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Preparation of α,ω-Diisopropenyloligopropylene by Thermal Degradation of Isotactic Polypropylene

Takashi Sawaguchi,* Tadashi Ikemura, and Manabu Seno

Department of Industrial Chemistry, College of Science and Technology, Nihon University, Kandasurugadai, Chiyoda-ku, Tokyo 101, Japan

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ABSTRACT: It was found that α,ω-diisopropenyloligopropylene (M_n = 3300−4800) is prepared as the nonvolatile oligomers isolated from the polymer residues resulting from the thermal degradation of isotactic polypropylene at 370 °C. Their structures were determined by ^1H and ^{13}C NMR spectroscopies in regard to the reactive end groups. Both the terminal vinylidene double bonds composed of an isopropenyl end group [CH_2=$C(CH_3)$−] and the saturated end group [$CH_3CH_2CH_2CH(CH_3)$−] were mainly detected with a molar ratio of about 9:1. The average number of isopropenyl end groups per molecule (f_t) is about 1.8, and therefrom it is indicated that about 80 mol % of the oligomer molecules is symmetric α,ω-diene-oligomer having two terminal isopropenyl groups. This oligopropylene retains highly the stereoregularity (microtacticity) of the original polymer and has a sharper dispersity of molecular weight (M_w/M_n: *ca.* 1.5) than the original polymer, in spite of lower molecular weights and T_m (*ca.* 150 °C). This compound is useful as a new telechelic oligomer. These oligomers are considered to be formed by the intramolecular hydrogen abstraction (back-biting) of secondary terminal macroradicals followed by β scission at the end of the main chain (eq 3) and the intermolecular hydrogen abstraction of secondary terminal volatile radicals (eq 4), which are formed by the back-biting and other elementary reactions, followed by β scission.

Introduction

The methods for introducing functional groups to polyolefins have been intensively explored to obtain a modifier to improve some properties such as chemical reactivity and affinity to adhesives or paints. Especially, terminal-functionalized polymers are useful not only to synthesize block copolymers but also to modify polymer properties. Some attempts have been carried out for the preparation of these polymers. For example, in the case of polypropylene, some end-reactive polypropylenes and block polymers with polar monomers are synthesized by utilizing a living active end of almost uniform syndiotactic polypropylene prepared by living polymerization with soluble vanadium-based catalysts.[1] More recently, it was found that a Kaminsky-type homogeneous catalyst produces polypropylene with a completely different stereoregularity depending on the organotransition-metal complex.[2] The polymer formed by this polymerization has a terminal vinylidene double bond,[3] and thereby some terminal-functionalized polypropylene as well as block copolymers were prepared by reactions of the isopropenyl end group.[4] However, these reactive polymers possess a functional group only at one chain end but not at the multichain end such as telechelics and polyfunctional telechelics.

Recently, the thermal degradation of polymers has been widely reinvestigated to synthesize new compounds including polymers, oligomers, and monomers.[5] It is very interesting as a unit reaction in synthetic chemistry. Moreover, the pyrolysis processes have being developed as useful methods for recovering carboneous compounds and fuel from waste polymers in view of the increasing crisis of the global environment.[6]

In a previous letter,[7] we reported that most of the nonvolatile oligomers obtained by the thermal degradation of isotactic polypropylene are composed of telechelic oligomers having two isopropenyl end groups from the precise analysis of end structure by ^1H and ^{13}C NMR spectroscopies. In this paper, we present details of the preparation and characteristics of the telechelic oligomers and discuss the mechanism of their formation.

Experimental Section

Sample. The isotactic polypropylene was commercially available and purified by precipitation with hot xylene−methanol. The precipitate was extracted for about 70 h with boiling *n*-heptane in an N_2 stream, and the residue was used as a sample after vacuum drying under heating. Characteristics of the sample are shown in Table 1.

