

Effect of Molecular Weight of Polyethylene on Its Flammability

Erika Nakashima,¹ Tomonaga Ueno,² Masao Yukumoto,¹ Kunihiro Takeda¹

¹Department of Mechanical Engineering, Graduate School of Engineering, Chubu University, Matsumoto-cho 1200, Kasugai, Aichi 487-8501, Japan

²Department of Materials Engineering, Graduate School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

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ABSTRACT: Polyethylene has been widely applied in our society and is known to burn well. Many researchers have been studying to control the flammability of polyethylene when adding several catalysts. However, this study has confirmed the effect of the molecular weight on the flammability of polyethylene. This article displays combustion states of two different molecular weights of polyethylene. The low molecular weight of polyethylene did not ignite and the high molecular weight of polyethylene ignited and burned well. From this result, it was difficult for polyethylene to continue combustion under limited conditions, such as the vertical configuration of the materials, air circumstance, and low molecular weight. To analyze such behaviors, the relationship between combustion state and degradation behavior of polyethylene was compared to that of polypropylene (PP) and polystyrene. PP and polystyrene decomposed into small molecules directly through chain-end scission and that low-molecular weight

scission products went to gas phase and reacted with oxygen and consequently fire around specimens during combustion. Polyethylene decomposed into relatively higher molecular weight scission products through random scission at primary degradation. The scission products further decomposed into lower molecular weight products with drip, which caused the combustion under specimens. There were no big differences in a weight loss temperature and scission products at high temperature between a low molecular weight of polyethylene and a high molecular weight of polyethylene. Therefore, the degradation and combustion behavior of scission products of polyethylene in primary degradation warrant further research on flame retardant of polyethylene. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 436–443, 2011

Key words: polyethylene; thermal degradation; flammability; molecular weight; polyolefin

INTRODUCTION

There are different types of polymeric materials, for example, natural materials such as woods and industrial material such as plastics, rubbers, and textiles. Both types have been widely applied in our society. One of the fatal drawbacks of man-made plastics is its flammability, which could be a cause of fire. Halogens, phosphorous compounds, and inorganic hydroxides have been extensively examined through experiments and theoretical studies on flame retardancy since the 1940s.^{1–4} These studies have elucidated several mechanisms that restrain the combustion of polymeric materials. Although the flame retardancy of polymeric materials is a very important matter in terms of industrial use, basic research is expected to obtain fundamental knowledge regarding the chain degradation paths at

higher temperatures, to decrease the environmental load caused by the treatment of disposed polymeric materials, and to construct a safer society by decreasing the possibility of fires.

Therefore, the authors have researched (1) the thermal degradation of polymers at the combustion temperatures,^{5–8} (2) the relation between the degradation products and flammability,^{9,10} (3) the relation between physical form and combustibility,¹¹ (4) the carbon layer on the polymer surface,⁸ and (5) theoretical analysis through computer simulation,^{12,13} to improve flame retardancy.

The combustion reaction appears to occur through the direct reaction between polymer chain and oxygen in a gas phase, but, actually, the degradation products are reacting with oxygen in the gas phase. The large amount of heat from this reaction irradiates the surface of the polymers, and thermal degradation occurs successively to continue the combustion.¹⁴ Namely, the degree and the rate of the combustion reaction can be expected to depend on (1) the thermal degradation products from the polymer and (2) the oxidation reaction between these products and oxygen.

Correspondence to: E. Nakashima (e-nakashima@isc.chubu.ac.jp).

