

## Preparation of telechelic oligomers by controlled thermal degradation of isotactic poly(1-butene) and poly(propylene-*ran*-1-butene)

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### Abstract

It was found that telechelic isotactic oligo(1-butene) and telechelic oligo(propylene-*ran*-1-butene) could be isolated as nonvolatile oligomers from polymer residues resulting from the thermal degradation of isotactic poly(1-butene) and poly(propylene-*ran*-1-butene), respectively. Their structures were determined by <sup>1</sup>H and <sup>13</sup>C NMR with attention being paid to their reactive end groups. The maximum average number of terminal vinylidene groups per molecule ( $f_{TVD}$ ) was 1.8, indicating that about 80 mol% were  $\alpha,\omega$ -diene oligomers having two terminal vinylidene groups. This useful new telechelic oligomer had a lower polydispersity than the original polymer, in spite of its lower molecular weight and  $T_m$ . The composition of end groups of nonvolatile oligomers obtained by thermal degradation of poly(propylene-*ran*-1-butene) could be explained by the differences in bond dissociation energy and activation energy of elementary reactions during thermal degradation, based on the monomer composition of the original polymer.

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**Keywords:** Controlled thermal degradation; Poly(1-butene); Poly(propylene-*ran*-1-butene); Telechelic oligomer

### 1. Introduction

Functionalization of polyolefins has been attempted in an effort to solve the problem of their lack of affinity to other polymers [1]. For example, functional groups have been added to the ends of polymer molecules, and olefins have been copolymerized with polar monomers [2–4]. Poly(1-butene) has been studied extensively for its exceptional creep characteristics, impact resistance, and flexibility. Its unique crystal forms have also been investigated. However, the functionalization of poly(1-butene) has hardly been studied. Ethylene and 1-butene

have been copolymerized with propylene, in general, using Ziegler–Natta catalysts [5,6]. Recently, however, these copolymers have been prepared using metallocene catalysts, yielding a narrower molecular weight distribution than with Ziegler–Natta catalysts, and forming homogeneous crystals [7–9]. If functional groups could be introduced into propylene copolymers, it is expected that the resulting materials would find many applications, but this has never been reported.

Recently, we have developed a controlled thermal degradation technology for efficient production of monochelic or telechelic oligomers having one or two terminal double bonds, respectively, from polypropylene [10]. The chief characteristic of this technology is to make products with ease by inhibiting secondary reactions of volatiles by rapidly removing these volatiles from the reactor. Because the structure of the obtained oligomers was simple, a clear relation of products to

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Table 1  
Yield of residue and characteristics of nonvolatile oligomers obtained by controlled thermal degradation of iPB

Degradation conditions		Yield of residue (wt%)	Nonvolatile oligomer					Microtacticity(pentad)							
Temperature (°C)	Time (h)		$M_n \times 10^4$	$M_w/M_n$	$T_g$ (°C)	$T_m$ (°C)	$f_{TVD}$	mmmm	mmmr	rmmr	mmrm	rrrm	rrrr	mrrr	mrrm
–	–	–	231	3.7	–25	113	–	0.89	0.04	0.02	0.02	0.00	0.01	0.01	0.01
330	1	99	4.11	1.8	–29	112	–	0.90	0.04	0.02	0.01	0.00	0.01	0.01	0.01
330	2	98	2.89	1.9	–32	111	–	0.90	0.04	0.03	0.01	0.00	0.01	0.01	0.01
330	3	98	2.48	2.0	–30	109	1.63	0.88	0.04	0.03	0.01	0.00	0.01	0.01	0.01
350	1	97	2.02	2.0	–32	110	1.71	0.89	0.04	0.03	0.01	0.00	0.01	0.01	0.01
350	2	97	1.67	1.9	–33	109	1.77	0.89	0.04	0.03	0.01	0.00	0.01	0.01	0.01
350	3	94	1.18	1.8	–35	106	1.79	0.89	0.04	0.03	0.01	0.00	0.01	0.01	0.01
370	1	95	1.02	1.9	–39	107	1.71	0.88	0.04	0.03	0.01	0.00	0.01	0.01	0.01
370	2	82	0.52	1.8	–46	105	1.66	0.86	0.04	0.04	0.02	0.00	0.02	0.01	0.01
370	3	78	0.49	1.7	–47	103	1.61	0.86	0.04	0.04	0.01	0.00	0.02	0.01	0.01

radical chain reactions was found [10]. We have previously reported the detailed mechanisms to account for the structures of products formed from the controlled thermal degradation of polyisobutylene [11] and polystyrene [12]. In addition, we have reported about the change in the terminal double bond functional groups of telechelic oligomers obtained by controlled thermal degradation of polypropylene [13–15].

In the present work, we report our attempts at selective preparation of telechelic oligomers (comparatively soft polymeric materials) having two terminal double bonds by controlled thermal degradation of isotactic poly(1-butene) and poly(propylene-*ran*-1-butene), and discuss their formation mechanism based on structural analysis of the oligomer termini.

## 2. Experimental

### 2.1. Materials

Isotactic poly(1-butene) and poly(propylene-*ran*-1-butene) (TAFMER<sup>®</sup>) from Mitsui Chemicals, Inc. were used as received. Characteristics of the polymers are shown in Tables 1 and 2.

