

# Effectively Terminal Functionalization of Precise Products Obtained by Controlled Thermal Degradation of Polypropylenes

D. Sasaki<sup>1,\*</sup>, Y. Yoshihiro<sup>1</sup>, T. Hoshi<sup>2</sup>, T. Hagiwara<sup>2</sup>, T. Sawaguchi<sup>2,\*</sup>

<sup>1</sup>San-ei Kogyo Corporation, Research and Development Division

<sup>2</sup>Nihon University, College of Science and Technology,

e-mail: sasaki@misato-net.com; phone: +08-48-955-1632 & fax: +08-48-952-5543

## Abstract

Developments of new chemical technologies for recycling of polypropylene wastes are desirable in order to meet the goals of a society that is based on resource recycling. In order to add values to polypropylene, we tried to synthesize end-reactive polymers by controlled thermal degradation of various polypropylenes. In the case of car battery wastes, the average number of double bonds per molecule of end-reactive polymer ranged from 1.54 to 1.31. This shows that 59 to 43 mol% of telechelic polymer having double bonds at either end. Thiol-ene reaction of end-reactive polymer and thiol compounds was a method of quantitatively and effectively terminal functionalization.

**Keywords:** polypropylene, controlled thermal degradation, end-reactive polymer, telechelic polymer, thiol-ene reaction.

## 1. Introduction

Plastic wastes are the environmental subject of highly developed societies. Mechanical recycling is the most desirable usage of plastic wastes. However, it has limits of decreasing quality after several cycles. Whereas liquefaction and gasification of polyolefins into hydrocarbons by pyrolysis with catalyst have been studied actively for many years, economical problems remain to be solved in their practical use. The development of new processes which change these plastic wastes to valuable chemical products is highly desirable.

Polypropylene is an environmental-friendly material because of its high recyclability. In addition, polypropylene is a broad class of materials ranging from high melting plastics to low melting elastomers, and their properties are controlled by their molecular structure and copolymerization composition. Polypropylene copolymers (random and impact copolymers) are industrially important as elastomers, impact modification materials, etc. There has been much effort to introduce polar groups into polyolefins using an appropriate catalyst technology in order to overcome their lack of affinity to other polymers.

We have developed a controlled thermal degradation technique for efficient production of end-reactive polymers having one or two terminal double bonds [1]. End-reactive polymers were functionalized by organic synthesis and copolymerized by living polymerization [2, 3].

In this study, the feature of end-reactive polymer obtained by controlled thermal degradation of vinyl polymers and synthesis of novel copolymers from end-reactive polymer are reported.

## 2. Materials and Methods

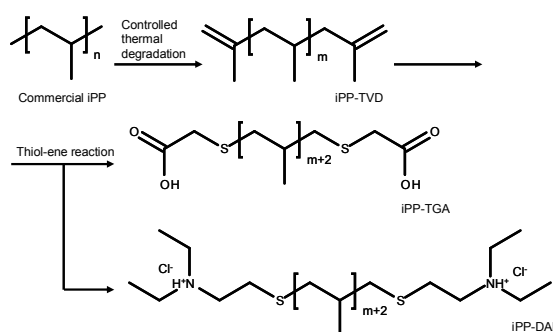
### 2.1 Controlled thermal degradation

Commercial polypropylene and polypropylene wastes (bottle cap, car battery and washer tank) were thermally degraded in glass-apparatus (5g scale) or laboratory-scale

apparatus (1-2 kg scale) under reduced pressure (ca. 10 mmHg) at 330-390 °C. In the reaction, molten polymer was stirred by bubbles of N<sub>2</sub> gas introduced. After the reaction, polymer residue in reactor was dissolved in hot xylene and nonvolatile polymer (PP-TVD) was reprecipitated with methanol.

### 2.2. Thiol-ene reaction of iPP-TVD

Thiol-ene reaction is focused as click reaction and applied to functionalization of polymer [4]. iPP-TVD was prepared by controlled thermal degradation of commercial iPP. The mixture of iPP-TVD, AIBN, and thiol compounds were stirred in toluene at 80 °C for 8h. The mixture was then poured into methanol, and the precipitate was filtered and dried under reduced pressure.



Scheme. Controlled thermal degradation of PP wastes and thiol-ene reaction of wPP-TVD.

## 3. Results and Discussion

### 3.1. Controlled thermal degradation of polypropylene waste

As an example of polypropylene wastes, the result of car battery waste is shown. Molecular structure of car battery waste was random PP with ethylene. The monomer

Table 1. Degradation condition, yield of residue and molecular characteristics of nonvolatile polymer obtained by controlled thermal degradation of car battery wastes.