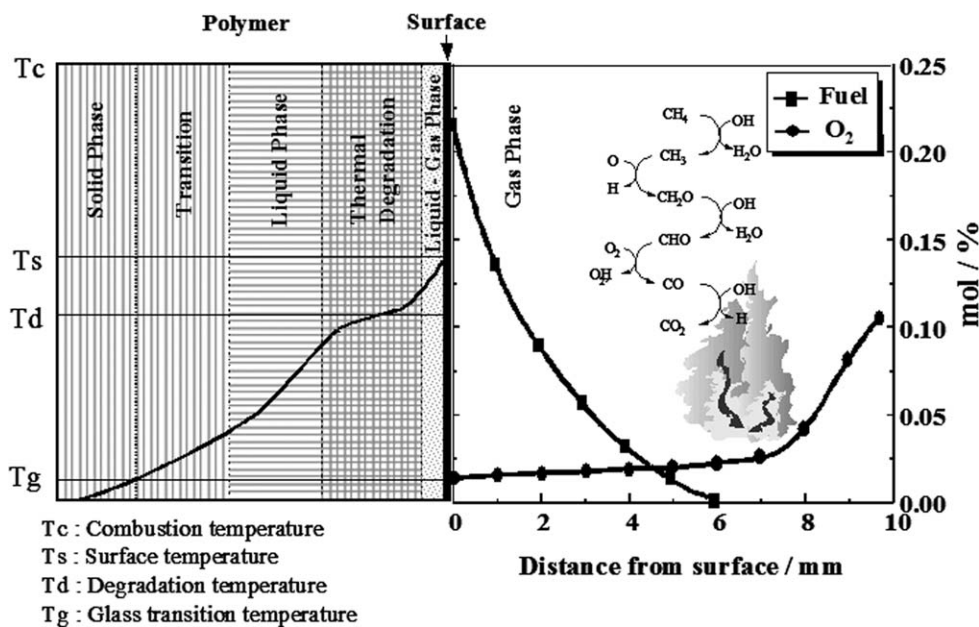


Figure 1 Oxidation reaction field.

The oxygen reaction does not occur without heat sources around the polymeric materials, because the oxygen ratio is not high enough. The oxygen is supplied to the surface with enough from air when the polymeric material ignites, but the oxygen is apt to lack during combustion, because the combustion reaction is intense and fast. The oxidation reaction field takes a distance little by little from the polymeric material when the combustion starts and forms it around 10 mm from the polymeric material surface (Fig. 1). Fuel gases gushing out from polymeric material and oxygen react intensely at the oxidation reaction field. The combustion causes to rise the temperature to about 1000–1200°C immediately by convection of air, radiation heat, and diffusion of substances such as gases and oxygen. At the first stage of combustion, the material surface is heated by this heat radiation, decomposes, and gases are generated. The surface is covered with soot, carbide, bubbles, and scission products, but the heat passes the surface covered with soot and reaches the material inside.¹⁵ The heated material reaching the decomposition temperature begins to decompose. Each polymer has a different decomposition temperature, but it is around 500°C, and the temperature is almost the same as the temperature of polymeric material surface at the early stage of fire. The decomposed gases are generated, diffuse into polymeric material, and reach the surface. Then, they disperse into the air and reach to oxidation reaction field. Figure 2 shows a basic concept of combustion reactions in the area of polymeric material. These six elementary reactions of combustion are series; (1) combustion reaction at the oxidation reaction field,

(2) heat transfer by the radiation and heating of the materials surface, (3) radiation into the material, (4) generation of volatile scission products at degradation reaction field, (5) volatile diffuse into the material, and (6) finally decomposed products disperse into the gaseous phase, and reaction and a physical process continue in “series.”¹⁶

The synergistic effects of halogen compounds and antimony oxide were discovered in the early stages and have been used to obtain flame retardancy.¹⁷ Studies on the effects of the carbon layer on the surface of polymeric materials have led to the studies on the effect of adding several kinds of phosphorous compounds such as red phosphorous and organic phosphoric esters to accelerate the formation of the carbon layer.^{18,19} PE also has studied on the effect of adding phosphorous compounds²⁰ and magnesium

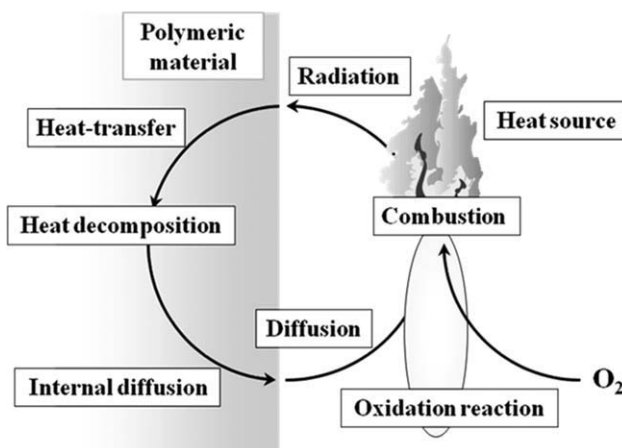


Figure 2 Combustion mechanisms.