### 2.2. Apparatus

The Pyrex glass apparatus used for thermal degradation has been described in our previous paper [10] and a 5-kg scale apparatus was newly designed for these tests. The degradation

Table 2  
Yield of residues and characteristics of nonvolatile oligomers obtained by controlled thermal degradation of poly(propylene-*ran*-1-butene)

Degradation conditions		Yield of residue (wt%)	Nonvolatile oligomer			
Temperature (°C)	Time (h)		$M_n \times 10^4$	$M_w/M_n$	$T_m$ (°C)	$f_{TVD}$
–	–	–	156	3.4	111	–
330	1.0	99	9.31	2.8	110	–
330	2.0	99	5.65	1.7	110	–
330	3.0	99	4.08	1.8	111	–
350	1.0	98	5.31	3.0	113	–
350	2.0	95	3.26	1.9	112	–
350	3.0	91	1.73	1.9	107	1.68
370	1.0	99	3.14	2.2	111	1.64
370	2.0	94	1.18	1.8	106	1.75
370	3.0	87	0.90	1.8	103	1.69
390	1.0	90	1.72	1.9	108	1.71
390	2.0	78	0.62	1.7	100	1.83
390	2.5	46	0.43	1.4	94	1.78
390	3.0	39	0.39	1.3	96	1.75
390	3.5	14	0.30	1.2	89	1.58

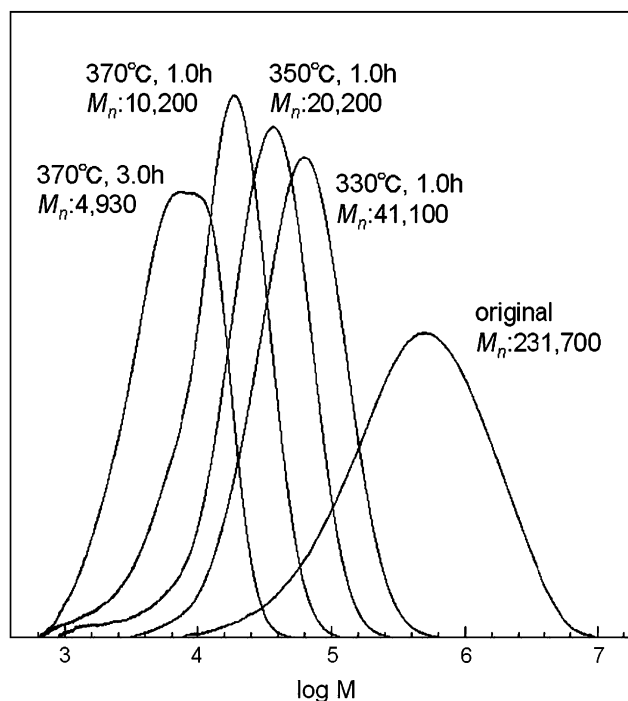


Fig. 1. GPC curves of original iPB and nonvolatile oligomers.

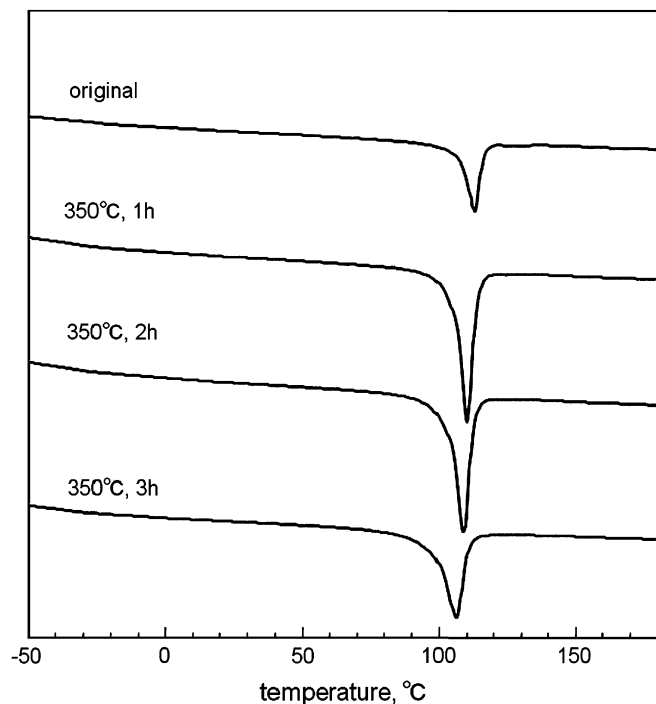


Fig. 2. DSC curves of original iPB and nonvolatile oligomers.

experiments were performed at 330–390 °C at 2 mmHg in a stream of N<sub>2</sub> gas. Part of the fractionating column in the apparatus was held at a specified temperature for rapidly removing the volatiles from the reactor. A certain quantity of sample was placed in the reactor, and the air in the apparatus was replaced by N<sub>2</sub> gas at 2 mmHg. The reactor was immersed in a bath maintained at a specified temperature as soon as the sample reached about 250 °C. The sample in the reactor was vigorously stirred by bubbling N<sub>2</sub> gas through the molten

polymer. After the reaction the volatiles, including volatile oligomers, were collected in a fraction trap chilled with liquid N<sub>2</sub>. Polymer residues in the reactor were dissolved in xylene and reprecipitated with methanol to remove the small amount of volatile oligomers remaining and were characterized after vacuum drying under heating. The nonvolatile oligomers that were the focus of this study were thus almost completely separated from the volatile oligomers.