Apparatus. The apparatus used was described in our previous paper.[8] The apparatus was made of Pyrex glass. The degradation experiments were done at 370 °C at 4 mmHg in a stream of N_2 gas. The reaction temperature was measured by an alumel−chromel thermocouple in a Pyrex glass tube

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Table 1. Yield of Polymer Residue and Characteristics of Nonvolatile Oligomers Obtained by Thermal Degradation of Isotactic Polypropylene at 370 °C

time, min	yield, wt %	nonvolatile oligomers								
					microtacticity (triad)[a]				density,[b]	functionality[c]
		$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	mm	mr	rr	T_m, °C	g/cm³	f_t
0	0	338	60.8	5.56	0.94	0.04	0.02	164.4	0.8771	-
45	82	7.83	4.76	1.64	0.93	0.05	0.02	151.9	0.8775	1.82
60	80	6.95	4.41	1.57	0.92	0.05	0.03	150.5	0.8776	1.80
90	67	4.94	3.29	1.50	0.90	0.07	0.03	146.0	0.8779	1.76

[a] Determined from the relative intensity of the triad peaks of the methyl carbon except for peaks of each end group in the ^{13}C NMR spectrum. [b] At 17.6 °C. [c] $2I_{TVD}/[I_{TVD} + I_{n-Pr}]$. I is the intensity of the ^{13}C NMR methyl signal of each end group.

installed at the bottom of the flask and controlled within ±2 deg. Part of fractionating column in the apparatus was held at a specified temperature to remove rapidly the volatiles from the reaction flask. One gram of sample was placed in a flask, and the air in the apparatus was replaced by a stream of N_2 gas at 4 mmHg, which was reported to be of 99.999% purity containing 0.0007% oxygen by volume. The flask was contacted with the metal bath maintained at a specified temperature and then immediately immersed in the bath, when the sample attained a temperature of about 250 °C. The reacting molten polymer in the flask was vigorously stirred with bubbles of N_2 gas introduced. After the reaction the volatiles including volatile oligomers were collected in a fraction trap chilled with liquid N_2 and the volatile oligomers, which are liquid at room temperature, were dissolved in acetone for GC analysis. Moreover, the polymer residue in the flask was dissolved in 10 cm³ of xylene and reprecipitated with 50 cm³ of methanol to remove a small amount of volatile oligomers. The reprecipitate was termed nonvolatile oligomers and used as a sample for characterization after vacuum drying under heating. The nonvolatile oligomers were almost completely separated from the volatile oligomers. The nonvolatile oligomers thus obtained are focused in this experiment.

Characterization. NMR. ^{13}C NMR spectra were measured with a JEOL JNM-FX100 spectrometer operating at 25.05 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 1:3 (v/v) mixture of 1,2,4-trichlorobenzene and benzene-d_6. Hexamethyldisiloxane (HMDS) was used as an internal standard (2.0 ppm from tetramethylsilane, Me_4Si). The 10-mm sample tubes were deaerated by several freeze–pump–thaw cycles and sealed after N_2 gas was admitted into the evacuated tube. Spectral widths were 2 kHz, with 8192 data points acquired on a JEC 980 computer. A pulse width of 45° and approximately 6 μs and pulse repetition times of 10 s were used. The experiments were generally performed within 20–45 h. These conditions presumed that equilibrium magnetization was attained and that saturation of a resonance of interest would not occur.[9]

^1H NMR spectra were also measured with a JEOL JNM-FX100 spectrometer operating at 99.6 MHz and 110 °C with an internal lock. Although sample concentrations and the preparation of sample tubes were the same as those for carbon-13 nuclei, 5-mm sample tubes were used for ^1H NMR spectra. The spectral width was 1 kHz, excluding the overflowing spectral region except for the chemical shift range of about 3–6 ppm, with 8192 data points acquired on a JEC 980 computer. Pulse widths of 8 μs (a 45° pulse) with a pulse repetition of 10 s and 2000–5000 scans were used.

The intensities of the peaks in the ^1H and ^{13}C NMR spectra were measured by cutting out and weighing each band area in five copies of the enlarged spectrum.

GPC. M_n, M_w, and molecular weight distribution were measured by a GPC (Toyo Soda HLC-811). The data were calibrated by standard polystyrene, and 26.4[10] was used as the Q factor without intrinsic viscosity measurements.

DSC. Melting points (T_m) were measured by a DSC (MAC SCIENCE DSC3100) in a stream of N_2 gas. Measurement conditions were as follows: sample weight, *ca.* 1 mg; heating rate, 5.0 °C/min.