TABLE I
Materials Used in the Present Study

Chemicals	C_nH_{2n+2} (n)	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	Manufacturer	Density (g/mL, 25°C)	Viscosity poise (150°C, Brookfield Thermosel) (L)	M_p (°C)
Eicosane	20	282	282	Kishida Chemical Co., Ltd.	–	–	34–37
PE	121	1,700	4,000	Aldrich	0.92	1.5	92
	393	5,500	15,000	Aldrich	0.93	37.2	112
	550	7,700	35,000	Aldrich	0.906	78	90
	786	1,1000	76,000	Tosoh Co.	0.964	–	–
	$2-4 \times 10^5$	–	$3-6 \times 10^6$	Aldrich	–	–	–
PP	–	–	210,600	Japan PP Co.	0.90	–	–
PS	–	–	240,000	PS Japan Co.	1.05	–	–

hydroxide²¹ to accelerate the formation of the carbon layer in flame retardant.

This article clarifies some points regarding the relation of cause and effect of molecular weight and combustibility of polyethylene, which has the frame of the hydrocarbon, the most basic frame of the polymeric materials. This article also compares the combustion behavior of polypropylene (PP) and polystyrene, which resemble polyethylene in structure.

EXPERIMENTAL

Specimens used in this study

Five kinds of HDPE (high density polyethylene) manufactured by Aldrich and Tosoh Co., Japan, with different M_w and M_n , and Eicosane manufactured by Kishida Chemical Co., a compound whose chemical structure is the same as PE with a molecular weight of 282, were used. PP manufactured by Japan Polypropylene Co. and PS (polystyrene) manufactured by Polystyrene Japan Co. were also used in this study. Their characteristics are listed from their catalog, and each specimen was measured M_w and M_n by gel permeation chromatography in Table I. There is recognition that molecular weight distribution is important knowledge to discuss molecular weight, but it is thought that the molecular weight distribution (M_w/M_n) is not an important factor in combustibility in this study.

Thermal gravimetric analysis

DTG-60 manufactured by Shimadzu Co. was used for thermal gravimetric analysis.^{22,23} Experiments were carried out on 5.0 mg of the samples under nitrogen at a flow rate of 50 mL/min and a furnace-heating rate of 90°C/min up to 800°C. The rate was much higher than that of, in general, degradation experiments, because the main purpose of this study was to analyze the degradation during fires

when the elevating rate of the temperature is about 100°C/min.

Pyrolyzer/gas chromatography/mass spectrometry

Pyrolyzer/gas chromatography/mass spectrometry (Py-GC/MS) made by Shimadzu Co. (GCMS-QP5000) were used to assign the fragmentations. The procedure was conducted according to the usual way in the degradation experiments of plastics. A 30-m-long capillary column (100% dimethyl polysiloxane) was used, and helium was used as a carrier gas. The minimum and the maximum mass numbers were set at 10 and 700, respectively. The interface temperature between the pyrolyzer and the gas chromatography was 280°C to prevent the gas from condensing. The column was heated at a rate of 5°C/min from 50 to 325°C. The quantitative values were obtained from the peak areas of total ion chromatography.

Combustion test

The ignition and burn times were measured by the Underwriters Laboratory UL-94 method, which has been well established as a burning test for plastics. Moreover, the heat of the combustion during the test was measured at the same time by a multicalorimeter (MCM-1 manufactured by Toyo Seiki Seisaku-Sho). MCM-1 measured the weight loss rate, total heat amount, heat flux, and combustion residue.

Regarding the heating time with a methane burner of the sample, the difference from the UL94-V examination was that the sample was heated until it ignited, and the methane burner was separated from the sample to a regulated position after ignition to conduct the experiment. The size of the test specimen was 12.7 mm × 127 mm × 3.2 mm, and the states of combustion and ignition of each resin were recorded with a video camera and observed, respectively.