### 2.3. NMR

<sup>13</sup>C NMR spectra were measured with a JEOL-EC500 spectrometer operating at 125.78 MHz and at 60 °C or 120 °C with an internal lock. The samples were dissolved in a 1:3 (v/v) mixture of benzene-*d*<sub>6</sub> and 1,2,4-trichlorobenzene (120 °C) or CDCl<sub>3</sub> (60 °C) (ca. 10% (w/v) concentration), and hexamethyldisiloxane (HMDS) was added as an internal standard (2.0 ppm with respect to TMS). The 10-mm sample tubes were deaerated by several freeze–pump–thaw cycles and sealed after N<sub>2</sub> gas was admitted into the evacuated tube. A pulse width of 18.8 μs (90° pulse) and 5000 scans were used.

<sup>1</sup>H NMR spectra were measured on the same spectrometer operating at 500.16 MHz and at 60 °C or 120 °C with an internal lock. The sample concentrations and the preparation of sample tubes were as above. A pulse width of 23 μs (90° pulse) and 5000 scans were used.

### 2.4. GPC

$M_n$  and  $M_w/M_n$  were measured by GPC (TOSOH HLC-821 GPC/HT), calibrated using polystyrene standards. The eluent was *o*-dichlorobenzene, and the measurement was performed at 145 °C.

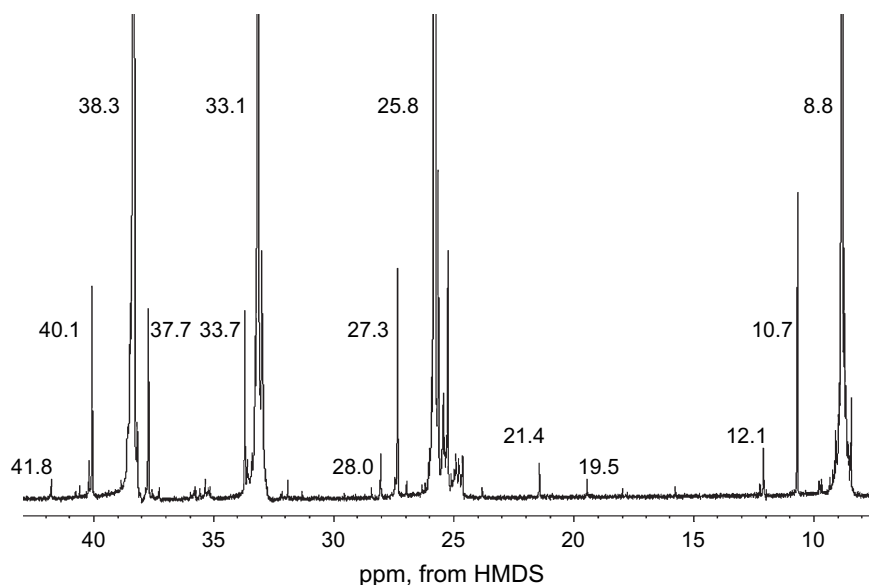


Fig. 3. <sup>13</sup>C NMR spectrum of main chain of nonvolatile oligomer obtained from isotactic poly(1-butene).

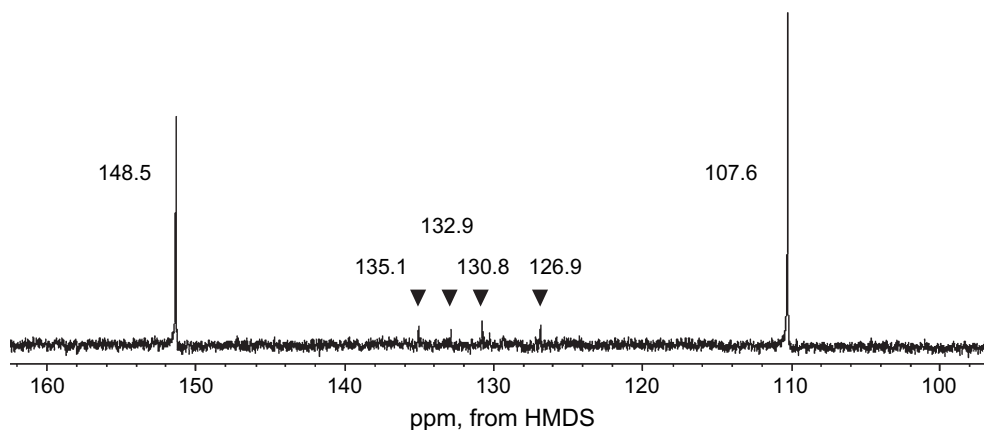


Fig. 4.  $^{13}\text{C}$  NMR spectrum of nonvolatile oligomer obtained from isotactic poly(1-butene).

