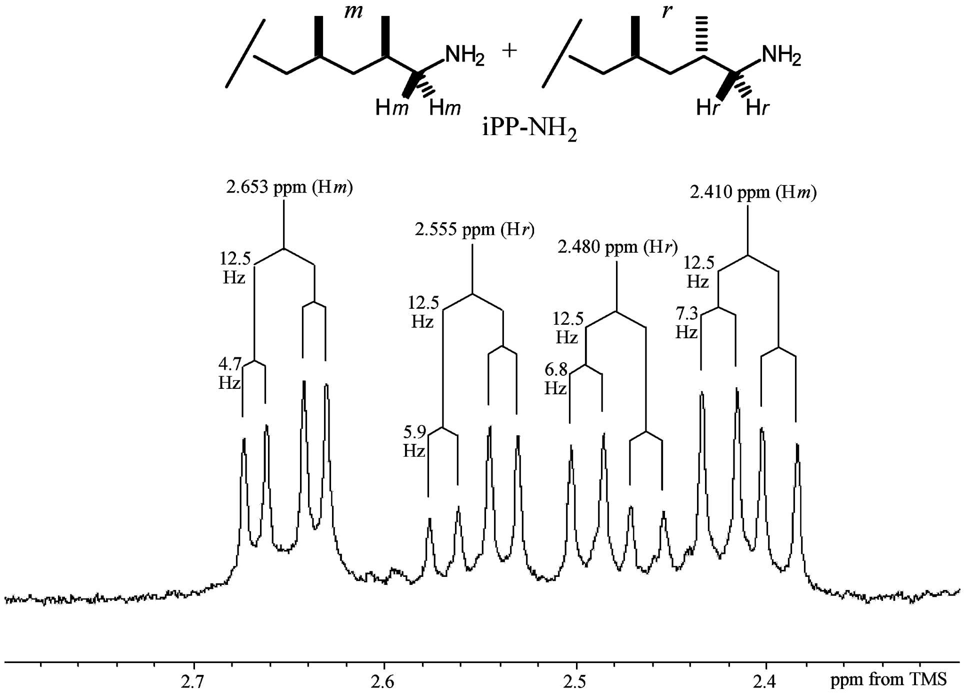
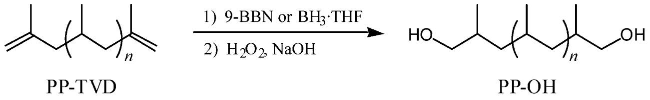


Figure 6. ^1H NMR assignment of α-methylene protons of iPP-NH_2 (frequency: 399.65 MHz; solvent: $CHCl_3$; reference: TMS; temperature: 23 °C).

2. Preparation of α,ω-Diaminooligopropylenes. For the preparation of α,ω-diaminooligopropylenes (PP-NH_2), we planned to convert the hydroxyl groups on PP-OH to amino groups via tosylates and azides.[8] iPP-OH (IV) was tosylated with *p*-toluenesulfonyl chloride, and the OTs groups were then converted to azide by reaction with NaN_3 in DMF. The desired product, iPP-NH_2, was then obtained in good yield by reduction of the azide with $LiAlH_4$ (Scheme 2).

Scheme 1



^1H NMR, ^{13}C NMR, and IR spectra of the iPP-OH precursor and the tosylate (iPP-OTs), azide (iPP-N_3), and iPP-NH_2 products are shown in Figures 1, 3, and 5. In the ^1H and ^{13}C NMR spectra, it is observed that

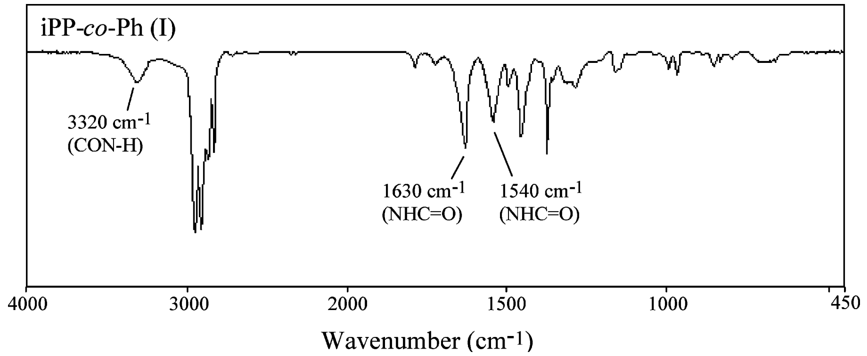
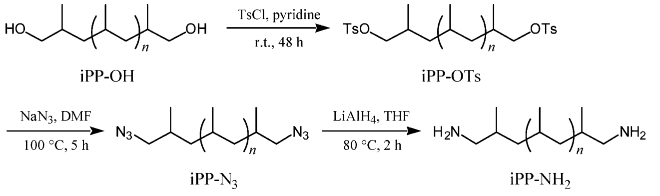
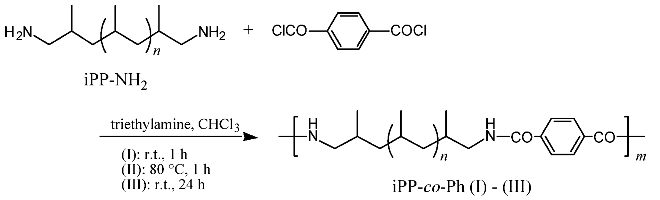


Figure 7. IR spectrum of iPP-*co*-Ph (I).