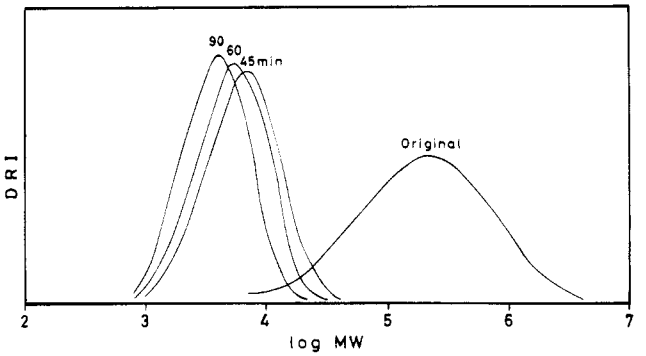


Figure 1. GPC curves of the original polypropylene and the nonvolatile oligomers.

Density. The densities were measured by a density-gradient method at 17.9 °C using the film.

FT-IR. FT-IR spectra were measured with a Perkin-Elmer 1600 FT-IR, using a casting film made of sample powder with a hot-press.

GC. A GC of the volatile oligomers was obtained on a Shimadzu GC-6A gas chromatograph equipped with a flame-ionization detector, and a 3000-mm × 3-mm i.d. glass column packed with OV-17 (5%) on Uniport KS (60–80 mesh) was used.

Hydrogenation of the Nonvolatile Oligomers. Hydrogenation was carried out in a 200-cm³ stainless-steel autoclave which was mechanically stirred at 70 rpm. Hydrogenation conditions were as follows: sample concentration, about 2% in decalin; catalyst, about 20% Pt–charcoal by sample weight; hydrogen added, 35 kg/cm²; temperature, 130 °C; time, 3 h. The reaction mixture was filtered and then dropped in ethanol. The precipitate was analyzed after vacuum drying under heating.

Results and Discussion

The yield of the polymer residues and the characteristics of the nonvolatile oligomers obtained by the thermodegradation of isotactic polypropylene at 370 °C for 45, 60, and 90 min are listed in Table 1. GPC and DSC curves of the original polymer and the nonvolatile oligomers are shown in Figures 1 and 2, respectively. The value of M_n of the nonvolatile oligomers ranges from 3000 to 5000 but the M_w/M_n ratio markedly decreases from 5.56 to *ca.* 1.5. The microtacticity (triad) of the nonvolatile oligomers is nearly the same as that of the original polymer and shows that the nonvolatile oligomers mostly retain the stereoregularity of the original polymer without random stereo-isomerization (epimerization) of the polymer chain during thermal degradation. The endothermic peak of the DSC curve (Figure 2) is caused by melting of crystallites and decreases largely from the original polymer to the oligomers, dependently on their molecular weight. As shown in Table 1, the melting point (T_m) reduces from 164.4 °C for the original polymer to *ca.* 150 °C for the oligomers, but the density at 17.6 °C approximately keeps the

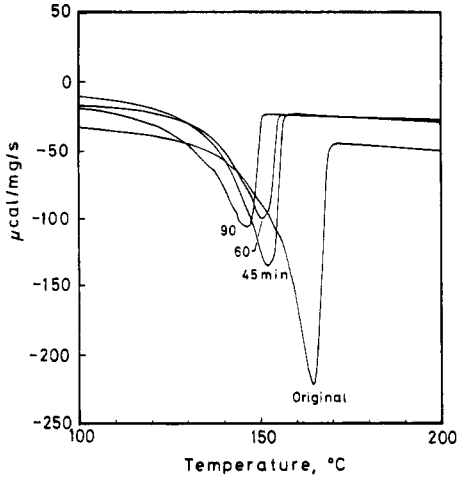
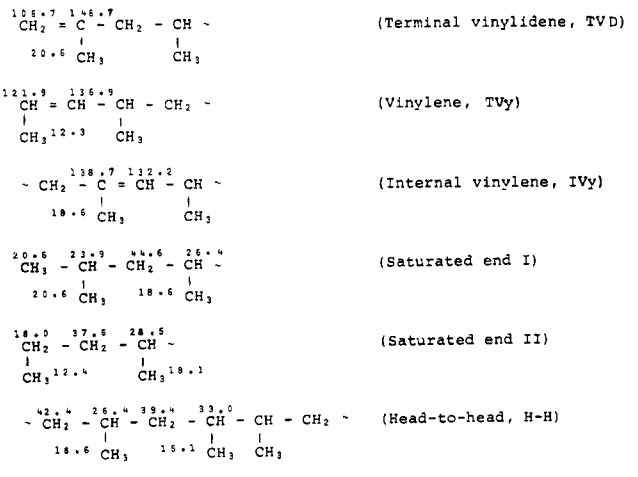