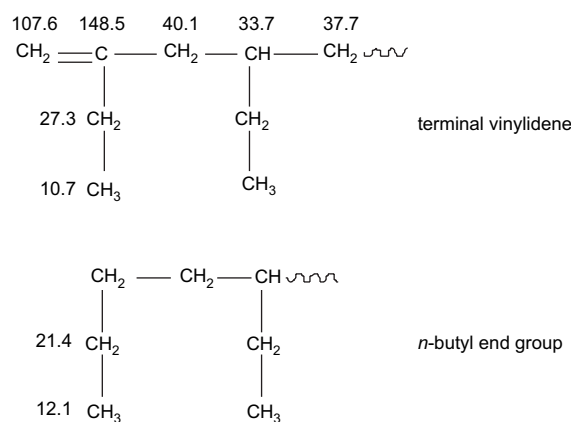
## 2.5. DSC

The melting temperature ( $T_m$ ) and glass transition temperature ( $T_g$ ) were measured by DSC (Seiko Instruments, Inc. DSC 6100) under  $\text{N}_2$  and in the second heating cycle after cooling at a rate of  $10^\circ\text{C}/\text{min}$ . The sample weight was ca. 5 mg, and the heating rate was  $10^\circ\text{C}/\text{min}$ .

## 3. Results and discussion

### 3.1. Isotactic poly(1-butene)

The yield of polymer residue and characteristics of the nonvolatile oligomers obtained under various conditions are shown in Table 1. Typical GPC and DSC curves of the original polymer and the nonvolatile oligomer are shown in Figs. 1 and 2, respectively. Although the  $M_n$  of the nonvolatile oligomer ranged from 5000 to 41 000 g/mol,  $M_w/M_n$  decreased markedly from 3.7 for the original polymer to 1.7 for the lowest molecular weight oligomer. The microtacticity of the oligomers was nearly the same as that of the original polymer and showed that these oligomers largely retained the stereoregularity of the original polymer without random stereo-isomerization of the polymer chain during thermal degradation. Although the microtacticity was determined from signals at 26.1 to 26.4 ppm [16] assigned to methylene carbons on the main chains, signals assigned to carbons near the terminal double bond were subtracted. The endothermic peak of the DSC curve (Fig. 1) was caused by melting of crystallites and was lower in the oligomers than in the original polymer, depending on their molecular weight. Glass transition temperatures were barely detectable and were higher for the original polymer than the oligomers, again dependent on their molecular weight. The values of  $f_{\text{TVD}}$  in Table 1 represent the average number of terminal vinylidene groups per molecule and are discussed below. Based on the mechanism of thermal degradation discussed in our former paper [10], possible chemical structures of the oligomers along with their  $^{13}\text{C}$  chemical shifts [10] were as follows:



The  $^{13}\text{C}$  NMR spectrum of main chain carbons of the nonvolatile oligomer is shown in Fig. 3, and  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of olefin carbons/protons are shown in Figs. 4 and 5, respectively. In Fig. 3, signals at 8.8, 25.8, 33.1, and 38.3 ppm were, respectively, assigned to methyl; methylene of side chain; methyne; and methylene of main chain. The methylene carbon resonance of the side chain was sensitive to the configuration of the polymer chain, and most peaks between 24.6 and 26.1 ppm were assigned to the pentad configurational sequence. The resonances at 107.6 and 148.5 ppm in Fig. 4 were assigned to the olefin carbons of terminal vinylidene (TVD) groups. In the  $^1\text{H}$  NMR spectrum (Fig. 5), the two strong signals at 4.66 and 4.70 ppm were assigned to the two olefin protons of TVD, and the weak signals at 5.12 and 5.33 ppm were assigned to internal trisubstituted double bonds and vinylene type double bonds, respectively. These double bonds were about 85 mol% terminal double bonds and about 15 mol% internal double bonds. The signals at 10.7, 27.3, 33.7, 37.7, and 40.1 ppm in Fig. 3 corresponded to the methyl and methylene carbon of side chain, and methyne, methylene, and adjacent methylene carbon of main chain side of TVD, in order. As for the saturated end group, methyl and methylene carbons of the *n*-butyl end

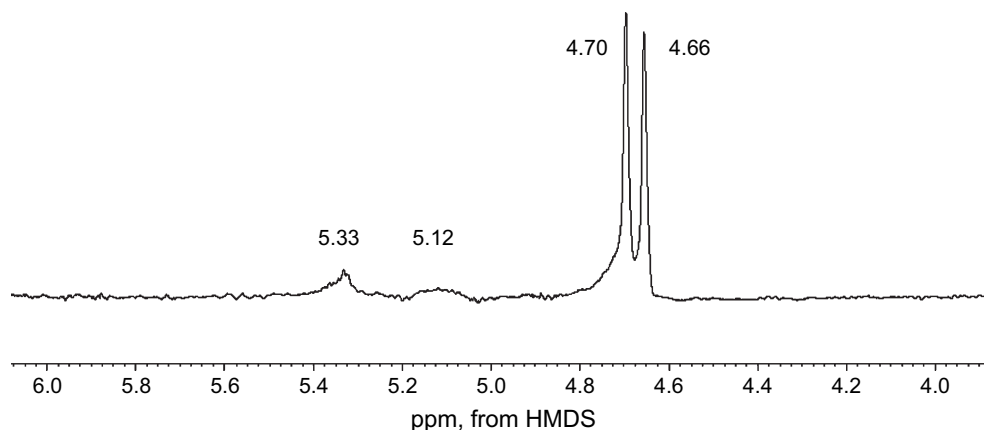


Fig. 5.  $^1\text{H}$  NMR spectrum of nonvolatile oligomer obtained from isotactic poly(1-butene).