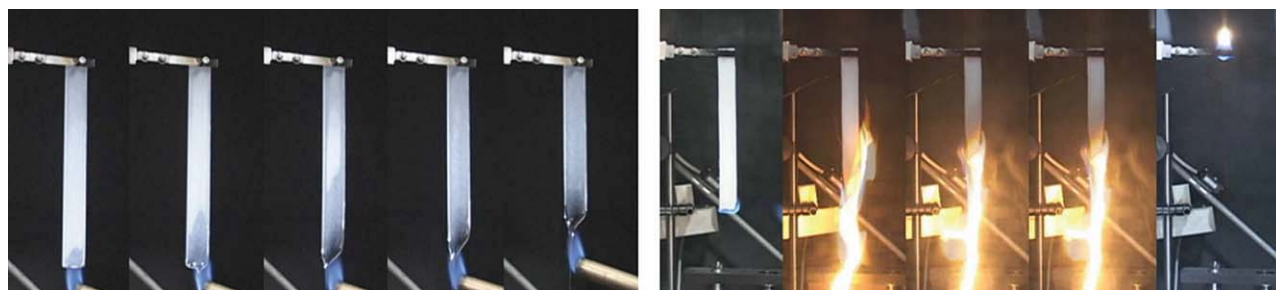


Figure 3 UL vertical test of PE (left: $M_w = 35,000$; right: $M_w = 76,000$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS

Combustion test by the UL-94 method

The flammability of materials strongly depends on the conditions of the combustion. This fact is completely different from what is commonly understood as “flammability” in the general sense. For example, carbon is thought to be easily flammable, but it actually burns when the concentration of oxygen in the air is 60% or more. The phenomenon was reported back in Fenimore et al., 1966, but it is still not well known after more than 40 years from the initial report¹⁸. Actually, almost all organic or polymeric materials composed mainly of carbon and hydrogen will burn if the combustion condition can be freely selected. Those materials burn under higher temperatures and a higher oxygen concentration, because they decompose into small fragments that vaporize and react with oxygen-like normal chemical reactions. The flammability of materials also depend on the arrangement during combustion. Useful experiments can be achieved under special conditions that resemble an actual fire. The key points are (1) a vertical position like a wall, (2) the same oxygen concentration in the air, and (3) no heat sources except the enthalpy of the combustion of the specimen. The UL method is the best method for conducting these tests and therefore was selected for the measurement of the combustion. Still, it is important to expand the application field of polymeric science to construct a safer society.

The PE specimen ($M_w = 35,000$) did not ignite after heating for 10 s by a butane burner repeatedly (five times). However, the PE specimen ($M_w = 76,000$) easily ignited and vigorously burned as shown in Figure 3.

As no ignition was observed in the case of PE specimen ($M_w = 35,000$) after heating by a butane burner, the fire of the burner was directly applied to heat the melted fiber about 2 mm in diameter under PE specimen. But it did not ignite.

The molecular weight range of the sample was expanded and tested. The PE specimens whose molecular weights were lower than PE specimen

($M_w = 35,000$) did not ignite, and the ones with higher molecular weight burnt like PE specimen ($M_w = 76,000$).

As mentioned in the Introduction section, the combustion phenomena occur when the scission products react with oxygen in a gaseous phase. The gasification ratio to the whole PE specimen calculated from the weights of the initial specimen, the dropped residue, and the residue that did not burn and drop are shown in Figure 4 along with the flaming combustion times.

The PE specimens whose molecular weights were relatively low did not burn, and the gasification ratios were nearly zero. On the other hand, the PE specimens of higher molecular weights burned easily, and those ratios were about 50–60%. The transitional M_w point was several tens of thousands.

Thermogravimetric test

To consider the reason why the combustion of PE differs according to molecular weight, several experiments to analyze the thermal degradation, the scission products, and other tests were conducted.

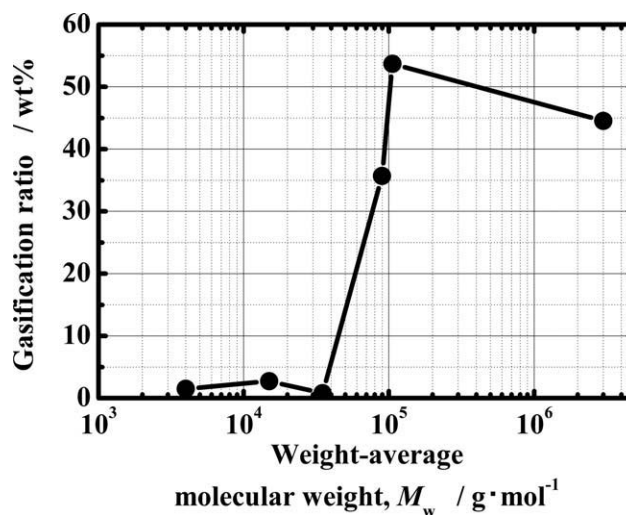


Figure 4 Flaming combustion time as a function of weight-average molecular weight.