Figure 2. DSC curves of the original polypropylene and the nonvolatile oligomers.

original value of *ca.* 0.877. The values of f_t in the right column of Table 1 represent the average number of isopropenyl end groups per molecule and are discussed later.

A gas chromatogram of the volatile oligomers obtained in this experiment shows many peaks ranging from dimers to about tridecamers and its pattern is extremely similar to that reported by Iida et al.[11] According to their results of identification for oligomers up to pentamers, most of the main peaks consist of about 72 wt % of terminal mono-olefins [CH_2=$C(CH_3)(CH_2CH(CH_3))_nCH_2CH_2CH_3$] and about 21 wt % of symmetric paraffins [$CH_3CH_2CH_2CH(CH_3)(CH_2CH(CH_3))_nCH_2CH_2CH_3$]. These main volatile oligomers are presumed to be formed *via* the transfer (back-biting) of the secondary terminal macroradicals to tertiary hydrogens followed by the two types of β scission,[12-17] and the stereoisomerization occurs *via* stepwise back-biting.[12,13,16] On the other hand, the amount of products expected from the transfer of primary terminal macroradicals is small. The results mentioned above reasonably suggest that the back-biting and intermolecular chain transfer followed by β scission to regenerate the secondary terminal macroradicals occur more frequently than the bond dissociation into two types of terminal macroradicals.[18] Consequently, the stationary concentration of the secondary terminal macroradicals should be much higher than that of the primary macroradicals.

Possible chemical structures of the polymer residues (nonvolatile oligomers) are deduced from the above mechanism as follows:



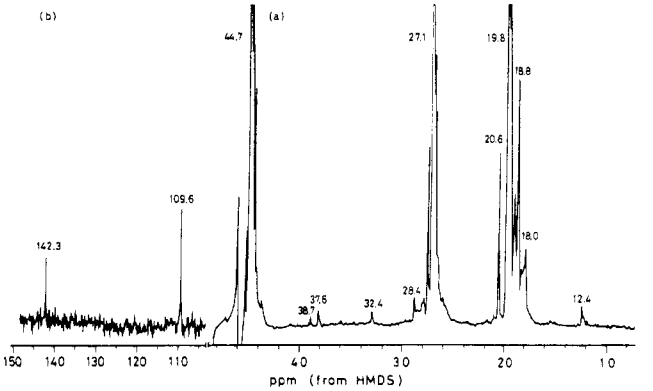


Figure 3. Part of ^{13}C NMR spectra of the nonvolatile oligomers before hydrogenation: (a) measurement conditions were described in the Experimental Section; (b) sample in 8% (w/v) decalin in an 8-mm tube, which was replaced with a 10-mm tube with dimethyl sulfoxide-d_6 for locking, measured with 5 kHz of spectral width and at 140 °C.

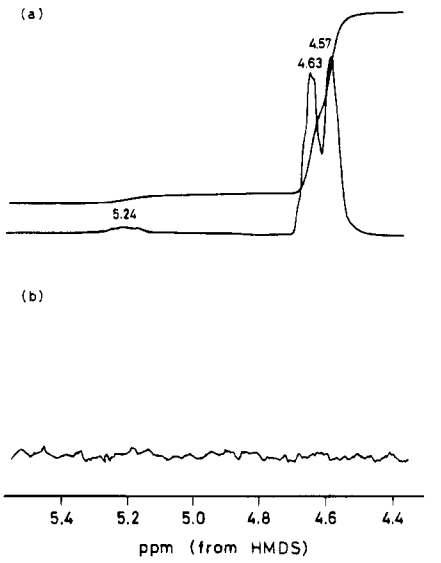


Figure 4. Part of ^1H NMR spectra of the nonvolatile oligomers before (a) and after (b) hydrogenation.