group (*n*-Bu) were detected at 12.1 and 21.4 ppm, respectively. Peaks from other carbons overlapped main chain signals and could not be assigned. In addition, signals detected at 19.5, 28.0, and 41.8 ppm were ignored because they were also present in the original polymer. Other saturated and unsaturated end groups and long chain branching were not observed. Assuming that all the nonvolatile oligomers were linear, the value of  $f_{\text{TVD}}$  was calculated from the following equation:

$$f_{\text{TVD}} = (2I_{\text{TVD}})/(I_{\text{TVD}} + I_{n\text{-Bu}}) \quad (1)$$

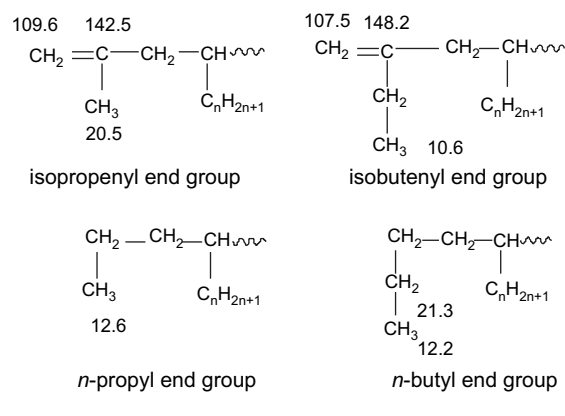
and was found to range from 1.6 to 1.8. Here,  $I_{\text{TVD}}$  and  $I_{\text{TVD}} + I_{n\text{-Bu}}$  were methyl carbon intensities of TVD and of all end groups, respectively. The maximum value of  $f_{\text{TVD}}$  was 1.8, indicating that about 80 mol% of the oligomer molecules were telechelic with two TVDs. Monochelics having one TVD and one *n*-Bu group each, and terminal saturated oligomers having two *n*-Bu groups, constituted about 19 and 1 mol% of the oligomers, respectively. Because these results corresponded closely to the results from telechelic oligopropylene made by the thermal degradation of polypropylene described in our former report [10] it was surmised that the same thermal degradation mechanism operated here.

### 3.2. Poly(propylene-*ran*-1-butene)

The yield of polymer residue and the characteristics of the nonvolatile oligomers obtained under various conditions are shown in Table 2. The GPC and DSC curves of the original polymer and nonvolatile oligomer are shown in Figs. 6 and 7, respectively.  $M_n$  of the nonvolatile oligomer ranged from 3000 to 90 000 g/mol, and  $M_w/M_n$  decreased markedly to 2.0 from 3.4 for the original polymer. The endothermic peak of the DSC curve in Fig. 7 was caused by melting of crystallites and occurred at a higher temperature in the original polymer compared to the oligomers, dependent on their molecular weight. As shown in Table 2, the melting temperature decreased from

110.9 °C for the original polymer to 89.0 °C for the shortest oligomer. The values of  $f_{\text{TVD}}$  in Table 2 indicated the average number of terminal double bonds per molecule and are discussed below.  $^{13}\text{C}$  NMR spectra of oligomer are shown in Figs. 8 and 9, and  $^1\text{H}$  NMR spectra in Fig. 10. The signal at 9.0 ppm was the methyl carbon of the 1-butene unit; at 19.8 ppm was the methyl carbon of the propylene unit; at 25.8, 26.0, and 26.2 ppm were methylene carbons of the side chain of the 1-butene unit; at 26.7 ppm was the methyne carbon of the propylene unit; at 33.3 ppm was the methyne carbon of the 1-butene unit; at 38.2 ppm was the methylene carbon of the main chain in the 1-butene sequence; and at 41.3, 41.6, 44.5, 44.7, and 45.1 ppm were methylene carbons of the main chain in different sequences. The composition of the main chain of the original polymer compared to literature [17] was propylene[P]:1-butene[B] = 75:25, [PP]:[PB]:[BB] = 55:36:9, and [PPP]:[PPB]:[PBP]:[PBB]:[BPB]:[BBB] = 46:23:12:8:9:2.

Based on the above results and the mechanism of thermal degradation described in our former paper [10] the structures of the end groups were postulated, and their corresponding  $^{13}\text{C}$  NMR chemical shifts were assigned based on literature [17] and estimated [18,19] values:



$n=1$  or 2

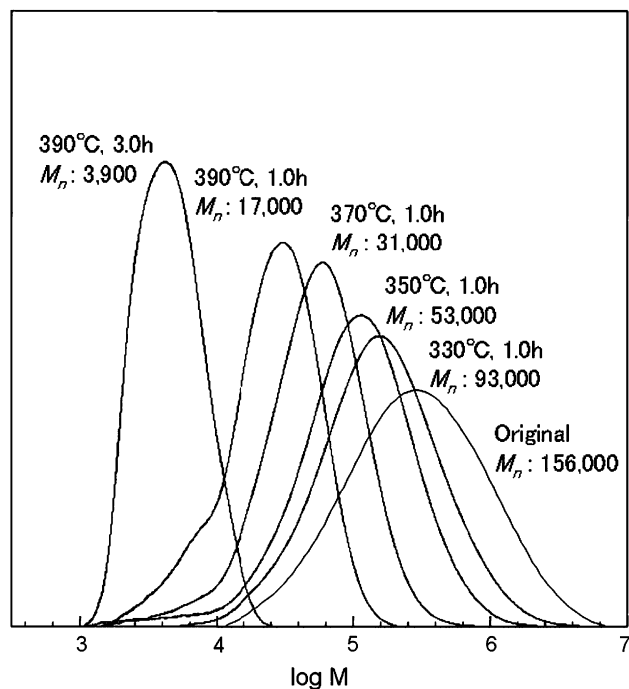


Fig. 6. GPC curves of original poly(propylene-*ran*-1-butene) and nonvolatile oligomers.

In Fig. 9, the signals at 143.2 and 109.6 ppm were assigned to olefin carbons of isopropenyl end groups, and the signals at 148.7 and 107.4 ppm were assigned to isobutenyl end groups. Moreover, methyl carbons' signals of these end groups were detected at 20.5 and 10.6 ppm. In the  $^1\text{H}$  NMR spectrum (Fig. 10), these olefin protons were assigned to 4.66 and 4.60 ppm; and to 4.62 and 4.69 ppm. In Fig. 9, the signals from the double bonds on the main chain were scarcely detected. These signals were from the internal trisubstituted and vinylene type double bonds, occurring around 5.32 and 5.10 ppm, respectively. The content of terminal and internal

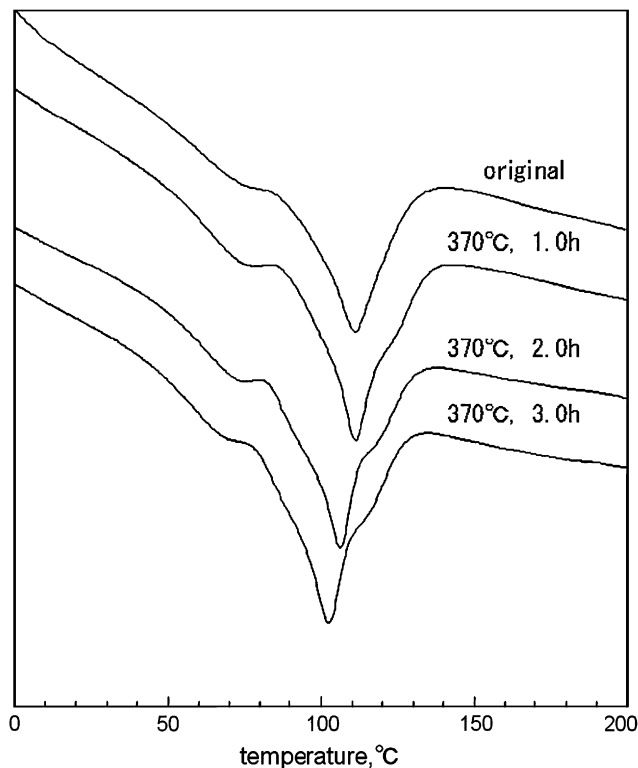


Fig. 7. DSC curves of original poly(propylene-*ran*-1-butene) and nonvolatile oligomers.

double bonds was 90 mol% of the former and about 10 mol% of the latter. Signals from saturated end groups were detected at 12.6 and 12.2 ppm in Fig. 8, corresponding to methyls of *n*-propyl and *n*-butyl moieties, respectively.

Assuming that all nonvolatile oligomers were linear, the value of  $f_{\text{TVD}}$  was calculated from the following equation:

$$f_{\text{TVD}} = (2I_{\text{US}} / (I_{\text{US}} + I_{\text{S}})) \quad (2)$$

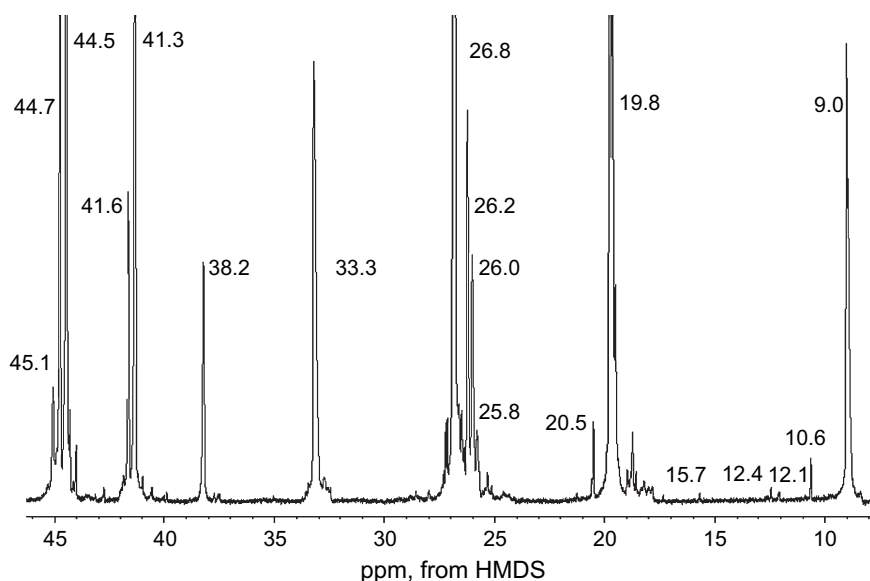


Fig. 8.  $^{13}\text{C}$  NMR spectrum of main chain of nonvolatile oligomer obtained from poly(propylene-*ran*-1-butene).