TABLE II
Weight Loss Temperatures of PE Obtained by TGA

C_nH_{2n+2} (<i>n</i>)	M_w (g mol ⁻¹)	Weight loss temperature (°C)			Residue (%)
		5%	50%	95%	
20	282	232	298	343	4
121	4,000	423	512	550	0
393	15,000	467	519	553	1
550	35,000	458	516	554	0
786	76,000	469	520	556	0
$2-4 \times 10^5$	$3-6 \times 10^6$	485	528	561	1

The 5, 50, and 95% weight loss temperatures (WLTs) obtained by TGA are shown in Table II.

The 5, 50, and 95% WLTs of Eicosane were lower than PE specimens. PE specimens whose molecular weights were above 4000 were nearly the same. All specimens had no residue after heating. PE has a relatively long carbon chain, and so the boiling point is either very high or does not exist. Therefore, the weight loss during heating is due to volatilization of scission products. The similar WLTs of the five PE specimens in Table II mean that the degradation rates were no different. On the other hand, the weight loss at lower temperatures of Eicosane is caused by the boiling temperature.

Quantitative analysis of scission products

The scission products of the two kinds of PE specimens ($M_w = 35,000$ and $M_w = 76,000$) were quantitatively measured by Py-GC/MS, and the results are shown in Figure 5.

Almost all scission products whose carbon number was below 43 could be specified. In thermal degradation of PE, the random scission is dominant.⁸ The boiling points of the scission products with higher carbon numbers were calculated using the relation between the molecular weight of hydrocarbons and the boiling point as shown in eq. (1).

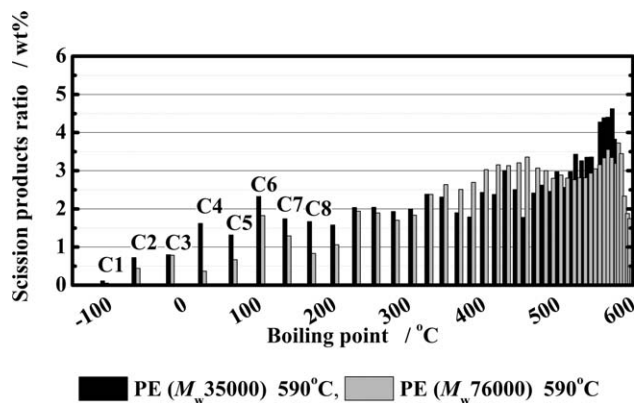


Figure 5 Difference of the scission products ratios of $M_w = 35,000$ and $M_w = 76,000$.

$$T_{bp} = 640 - 807 \times \exp\left(\frac{-M_w}{207}\right) \quad (1)$$

The amount of the scission products below $C = 8$ for PE ($M_w = 35,000$) was larger than for PE ($M_w = 76,000$), and the amount of scission products whose boiling points were between 530 and 580°C for PE ($M_w = 35,000$) was greater than that of PE ($M_w = 76,000$). However, there were no big differences in distribution of scission products. Therefore, it was assumed that the influence of the difference in distributions on combustion was small.

Combustion state analysis

It is important to compare the combustion state of PE with PP and PS having structures similar to PE. PP ($M_w = 210,600$) and PS ($M_w = 240,000$) were generally used for ejection grade that same as PE ($M_w = 76,000$), and those combustion states were observed. Figure 6 shows the combusting states of PE, PP, and PS 40 s after ignition in the combustion test by the UL-94 method.

