NOTES

Preparation of Telechelic Oligomers by the Thermal Degradation of Syndiotactic Polypropylene

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Terminal-functionalized polyolefins are useful for the synthesis of block copolymers and modifications of polymer properties. Some attempts have been made to prepare of these polymers. Some end-reactive polypropylenes are synthesized by utilizing the living active end of almost uniform syndiotactic polypropylene prepared by living polymerization with soluble vanadium-based catalysts.¹ Recently, the Kaminsky-type homogeneous catalyst was found active for the synthesis of polypropylenes with completely different stereoregularities depending on the kind of organotransition-metal complex.² The polymer prepared by this method of polymerization has a terminal vinylidene double bond³ and thereby some terminal-functionalized polypropylenes are prepared by reactions of the isopropenyl end group.⁴ However, these reactive polymers possess a functional group not at both chain end but at one chain end.

More recently, we found that almost all nonvolatile oligomers isolated from the polymer residue by the thermal degradation of isotactic polypropylene at 370°C are α,ω -diene-oligomers having two isopropenyl groups at both chain ends.⁵ These oligomers are expected to be useful as new telechelic oligomers, since they retain the stereoregularity (microtacticity) of the original polymer.

The physical properties of highly syndiotactic polypropylene with a relatively low crystallinity prepared by a Kaminsky-type homogeneous catalyst markedly differ from those of isotactic polypropylene.⁶

This note demonstrates that syndiotactic α,ω -diene-oligomers are prepared by the thermal degradation of syndiotactic polypropylene.

EXPERIMENTAL

Sample

The syndiotactic polypropylene used was "SPT-0071" supplied by Mitsui Toatsu Chemicals, Inc. and used without further purification. Characteristics of the sample are shown in Table I.

Apparatus

The apparatus and procedure for thermal degradation are described in detail in a previous paper.⁵ After the reaction, the polymer residue in the flask was dissolved

in 10 cm³ of xylene and reprecipitated with 50 cm³ of 2-propanol to remove small amounts of volatile oligomers. The reprecipitates were termed nonvolatile oligomers and used as samples for characterization after vacuum drying under heating.

Characterization

¹³C NMR spectra were measured with a JEOL JNM-GX400 spectrometer operated at 100.40 MHz and 110°C with an internal lock. The protons were decoupled from the carbon nuclei using a random noise decoupling field. The concentration of the sample was approximately 10% (w/v) in a 2:1 (v/v) mixture of 1,2,4-trichlorobenzene and benzene-*d*₆. Hexamethyldisiloxane (HMDS) was used as the internal standard (2.0 ppm from tetramethylsilane, Me₄Si). Pulse angle of 90° and pulse repetition times of 16.363 s were used. Measurement was generally carried out for about 50 h. These conditions promised that the equilibrium magnetization was attained and saturation of resonance of interest would not occur. ¹H NMR spectra were also measured with a JEOL JNM-GX400 spectrometer operated at 399.65 MHz and 110°C with internal lock. Pulse angle of 45° with a pulse repetition of 22.81 s and about 1000 scans were used. The intensities of the peaks in ¹H and ¹³C NMR spectra were measured by the area method.

M_n, *M_w* and molecular weight distribution were measured by a GPC (SSC-7100). The data were calibrated by standard polystyrene, and 26.4⁷ was used as the *Q* factor without intrinsic viscosity measurement. The melting point (*T_m*) and heat of melting (ΔH) were measured by DSC (Seiko DSC 220) in a stream of N₂ gas. Measurement conditions were as follows: sample weight, ca. 10 mg; heating rate, 5.0°C min⁻¹.

RESULTS AND DISCUSSION

Yield of the polymer residue and characteristics of the nonvolatile oligomers obtained by the thermal degradation of syndiotactic polypropylene at 370°C are listed in Table I. GPC curves of the original polymer and nonvolatile oligomers are shown in Figure 1. *M_n* of the nonvolatile oligomers ranged from 3000 to 3500 and the *M_w*/*M_n* ratio markedly decreased to ca. 2 from 4.18 of the original sample. The microtacticity (triad) of the nonvolatile oligomers is nearly the same as that of the original polymer, that is, the nonvolatile oligomers

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Table I. Yield of polymer residue and characteristics of nonvolatile oligomers obtained by the thermal degradation of syndiotactic polypropylene at 370°C

Time min	Yield wt%	Nonvolatile oligomers									Functionality, ^b f_t
		$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$\frac{M_w}{M_n}$	$\frac{M_{n0}}{M_n} - 1$	Microtacticity (triad) ^a			T_m °C	ΔH J g ⁻¹	
						<i>mm</i>	<i>mr</i>	<i>rr</i>			
0	0	233	55.8	4.18	—	0.04	0.18	0.78	128.2	26.4	—
30	90	13.6	4.59	2.97	11.1	0.04	0.08	0.88	131.9	48.9	1.76
60	78	8.51	3.52	2.42	14.8	0.04	0.12	0.84	127.5	53.3	1.78
90	65	6.38	3.20	1.99	16.5	0.05	0.12	0.83	124.8	67.7	1.72

^a Determined from the relative intensity of triad peaks of methyl carbon except for peaks of each end group in the ¹³C NMR spectrum.^b $2 \times I_{TVD} / [I_{TVD} + I_{n-Pr}]$; I : Intensity of the ¹³C NMR methyl signal of each end group. **Figure 1.** GPC curves of the original polypropylene and nonvolatile oligomers.

mostly retain the stereoregularity of the original polymer without random epimerization during thermal degradation. A relatively broad endothermic peak of DSC curve, possibly caused by melting of crystallites, increased largely for the oligomers compared to the original polymer. As shown in Table I, the melting point (T_m) slightly reduces from 128°C for the original polymer to ca. 125°C for the oligomers. The right column of Table I represents the average number of isopropenyl end groups per molecule (f_t).