The numeral on each carbon is the value of ^{13}C chemical shift from HMDS calculated from parameters of Lindeman–Adams[19] and Roberts et al.[20] Parts of the ^{13}C and ^1H NMR spectra of the nonvolatile oligomers before or/and after hydrogenation are shown in Figures 3–5. In Figures 3a and 5, the signals at 19.8, 27.1, and 44.7 ppm are assigned to *meso* methyl, *meso* methine, and *meso* methylene carbons, respectively. The methyl carbon resonance is sensitive to the configuration of the polymer chain,[21a] and most in the resonance range 18.0–19.8 ppm are assigned to pentad configurational sequences of the methyl carbon.[21] The resonances at 109.6 and 142.3 ppm shown in Figure 3b are assigned to the olefin carbons of the terminal vinylidene (TVD) type.[3,22,24d] No signals corresponding to the other olefin carbons (TVy, IVy) were detected. On the other hand, the two strong signals around 4.57 and 4.63 ppm and a very weak signal around 5.24 ppm were recognized in the ^1H NMR spectrum (Figure 4a) of the nonvolatile oligomers before hydrogenation, and these signals disappeared in the spectrum (Figure 4b) after hydrogenation. Thereby, these two strong signals are assigned to two nonequivalent olefin protons of TVD[4c-f,24d] and the very weak signal may be owing to one olefin proton of TVy or IVy.[23] The content of these double bonds was about 95 mol % of the former and about 5 mol % of the

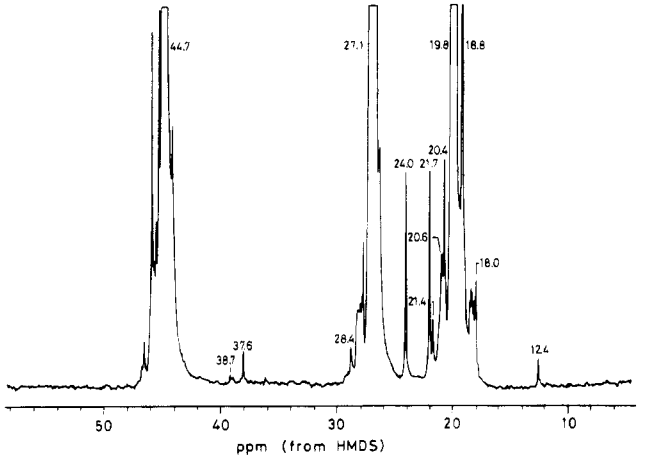


Figure 5. Part of ^{13}C NMR spectra of the nonvolatile oligomers after hydrogenation; measured with 4 kHz of spectral width and double precision memory method.

latter. Because no resonance corresponding to 23.9 ppm was detected, as shown in Figure 3a, the isopropyl end group (*i*-Pr) is negligibly small. The signals at 20.4, 20.6, 21.4, 21.7, and 24.0 ppm in Figure 5 correspond to the respective carbons of *i*-Pr converted from TVD by hydrogenation. The resonances at 20.4, 20.6, 21.4, and 21.7 ppm are caused by conformationally asymmetric methyl carbons,[24] depending on the different stereoregularities of adjacent monomer sequences, respectively, and the resonance at 24.0 ppm is for the methine carbon. Accordingly, a signal at 20.6 ppm in Figure 3a is exactly assigned to the α-methyl carbon[3,22,24d] to the olefin carbon of TVD. Because the calculated values of 18.0 and 18.1 ppm are recognized to be in the resonance range of the configurational methyl carbons, the signals at 12.4, 28.4, and 37.6 (plus 38.7) ppm arising with roughly equal intensities in Figure 3a correspond to carbons of the *n*-propyl end group (*n*-Pr), respectively, and the signals at 37.6 and 38.7 ppm are assigned to the triad methylene carbons.[3,24] The signals at 15.1, 32.0, and 32.5 ppm calculated for the head to head (H−H) linkage formed by the recombination termination between the secondary terminal macroradicals were not detected. The resonances for the branching structure formed *via* the recombination between the secondary terminal macroradical and tertiary on-chain macroradical were also not recognized. The signal at 32.4 ppm in Figure 3, which disappears in Figure 5, is not yet assigned but may be due to an allylic methine carbon of TVy or IVy. Consequently, both TVD and *n*-Pr were detected only in the nonvolatile oligomers isolated from the polymer residues. The chemical shift values of characteristic signals assigned to these partial structures are summarized in Table 2.