Each specimen burned well, but it can be seen that the position of the flames is different relative to the specimen. When the bottom of PE specimen was ignited by the burner, a small flame was observed on the bottom of it, and, 20 s later, it spread downward from the bottom. The flame did not ignite in the neighborhood of the PE specimen itself; rather, the flame ignited around the molten product dripping downward from the specimen. About one-third of the specimen disappeared about 40 s later, and the flame surrounded the surface of the dripping molten product and developed. Eighty second before the specimen completely burned out, the flame appeared to wind itself around the molten product dripping downward than around the specimen itself. Meanwhile, in the PS specimen, after ignition, the flame crawled upward around the PS specimen that maintained a solid shape, covering more than half of it. The flame developed around the upper part until

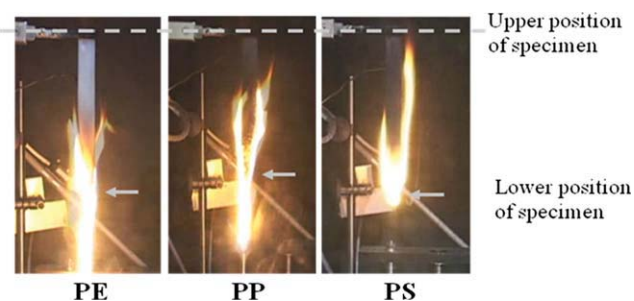


Figure 6 Flames of combusting PE ($M_w = 76,000$), PP ($M_w = 210,600$), and PS ($M_w = 240,000$) 40 s after ignition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Weight Loss Temperature Obtained by TGA

Sample	M_w (g mol ⁻¹)	Weight loss temperature (°C)			Residue (%)
		5%	50%	95%	
PE	76,000	469	520	556	0
PP	210,600	460	509	547	1
PS	240,000	421	462	505	0

the sample finally burned out. The combusting state of PP specimen was like the middle ground between PS and PE specimen, and the shape and position of the PP flame were closer to those of PE.

To analyze this phenomenon, the scission products of three kinds of polymeric materials were analyzed, and the following results were obtained. The decomposition temperature was set 50°C higher than the 50% WLT, which is equivalent to the combustion temperature. Table III shows the results of the thermogravimetric test of PE, PP, and PS. The temperature in which weight loss began was lowest for PS specimen, and its 50% WLT was 462°C. PE specimen had the highest temperature at 520°C.

The results in Table IV indicate that PE specimen has more compounds of C2, C3, and C6 with low molecular weight in terms of the mol ratio of the scission products compared to the other scission products. However, if the distribution of scission products is described by combustion heat on the

vertical axis, shown in Figure 7(a), the shape of the distribution is changed. The scission products with high boiling points between 400 and 600°C, corresponding to higher molecular weight scission products, showed high combustion heats. Figure 7(b) indicates that there are exceedingly more C9 compounds compared to other scission products in PP specimen, because the terminal of main chain forms a pseudo-six-membered ring, and a radical transfer occurs.²⁴ Aside from C9, there are little scission products with low boiling points, and there are more scission products with boiling points between 400 and 600°C than the ones with low boiling points. The combustion heat of these two kinds of polyolefin calculated from the entire amount of scission products is almost the same, 46.4 kJ g⁻¹ for PE specimen and 46.5 kJ g⁻¹ for PP specimen, and it is estimated that the combusting states strongly resemble each other. On the other hand, Table IV shows that PS specimen mostly produces three kinds of scission products: monomer, dimer, and trimer. These products were produced by the chain-end scission.²⁵ The boiling point of the monomer is 170°C, the dimer is 340°C, and the trimer is 460°C. The most of combustion heat was produced by monomer. The trimer is next in efficiency in terms of combustion heat. Furthermore, Table III shows that the 50% WLT of PS specimen is 462°C, which means that it is highly possible that all three scission products goes to gas phase during the initial stages of combustion and combine with oxygen.