Degradation condition		Yield of Residue, wt%	Nonvolatile polymer			
Temp., °C	Time, h		$M_n, \times 10^3$	$M_w/M_n$	$T_m, ^\circ\text{C}$	$f_{\text{TVD}}$
Original sample			64.0	5.2	167.7	-
370	1	96.9	20.5	1.9	157.9	1.31
370	2	87.2	7.7	1.7	148.8	1.52
370	3	87.7	7.5	1.8	146.0	1.47
390	1	85.2	7.3	1.7	151.1	1.54
390	2	66.0	6.5	1.6	136.6	1.46
390	3	37.6	4.4	1.6	117.1	1.33

composition is propylene[P]: ethylene[E]=87.9:12.1 mol% and triad monomer composition is [EEE]:[PEE+EEP]:[PEP]:[EPE]:[PPE+EPP]:[PPP]=8.4:2.0:1.7:1.7:2.1:84.1 mol%. Degradation condition, yield of residue and molecular characteristics of nonvolatile polymer are shown in Table 1. The yield of residue and  $M_n$  of nonvolatile polymer decreased depending on degradation temperature and time.  $M_w/M_n$  values of nonvolatile polymer ranged from 1.6 to 1.9, lower than original sample.  $T_m$  determined by DSC decreased from 165.7 °C to about 130 °C. The  $f_{\text{TVD}}$  value in right column of Table 1 is average number of terminal double bond per molecule and estimated by  $^{13}\text{C}$ -NMR spectrum (Fig. 1). The saturated end groups (n-propyl and long chain n-alkyl groups) were detected at 12.5 and 12.0 ppm. The signals at 20.4 and 20.5 ppm were assigned to methyl carbons of terminal vinylidene moieties adjacent to propylene and ethylene.

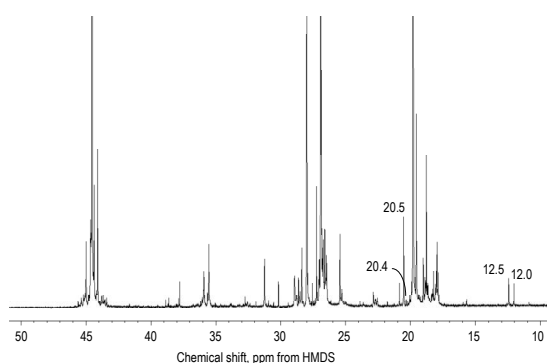


Fig. 1.  $^{13}\text{C}$ - NMR spectrum of nonvolatile oligomer obtained by controlled thermal degradation of car battery waste at 390 °C for 3h

Nonvolatile polymer with  $f_{\text{TVD}}=1.54$  consisted of 59 % telechelic polymer, 36 % monochelic polymer and 5 % paraffin. On the other hand,  $f_{\text{TVD}}$  value is 1.8 in the case of nonvolatile polymer obtained by controlled thermal degradation of commercial iPP. The low  $f_{\text{TVD}}$  value is considered as due to copolymer with ethylene and original sample with low  $M_n$ .

### 3.2. Thiol-ene reaction of iPP-TVD

Although terminal vinylidene group of iPP-TVD showed little or no polymerization reactivity, it was convertible for functional groups, such as hydroxyl, carboxyl and epoxy groups. The thiol-ene reaction of iPP-TVD and various thiol

compounds were converted into various functional groups in one step. Thioglycolic acid (TGA) showed high reactivity on thiol-ene reaction (Fig. 2). The reaction quantitatively proceeded on iPP-TVD (1mmol, 2mmol/C=C), AIBN (0.2 mmol), and TGA (3 mmol) for 4 h. On the other hand, 2-dimethylaminoethanethiol hydrochloride (DAE) had very low thiol-ene reactivity, required for quantitative reaction of excess of AIBN. This reaction without side reaction is regarded as the important method for functionalized polypropylene with controlled structure.

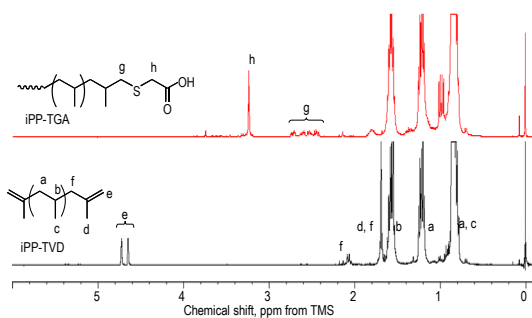


Fig. 2.  $^1\text{H}$ -NMR spectra of iPP-TVD and iPP-TGA.

## 4. Conclusions

The nonvolatile polymer obtained by controlled thermal degradation of polypropylene waste had  $M_n=4,000$  to 20,500 and  $f_{\text{TVD}}=1.31$  to 1.54. The  $f_{\text{TVD}}$  value lower than the case of commercial iPP is considered as due to copolymer with ethylene and original sample with low  $M_n$ . Thiol-ene reaction of iPP-TVD showed widely different reactivity depend on thiol compounds. The low reactivity compounds required excess AIBN as radical source. The thiol-ene reaction is an efficient synthetic method of functionalized polypropylene.

## References

- [1] T. Sawaguchi, T. Ikemura and M. Seno, *Macromolecules* 28 (1995) 7973-7978.
- [2] T. Hagiwara, H. Saitoh, A. Tobe, D. Sasaki, S. Yano and T. Sawaguchi, *Macromolecules*, 38 (2005) 10373-10378.
- [3] D. Sasaki, Y. Suzuki, T. Hagiwara, S. Yano and T. Sawaguchi, *Polymer* 49 (2008) 4094-4100.
- [4] C. E. Hoyle and C. N. Bowman, *Angew. Chem. Int. Ed.*, 49 (2010) 1540-1573.