Portions of ¹³C and ¹H spectra of the nonvolatile oligomers are shown in Figures 2 and 3, respectively. Characteristic signals in these figures are extremely similar to those of end groups of the nonvolatile oligomers prepared from isotactic polypropylene.⁵ According to identification of these end groups,⁵ a signal at 20.52 ppm in Figure 2 was exactly assigned to α methyl carbon^{3,8,9d} of the terminal vinylidene double bond (TVD) of isopropenyl end group [$\text{CH}_2=\text{C}(\text{CH}_3)-$] and the resonances at 109.64 and 142.57 ppm were assigned to the olefinic carbons of TVD.^{3,8,9d} No signal corresponding to the internal olefinic carbons was detected. Two strong signals around 4.601 and 4.661 ppm and a very weak signal around 5.262 ppm were recognized in the ¹H NMR spectrum of each nonvolatile oligomer (Figure 3). These two strong signals were assigned to two non-equivalent olefinic protons of TVD^{4c-f,9d} and the very weak signal may be due to one olefinic proton of the internal double bond.⁹ The contents of these double bonds are about 95 mol% of the former and about 5 mol% of the latter. The signals at 12.46 and 38.71 ppm in Figure 2 correspond to methyl and methylene carbons from the end of the *n*-propyl group (*n*-Pr) [$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)-$], respectively, and the signals

at 38.71 ppm was assigned to the tetrad (*rrr*, *r*: racemo) methylene carbons.^{3,9} Because no resonance was detected at 20.4, 20.6, 21.4, 21.7, and 24.0 ppm as shown in Figure 2,⁹ the existence of isopropyl end group is negligible. The methyl carbon resonance is sensitive to the configuration of polymer chain^{11a} and most of the resonance between 18.00–19.85 ppm was assigned to the pentad and heptad configurational sequence of methyl carbon.^{9c,d} Consequently, both TVD and *n*-Pr were detected only in the nonvolatile oligomers isolated from the polymer residues resulting from the thermal degradation of syndiotactic polypropylene.

The intensities of signals of α methyl carbon (20.52 ppm) of TVD and methyl carbon (12.46 ppm) of *n*-Pr in Figure 2 were measured by the area method. The results show certainly that the end groups of the nonvolatile oligomers consist of about 88 mol% of isopropenyl group (TVD) and about 12 mol% of *n*-Pr. Assuming all nonvolatile oligomers are linear, f_t was calculated as 1.76 from the following equation⁵

$$f_t = \frac{2 \times (\text{methyl signal intensity of isopropenyl end group, } I_{TVD})}{(\text{methyl signal intensity of all end groups, } [I_{TVD} + I_{n-Pr}])}$$

This f_t indicates that about 77 mol% of the oligomer molecules is a structurally symmetric α,ω -diene-oligomer having two isopropenyl end groups. The contents of macromonomers having an isopropenyl end group and an *n*-Pr end group and the terminal-saturated oligomer having two *n*-Pr groups are about 21 mol% and 2 mol%, respectively. These values were derived by statistical fitting, as described previously.⁵ As suggested from changes in GPC curves (Figure 1), the scission reaction of the main chain occurs at random positions of the polymer. Average numbers of scission (M_{n0}/M_{n-1}) are 11, 15, and 17 after 30, 60, and 90 min at 370°C, respectively. Therefore, over 92% of the end groups of these oligomers are formed during scission reactions.

Thus, it was concluded that syndiotactic telechelic oligopropylenes having two isopropenyl end groups could be synthesized in good yield by the thermal degradation of syndiotactic polypropylene. These oligomers are also expected as new telechelic oligomers.⁵ We prepared multiblock copolymers of α,ω -dihydrosilylpolydimethylsiloxane with these telechelic oligomers with different stereoregularities.¹²

The degradation products are produced *via* various elementary reactions of secondary terminal macro-

Figure 2. A portion of ^{13}C NMR spectra of the nonvolatile oligomers.

Figure 3. A portion of ^1H NMR spectra of the nonvolatile oligomers.

radicals in the depropagation step, as discussed previously.⁵ A possible mechanism for the predominant formation of TVD of nonvolatile oligomers (polymer residue) is as follows: telechelic oligomers are formed by intramolecular hydrogen abstraction (back-biting) of secondary terminal macroradicals followed by β scission at the end of main chain and intermolecular hydro-

gen abstraction of secondary terminal volatile radicals formed by the back-biting and other elementary reactions, followed by β scission.

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