TABLE IV
Major Scission Products of Respective Polymers

Polymer	M_w (g mol ⁻¹)	Scission products		Molecular weight (g mol ⁻¹)	Boiling point (°C)	Scission products ratio (mol %)	Combustion heat			Total Combustion heat (kJ mol ⁻¹)
		Abbreviation	Structure				Calculated (kJ mol ⁻¹)	Observed (kJ mol ⁻¹)	Correlated (kJ mol ⁻¹)	
PE	76,000	C2	CH ₂ =CH ₂	28	-65	4.0	1,248	1411	1,370	55
		C3	CH ₂ =CH-CH ₃	42	-19	4.8	1,836	2058.47	2,010	96
		C6	CH ₂ =CH(CH ₂) ₃ CH ₃	84	102	5.5	3,600	n.a.	3,940	217
		C38	CH ₂ =CH(CH ₂) ₃₅ CH ₃	532	578	1.8	22,409	n.a.	24,500	441
PP	210,600	C3		42	-19	16.0	1,836	2058.47	2,010	322
		C9		126	201	21.0	5,363	n.a.	5,860	1231
		C55		770	620	1.8	32,402	n.a.	35,400	651
PS	240,000	S		104	152	73.4	4,120	4395.2	4,510	3312
		SS		208	345	7.3	8,325	n.a.	9,100	662
		SSS		312	461	15.8	12,531	n.a.	13,700	2158



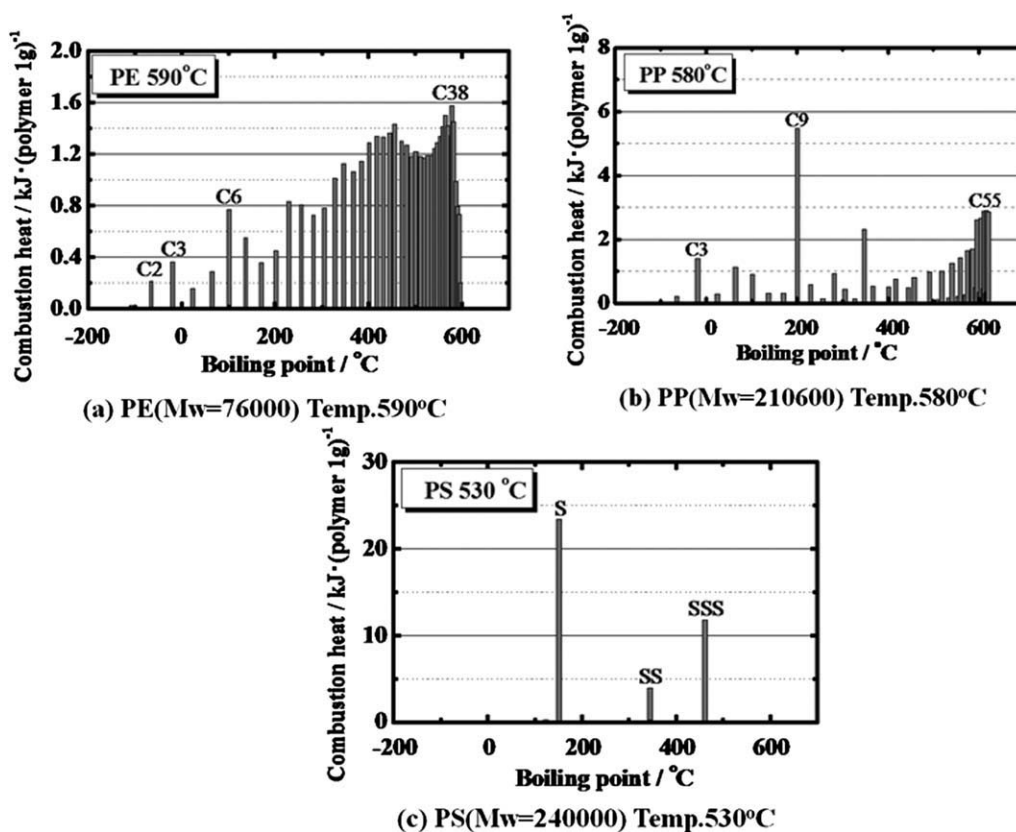


Figure 7 Combustion heat distribution of scission products.

DISCUSSION

The combustion tests simply showed that PE, which is known to be an easily burnable material, did not burn under limited conditions, namely the configuration of the materials (vertical), in the air (oxygen density 21%), and low molecular weight. The experiments were repeated several times at two laboratories in different universities, Nagoya University and Chubu University, to confirm the reliability of the

experiment result, and the same combustion results were obtained from each university. The most notable result of these experiments was that when the molten sample created by directly heating of the PE specimen ($M_w = 35,000$) with a flame of a butane burner was reheated, it did not burn at all. As the flame did not change the characteristics of the molten sample, this could become a new molding method by using open fire²⁶.