We have then tried to estimate quantitatively the two end groups by ^{13}C NMR. For this purpose, the intensities of signals of the α-methyl carbon (20.6 ppm) of TVD, the methyl carbon (21.4 and 21.7 ppm) or methine carbon (24.0) of *i*-Pr, and the methyl carbon (12.4 ppm) or configurational methylene carbons (37.5 and 38.7 ppm) of *n*-Pr in Figures 3a and 5 were measured by the area method. An example of the results of these analyses is shown in Table 3. Although the differences in the spin−lattice relaxation time and the nuclear Overhauser enhancement factor for carbons of interest were not considered in this analysis,[21a,25] the results show certainly that the end groups of the nonvolatile oligomers consist of about 90 mol % isopropenyl group (TVD) and about 10 mol % *n*-Pr in all the cases

Table 2. Summary of NMR Characteristic Signals Assigned to Partial Structures of the Nonvolatile Oligomers[a]

partial structures[b]	observed chemical shifts: carbon-13	observed chemical shifts: proton
$CH_2{=}C(CH_3)-CH_2-$ (106.7, 146.7, 20.6)	109.6, 142.3, 20.6	4.63, 4.67 ($CH_2{=}$)
$CH_3-CH_2-CH_2-CH(CH_3)-$ (12.4, 18.0, 37.6, 28.5, 18.1)	12.4, 18.0, 18.1, 28.5, 37.6, 38.7	

[a] ppm downfield from internal HMDS. [b] Calculated carbon-13 chemical shifts.

examined. Assuming all the nonvolatile oligomers are linear, the value of f_t is calculated from the following equation

$$f_t = \frac{2I_{TVD}}{I_{TVD} + I_{n\text{-Pr}}}$$

and is about 1.8 (Table 1). I_{TVD} is the methyl signal intensity of the isopropenyl end group, and $I_{TVD} + I_{n\text{-Pr}}$ is the methyl signal intensity of all end groups. This f_t value indicates that about 80 mol % of the oligomer molecules is a structurally symmetric α,ω-diene-oligomer having two isopropenyl end groups and, on the other hand, that the macromonomer having an isopropenyl end group and an *n*-Pr and the terminal-saturated oligomer having two *n*-Pr are about 19 and 1 mol % of the oligomers, respectively. This conclusion is confirmed by the statistical fitting of the observed f_t values with those calculated using the composition of end groups among three types of linear oligomers; paraffins, terminal mono-olefins, and terminal di-olefins. It is very interesting that such novel telechelic oligomers having two TVD are formed by the thermal degradation. The IR spectra of the original polypropylene and the nonvolatile oligomers are shown in Figure 6. A band at 887.4 cm^{-1}, which is owing to TVD[26] of the telechelic oligomers, is not detected in the original polymer. As shown from the change in GPC curves (Figure 1), the scission reaction of the main chain occurs at random positions of the polymer. The average number of scission ($M_{n_0}/M_n - 1$) becomes about 12, 13, and 17 for 45, 60, and 90 min, respectively. Thereby, over 90% of the end groups of these oligomers are formed by the scission reaction. In the present stage, little is known on the syntheses of telechelic oligopropylenes having two functional end groups, except for the introduction of a hydroxyl group[27] and carboxyl group[28] *via* ozonolysis of atactic polypropylene. Recently, Lattimer[17] has analyzed isotactic polypropylene by pyrolysis field ionization mass spectrometry and has found that most of the volatile pyrolyzates with higher molecular weights from *ca.* 550 to 1400 are of dialkenes. This is very interesting and may be the minor part of lower molecular weight portion of the telechelic oligomers prepared in this experiment. We have prepared some terminal-functionalized oligopropylene as well as block copolymers by reactions of isopropenyl groups of the telechelic oligomers, and these results will be reported later.