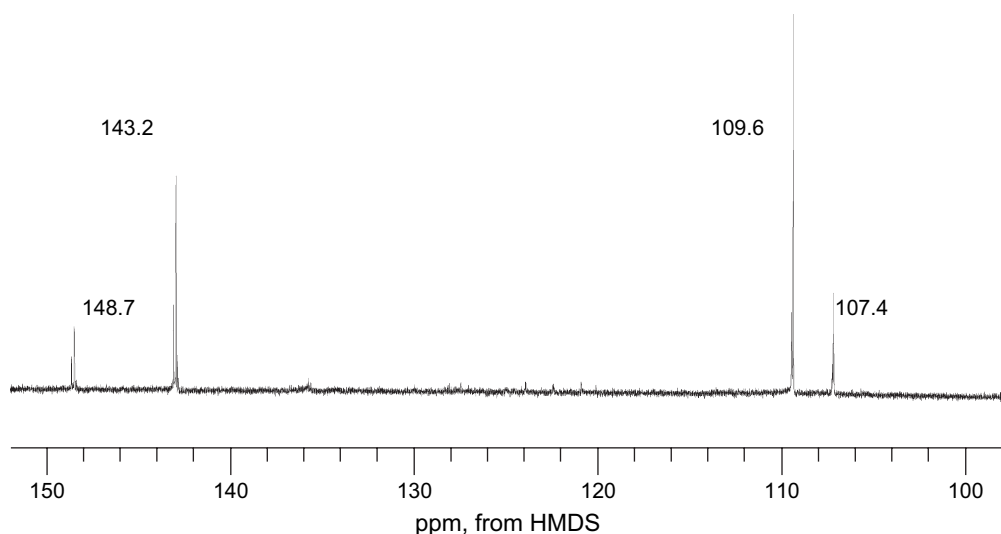


Fig. 9.  $^{13}\text{C}$  NMR spectrum of nonvolatile oligomer obtained from poly(propylene-*ran*-1-butene).

and ranged from 1.7 to 1.8 (Table 2). Here,  $I_{\text{US}}$  was the signal intensity of the methyl group (20.5 and 10.6 ppm) adjacent to terminal double bonds, and  $I_{\text{S}}$  was the methyl signal intensity of saturated end groups (12.6 and 12.2 ppm). This  $f_{\text{TVD}}$  value

indicated that about 70–80 mol% of the oligomer molecules were telechelic with two terminal double bonds.

The characteristic formation reactions of end groups will now be described. The reaction in Schemes 1 and 2 was

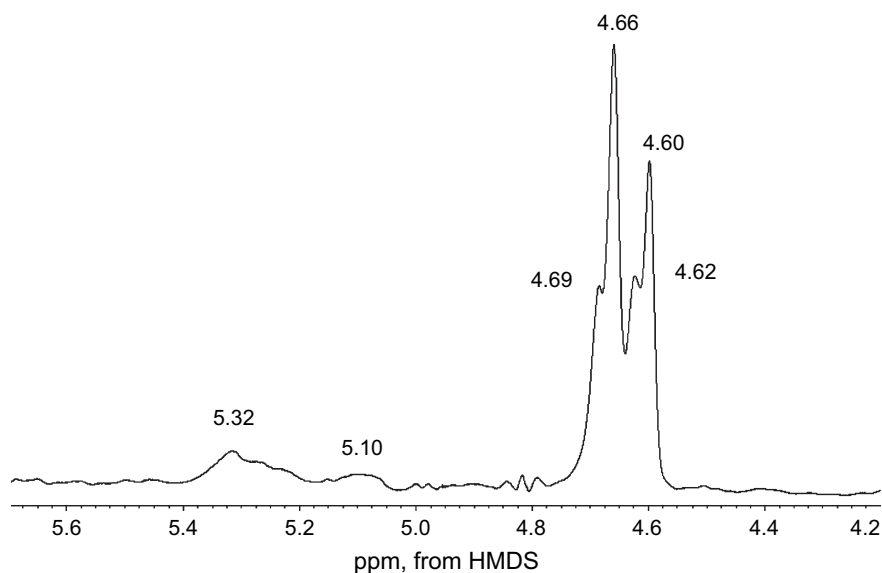
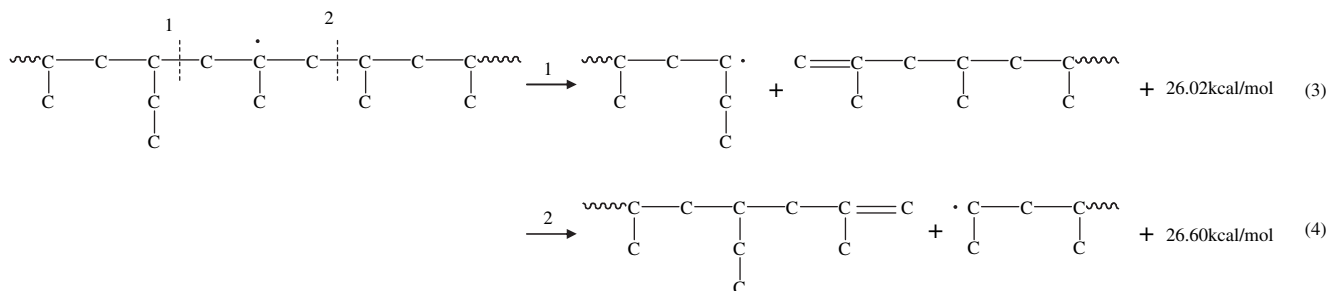
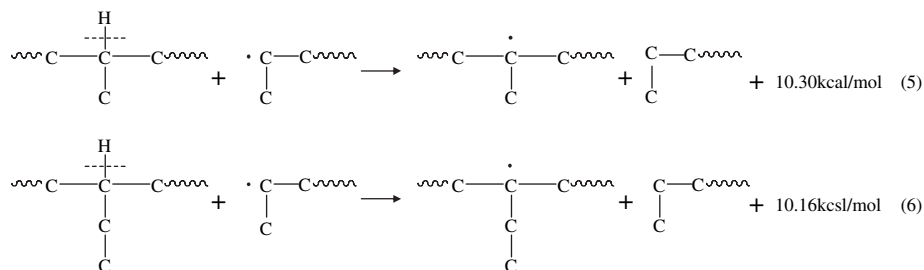