Scheme 2



Scheme 3



chemical shifts of the signals vary with changes in functional group. The α-methylene protons appear at 3.70−3.88 ppm for iPP-OTs and 2.26−2.55 ppm for iPP-NH_2 (Figure 1). The signals of the protons split into a pattern similar to that obtained for iPP-OH. In Figure 6, ^{1}H NMR assignments for the multiplet signal of iPP-NH_2 are shown. ^{13}C signals corresponding to the *β*-methyl carbons are observed at 14.53−15.78 ppm for iPP-OTs and 15.70−16.75 ppm for iPP-NH_2, with retention of the four-signal pattern referred to earlier (Figure 3). The IR spectra (Figure 5) also indicate conversion of the OH group to an OTs group (disappearance of a band at 3350 cm^{-1} (O−H stretching) and appearance at 1175 cm^{-1} (S=O stretching)), conversion of OTs to N_3 (the appearance of a band at 2095 cm^{-1} due to N=N=N stretching), and conversion of N_3 to NH_2 (disappearance of the band at 2095 cm^{-1} and appearance at 3200 cm^{-1} (N−H stretching)).

3. Copolymerization of iPP-NH_2 with Terephthalic Acid. The first prepared telechelic diamino-oligopropylene, iPP-NH_2, may be useful in the preparation of novel recyclable polyolefin copolymers. For example, amidation with dicarboxylic acids gives unique copolymers with PP chains and amide bonds alternating in the main chain. Reactions of iPP-NH_2 and terephthaloyl chloride with triethylamine were carried out in $CHCl_3$ (Scheme 3).

In the IR spectrum of iPP-*co*-Ph (I) (Figure 7), bands corresponding to CON−H (3320 cm^{-1}, stretching) and NHC=O (1630 and 1540 cm^{-1}, stretching) can be seen. GPC curves for iPP-NH_2 and iPP-*co*-Ph (I−III) are shown in Figure 8. The molecular weight of iPP-*co*-Ph shifts to become higher than that of iPP-NH_2, and clear peaks assigned to stepwise growth of the molecular weight are observed. In the DSC curves of iPP-NH_2 and iPP-*co*-Ph (I−III) (Figure 9), the endothermic peak due to melting (T_m) shifts to a higher temperature and the melting enthalpy (ΔH_m) decreases after copolymerization. From these results, it was concluded that iPP-NH_2 was copolymerized with terephthalic acid, and condensed copolymers iPP-*co*-Ph were obtained.

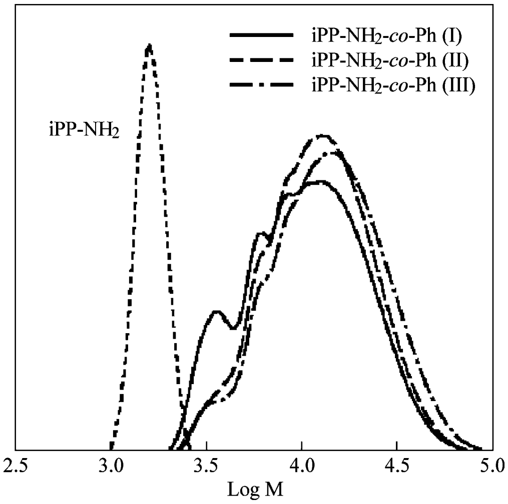


Figure 8. GPC curves for iPP-NH_2 and iPP-*co*-Ph.

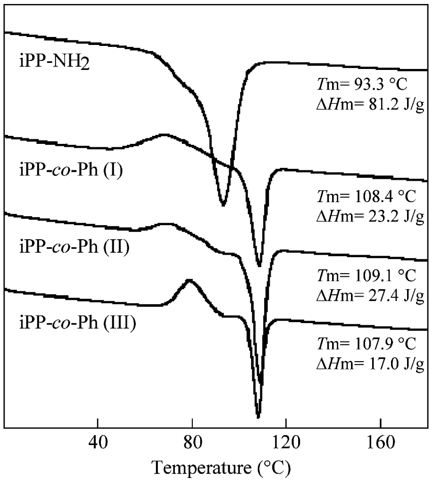


Figure 9. DSC curves for iPP-NH_2 and iPP-*co*-Ph.