A possible mechanism for the formation of end groups of the nonvolatile oligomers (polymer residues) is given in Scheme 1. The degradation products are produced *via* various elementary reactions of secondary terminal macroradicals in the depropagation step, as mentioned

Table 3. Example of Relative Intensity of ^{13}C NMR Signals and Composition of End Groups of the Nonvolatile Oligomers[a]

	before hydrogenation			after hydrogenation				
	relative intensity		composition, mol %	relative intensity			composition, mol %	
partial structures	methyl	methylene	using (1)	methyl	methylene	methine	using (2)	using (3)
$CH_2{=}C(*CH_3)-CH_2-$	7.1 (1)		88					
$CH_3-*CH(*CH_3)-CH_2-$				10 (2)		11 (3)	91	92
$*CH_3-CH_2-*CH_2-CH(CH_3)-$	1.0 (1)	1.1	12	1.0 (2) (3)	0.98		9	8

[a] Asterisks show carbons of interest.

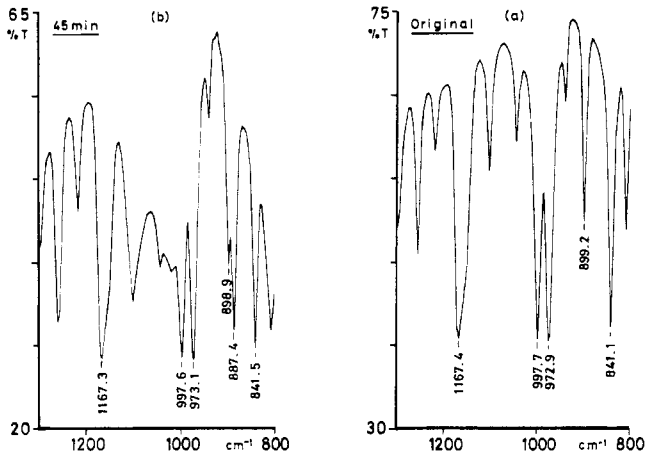


Figure 6. IR spectra of the original polypropylene (a) and the nonvolatile oligomers (b).

above for the formation of volatile oligomers. If the intermolecular radical transfer (eq 1) followed by β scission plays an important role in determining the end groups and the molecular weight of the polymer residues, the value of f_t should statistically tend toward 1 because of the formations of both *n*-Pr and TVD. However, the observed f_t value shown in Table 1 could not be interpreted only by eq 1. So we have directed our attention to volatile radicals, which have been neglected in the consideration hitherto. The formation of terminal mono-olefins and structurally symmetric paraffins in the volatile oligomers is dependent on the positions of β scission of the C−C bond of tertiary on-chain macroradicals, as shown by 1 (eq 2) or 2 (eq 3). Especially, if besides eq 3 the intermolecular hydrogen abstraction (eq 4) of terminal secondary volatile radicals formed by eq 3 occurs, one molecule of the structurally asymmetric paraffins (volatile oligomers) and two molecules of polymer having an isopropenyl end group (TVD) are produced. If the rates of both the reactions eqs 3 and 4 are much faster than that of eq 1, the value of f_t should statistically approach 2. The observed f_t value of 1.8 suggests that the rates of eqs 3 and 4 are greater than that of eq 1. The mono-olefins:paraffins content ratio (*ca.* 72:21 by weight)[11] approximately represents the rate ratio of the reaction eq 2 to eq 3. Thereby, at least, the total amount of *n*-Pr of the paraffins in the volatile oligomers should be comparable to that of TVD of the nonvolatile oligomers. Excess *n*-Pr to TVD is confirmed by comparing roughly calculated values when M_n of the paraffins is assumed to be 240 as hexamer. Thus, the reactions of eqs 3 and 4 are a main route of thermal degradation, determining the f_t

Scheme 1. Reaction Scheme for the Formation of End Groups of the Nonvolatile Oligomers