Fig. 10.  $^1\text{H}$  NMR spectrum of nonvolatile oligomer obtained from poly(propylene-*ran*-1-butene).



Scheme 1. The bond dissociation energies for  $\beta$  scission of tertiary radicals on the main chain of poly(propylene-*ran*-1-butene).



Scheme 2. The activation energies for intermolecular tertiary hydrogen abstraction of secondary terminal radicals.

conjectured to occur in the copolymer used in this study. The correct values in each equation are the bond dissociation energy for  $\beta$  scission of tertiary radicals and the activation energy of the hydrogen abstraction reaction. The heats of formation of compounds and radicals were estimated by the ABW method [20] and that of Franklin [21], respectively. Although the bond dissociation energy of  $\beta$  scission was used heat of reaction, the activation energy of the hydrogen abstraction reaction was obtained by the conversion of heat of reaction, according to the method of Semenov [22].

The ratio ([P]:[B]) of the signal intensity of saturated end groups (*n*-Pr and *n*-Bu) was about 60:40. This ratio did not reflect the composition (75:25) of each unit in the main chain, showing that scission near the 1-butene units was favored.

Saturated end groups were formed by intermolecular hydrogen abstraction reactions of secondary radicals formed by  $\beta$  scission of tertiary radicals. The formation reaction for the saturated end groups inferred here is shown in Scheme 1.

As shown in Eqs. (3) and (4), the bond dissociation energy for  $\beta$  scission of tertiary radicals of propylene units adjacent to 1-butene units was about 0.6 kcal/mol more favorable than that for the 1-butene unit. These estimates showed why the composition of the main chain of the original polymer ([P]:[B] = 75:25) was different from that of the saturated end groups ([P]:[B] = 60:40), and satisfactorily explained why the content of 1-butene units in the end groups increased during thermal degradation. On the other hand, the composition ratio of terminal double bonds analyzed by  $^{13}\text{C}$  NMR was [P]:[B] = 75:25, almost the same as that in the main chain. These terminal double bonds were produced by  $\beta$  scission of tertiary radicals formed by hydrogen abstraction from the main chain (Scheme 2).

The composition of terminal double bonds depended on the activation energy of hydrogen abstraction for each monomer unit. Although the activation energy of hydrogen abstraction was about 0.14 kcal/mol more favorable for 1-butene units (6) than for propylene units (5), this difference in activation energy did not influence the composition of terminal double bonds. This result indicated that this process was insensitive to the activation energy because of the low concentration of 1-butene units. This constitutes a reasonable explanation for the difference in composition between end groups and main chain, based on the estimated values of bond dissociation energies for  $\beta$  scission and activation energies for hydrogen abstraction. The composition of end groups in the oligomer

could therefore be predicted from the structure of the original polymer.

#### 4. Conclusion

In conclusion, it was clear that about 80 mol% of the non-volatile oligomers isolated from the polymer residues resulting from the thermal degradation of isotactic poly(1-butene) and poly(propylene-*ran*-1-butene) consisted of  $\alpha,\omega$ -diene oligomers having two terminal double bonds. These oligomers are expected to find uses as new telechelic oligomers. This paper is the first report of the synthesis of such isotactic oligo(1-butene) and oligo(propylene-*ran*-1-butene) compounds having two reactive end groups. The thermal degradation results reported here were mostly consistent with the results for polypropylene previously reported by us. Therefore, a similar thermal degradation mechanism is probably in effect here. The composition of the end groups in the nonvolatile oligomer obtained by thermal degradation of poly(propylene-*ran*-1-butene) was explained by an examination of bond dissociation energies and activation energies based on the structure of the original polymer and its simple thermal degradation reactions.

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