Conclusions

Novel α,*ω*-difunctional oligopropylenes were prepared from α,*ω*-bis(2-propenyl)oligopropylene (PP-TVD). PP-OH oligomers obtained from PP-TVD by hydroboration and subsequent oxidation were converted to PP-NH_2 via tosylate and azide. PP-NH_2 was copolymerized with terephthalic acid to give copolymers with higher molecular weights. It was shown that the products PP-OH and PP-NH_2 may be used to prepare macromonomers for unique polyolefin copolymers.

Experimental Section

General. PP-TVDs were prepared by controlled thermal degradation of commercially available polypropylenes. THF was dried over CaH_2 and distilled under N_2 before use. The other reagents were used without further purification. FT-IR spectra were measured with a Perkin-Elmer 1600 spectrometer. Melting points (T_m) and melting enthalpies (ΔH_m) were determined by DSC measurement (Seiko Instruments Inc., DSC6100).

NMR Measurement. A JEOL JNM-ECP500 spectrometer was used for ^1H NMR (500.0 MHz) and ^{13}C NMR (125.0 MHz) measurements. The samples were dissolved in 1:3 (v/v) mixture of benzene-d_6 and 1,2,4-trichlorobenzene (ca. 10% (w/v) concentration), and HDMS was added as an internal standard. The solutions were sealed in 10 mm o.d. sample tubes under N_2 and measured at 110 °C. For quantitative ^{13}C NMR spectroscopy, 15.0 s pulse delay times were used.[7] ^1H NMR spectra were also measured with a JEOL JNM-GX400 spectrometer (399.65 MHz). The samples were dissolved in $CDCl_3$ with TMS and measured at 23 °C.

Molecular Weight Determination. M_n, M_w, and M_w/M_n were determined by high-temperature GPC (TOSOH HLC-8121GPC/HT) with a TOSOH TSKgel G2000H_{HR}(20)HT/GMH_{HR}-HHT column system. The molecular weight was calibrated using standard polystyrene, and 26.4 was used as the Q factor. *o*-Dichlorobenzene was used as an eluent, and the measurement was performed at 140 °C.

Preparation of PP-OHs. A four-necked flask equipped with reflux condenser, thermometer, two-way stopcock, and septum cup was charged with 1.0 g of PP-TVD and 20 mL of dried THF. Boranes (1 M BH_3·THF complex or 9-BBN, see Table 2) in THF solution were added dropwise to the mixture by syringe with stirring. The reaction mixture was stirred at 55 °C for 5 h under an atmosphere of N_2. After cooling the mixture to room temperature, 5 M NaOH (8 equiv of boranes) and methanol (1/4 volume of aqueous NaOH) were added. The mixture was chilled with ice, H_2O_2 (35% solution, 12 equiv of boranes) was added dropwise, and oxidation was carried out at 40 °C for 6 h. The mixture was then poured into methanol to precipitate the oligomer, which was filtered. The oligomer was washed in refluxed methanol for 2 h, filtered, and dried under reduced pressure. In almost all cases, 80% of the oligomers were recovered.

Tosylation of iPP-OH. To a mixture of 0.95 g of iPP-OH and 1.0 mL of anhydrous pyridine in 30 mL of $CHCl_3$, *p*-toluenesulfonyl chloride (15 equiv of iPP-OH) was added, and the mixture was stirred at room temperature for 24 h under an N_2 atmosphere. After the reaction, the mixture was poured into methanol. Precipitated iPP-OTs was filtered and dried under reduced pressure. The yield of iPP-OTs was 1.08 g.

Azidation of iPP-OTs. A mixture of 0.74 g of iPP-OTs and sodium azide (10 equiv of iPP-OTs) in 20 mL of DMF was stirred at 100 °C for 5 h under an N_2 atmosphere. The reaction mixture was poured into water, and azidated polymer was precipitated. After filtration and drying under reduced pressure, 0.46 g of iPP-N_3 was obtained.

Preparation of iPP-NH_2. To 0.46 g of iPP-N_3 in 60 mL of dry THF, lithium aluminum hydride (iPP-N_3:$LiAlH_4$ = 1:5 molar ratio) was added, and the mixture was stirred at 80 °C for 2 h under an N_2 atmosphere. After adding methanol to inactivate the hydride, the solvent was evaporated under reduced pressure. Xylene was added to the residue, and the oligomer was dissolved by heating. The solution was hot-filtered, and the oligomer was reprecipitated by dropping the solution into methanol. The obtained iPP-NH_2 was filtered and dried under reduced pressure. The yield of iPP-NH_2 was 0.33 g.

Copolymerization of iPP-NH_2 with Terephthalic Acid. Equimolar amounts of iPP-NH_2 and terephthaloyl chloride were reacted in $CHCl_3$ with an excess of triethylamine (see Scheme 3). The copolymer was reprecipitated in methanol, filtered, and dried under reduced pressure.

References and Notes

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