Intermolecular chain transfer of secondary terminal macroradical followed by ß-scission

$$\sim CH_2-\dot{C}H(CH_3)-CH_2-\dot{C}H(CH_3) \bullet \sim CH_2-\dot{C}H(CH_3)-CH_2\sim \longrightarrow \sim CH_2-CH(CH_3)-CH_2-CH_2 \bullet \sim CH_2-C(CH_3)=CH_2 \bullet \dot{C}H(CH_3)-CH_2-CH(CH_3)\sim \quad (1)$$

Intramolecular chain transfer (back biting) and stepwise back biting (stereoisomerization, *) of secondary terminal macroradical followed by ß-scission

$$\sim CH(CH_3)-CH_2-\dot{C}(CH_3)-(CH_2-CH(CH_3))_m-CH_2-\dot{C}(CH_3)-(CH_2-CH(CH_3))_n-CH_2-\dot{C}H(CH_3) \quad (m,n=0\sim 2)$$

$$\xrightarrow{1} \sim CH_2-CH(CH_3)-CH_2-CH(CH_3) \bullet CH_2=C(CH_3)-(CH_2-CH(CH_3))_m-CH_2-*CH(CH_3)-(CH_2-CH(CH_3))_n-CH_2-CH_2 \quad (2)$$

$$\xrightarrow{2} \sim CH_2-CH(CH_3)-CH_2-C(CH_3)=CH_2 \bullet \dot{C}H(CH_3)-(CH_2-CH(CH_3))_{m-1}-CH_2-*CH(CH_3)-(CH_2-CH(CH_3))_n-CH_2-CH_2 \quad (3)$$

Intermolecular chain transfer of secondary terminal volatile radical followed by ß-scission

$$\dot{C}H(CH_3)-(CH_2-CH(CH_3))_{m-1}-CH_2-*CH(CH_3)-(CH_2-CH(CH_3))_n-CH_2-CH_2 \bullet \sim CH_2-CH(CH_3)-CH_2\sim$$

$$\longrightarrow CH_2(CH_3)-(CH_2-CH(CH_3))_{m-1}-CH_2-*CH(CH_3)-(CH_2-CH(CH_3))_n-CH_2-CH_2 \bullet \sim CH_2-C(CH_3)=CH_2 \bullet \dot{C}H(CH_3)-CH_2\sim \quad (4)$$

Other volatile radicals

End-initiation

$$\sim CH(CH_3)-CH_2-C(CH_3)=CH_2 \longrightarrow \sim CH(CH_3)-CH_2-\dot{C}H(CH_3) \bullet CH_2-C(CH_3)=CH_2 \quad (5)$$

Depolymerization, or back biting followed by ß-scission

$$\sim CH_2-CH(CH_3)-CH_2-\dot{C}H(CH_3) \longrightarrow \text{monomer or oligomer} \bullet \sim CH_2-\dot{C}H(CH_3) \quad (6)$$

value and the molecular weight of the polymer residues. The volatile radicals are also produced *via* eqs 5 and 6. Equation 5 represents the formation of an allylic radical by end initiation.[29] In eq 6 the volatile radicals are produced when the size of the terminal macroradicals just becomes volatile during depolymerization, or the back-biting followed by β scission (eq 2). Although the concentration of these volatile radicals is considered to be lower than that produced by eq 3, their formation also contributes to an increase in the f_t value.

In conclusion, it becomes clear that about 80 mol % of the nonvolatile oligomers isolated from the polymer residues resulting from the thermal degradation of isotactic polypropylene at 370 °C is α,ω-diene-oligomers having two terminal isopropenyl groups. These oligopropylenes retain the stereoregularity (microtacticity) of the original polymer and are expected to be used as new telechelic oligomers. The synthesis of such oligo-

mers having two reactive end groups and a highly isotactic block chain is firstly reported in this paper. Thus, it was proved that the thermal degradation of polymers provides a simple and useful synthetic method for telechelic oligomers. The formation of telechelic oligomers is interpreted as resulting from a major contribution of both the back-biting of secondary terminal macroradicals followed by β scission (eq 3) and the intermolecular chain transfer of secondary terminal volatile radicals followed by β scission (eq 4), in addition to a minor contribution from the intermolecular chain transfer of secondary terminal macroradicals followed by β scission (eq 1).

References and Notes

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