

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

Daisuke Sasaki^{a,*}, Yasushi Okada^b, Yoshihiro Suzuki^a, Toshiki Hagiwara^b,
Shoichiro Yano^b, Takashi Sawaguchi^{b,**}

^a Research and Development Division, San-ei Kogyo Corporation, 3-302 Togasaki, Misato-shi, Saitama 341, Japan

^b Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, 1-8-14 Kanda-Surugadai, Chiyoda-ku, Tokyo 101, Japan

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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 ¹H and ¹³C 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 α,ω -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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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

* Corresponding author.

** Corresponding author.

E-mail addresses: sasaki@misato-net.com (D. Sasaki), sawaguti@chem.cst.nihon-u.ac.jp (T. Sawaguchi).

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.

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

2. Experimental

2.1. Materials

Isotactic poly(1-butene) and poly(propylene-*ran*-1-butene) (TAFMER[®]) 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

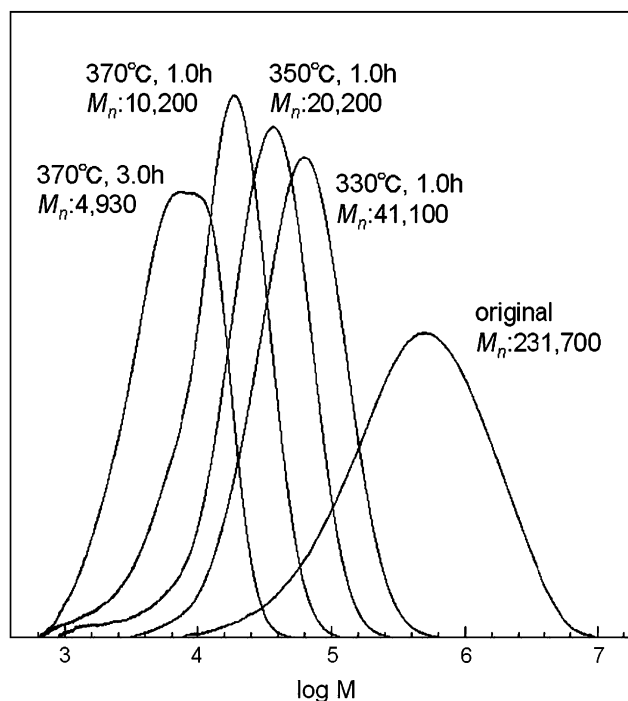


Fig. 1. GPC curves of original iPB and nonvolatile oligomers.

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