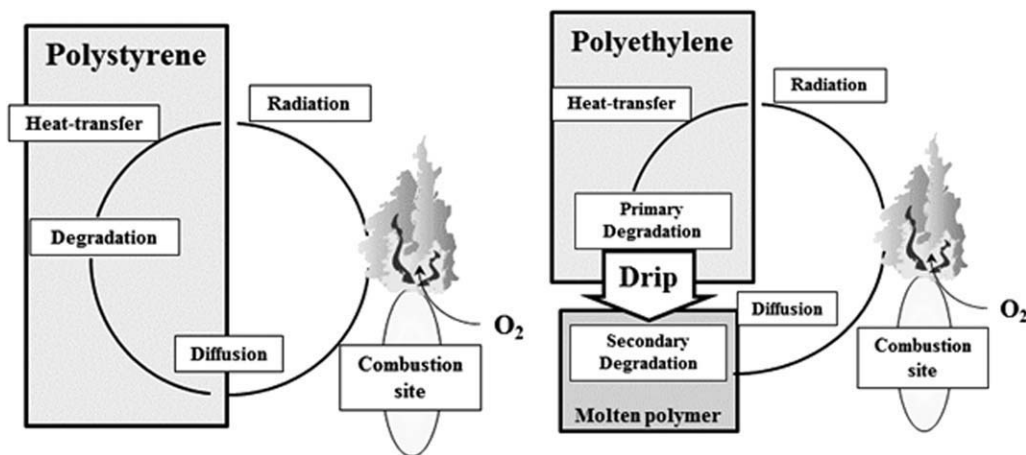


Figure 8 Block diagram of polymer degradation.

A major difference in the pyrolysis process on the combustion of polymer was expected, because the polymer did not react directly with oxygen, but rather the scission products reacted with oxygen in gas phase. However, there were no remarkable differences of degradation behaviors of respective polyethylene with different molecular weight as far as the analysis by TGA and Py-GC-MS.

Therefore, this experiment has taken a cross section approach to the combustion tests of not only PE but also PP and PS. Comparisons between the combustion state of PE to those of PP and PS suggested the reason why the combustion state of PE is clearly different according to its molecular weight. The flame appears around the specimen in the combustion test of PS. In the case of PP, not only did the flame appear around the specimen, but it also appeared in the lower part of specimen. When the combustion state of PE was observed in detail, flames were hardly seen around the specimen, and they appeared around the materials that fell to the lower part of the specimen. The block diagram of PS and PE degradation is shown in figure 8.

Normally, concept of combustion or flammable is the meaning of specimen that is burned. Based on this concept, any molecular weight of PE would be classified as nonflammable even so the specimen of which molecular weight is 76,000 did not burn. However, the thermally decomposed products falling to the lower part of the specimen and it burned when a flame was around it. Until now, such phenomena have led to the general understanding that PE burns, but it should be classified into the nonflammable category according to the normal concept of combustion. In particular, when the molecular weight of the PE was equal to or less than a specific number, it did not ignite at all in air in this study.

Whether the specimen itself burns or the products that are the primary degraded products or the fusion product burn create an extremely serious difference in controlling the combustibility of polymeric materials. The PS flame seems to surround the specimen and goes up, because more than half of the scission products are monomer that has a boiling point of 170°C, which goes to gas phase and reacts with oxygen immediately. Furthermore, the PP flame also goes up more than PE, because the volatile C9 compounds produce a lot. In the case of PE, there is an overwhelming amount of combustion heat from the generated high-boiling scission products, and so the primary degradation products do not immediately go to gas phase but fall down to the lower part of specimen, reacting with oxygen after the secondary degradation. In other words, polyolefin does not simply burn; it strongly depends on the generated scission products, their boiling points, and secondary degradation.

The controlling of the combustion state is not merely dependent on only molecular weight, because the primary degradation products or the fusion product has smaller molecular weight than the PE that constitutes the molding specimen. Combustion of PE specimen is determined by molecular weight and how the combustion fields are given, and it was shown that these phenomena were extremely complicated compared to those of PP and PS.

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