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Effect of porous solid in catalytic degradation of polymers

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Abstract

In this study the author investigated the effect of non-acidic porous solid (silicalite) on the thermal degradation behavior of polypropylene and polystyrene, and found that silicalite affects the thermal degradation behavior of polypropylene and polystyrene as well as polyethylene, respectively. And for comparison with silicalite, the thermal degradation behavior with silica-alumina was studied.

Experimental results obtained by the continuous reactor showed that not only the configuration of porous solids affected the thermal degradation behavior of polymer, but also the configuration of macromolecules affected it.

Keywords: Thermal degradation; Polymer; Porous solid; Configuration; Continuous flow reactor

1. Introduction

A lot of studies on the thermal degradation of polymers in the presence of solid oxide have been reported since the late 1970s [1, 2, 3]. Among solid oxides, silica-alumina and zeolites are mainly tested to degrade polyolefins. However, no studies in the presence of non-acidic porous solid have been conducted. It is in 1999 that Sakata et al. firstly reported that the non-acidic porous solid also had a catalytic effect on the thermal degradation of polymers [4].

In the previous work [5], the author conducted the thermal degradation of polyethylene in the presence of silicalite (a non-acidic porous solid) by a continuous flow reactor, and reported that silicalite significantly affected the pyrolysis behavior of polyethylene. It increases the chain-end scission of macromolecule and changes the composition of decomposition products with small effect on mass rate. The experimental fact that silicalite has similar catalytic effect as silica-alumina indicates that the catalytic degradation of polymer occurs without active centers of the catalyst. It was concluded the catalytic effect exhibited by the porous solid was based on the configuration derived from pore size, pore distribution and specific surface area.

In this study, the author investigated the effect of silicalite on the thermal degradation behavior of polypropylene and polystyrene to confirm that silicalite affected the pyrolysis behavior of polypropylene and polystyrene as well as polyethylene. In addition, for comparison with silicalite, the thermal decomposition behaviors of polyethylene, polypropylene and polystyrene in the presence of silica-alumina were also shown. As an experimental result, it was found that not only the configuration of porous solid affected on the thermal degradation behavior of polymer, but also the configuration of macromolecule affected on it.

2. Experimental

2.1 Material

Polyethylene (PE), polypropylene (PP) and polystyrene (PS) were made by Mitsui Chemicals, Inc. The physicochemical properties of polymers are shown in Table 1. The non-acidic porous solid, silicalite was made by Fuji Silicia Chemical. The properties of silicalite and silica-alumina tested in this study are shown in Table 2. Furthermore, NH3-TPD spectra of the silicalite and silica-alumina has been presented in reference [4], which shows that silicalite does not have any acid site in the temperature range of 300–500°C.

Table 1 Properties of original polymers

Property		PE	PP	PS
Density	g/cm3	0.968	0.906	1.050
Ash	wt%	0.03	0.04	0.02
Conradson carbon	wt%	0.10	0.10	0.06
Higher calorific value	joule/g	48,950	46,400	43,300
av. Molecular weight, Mw	–	1.12E+05	2.17E+05	1.35E+05

Table 2 Property of the porous solid

Porous solid		Al2O3/SiO2	BET surface area
		(mole ratio)	(m^2/g)
Silica alumina	SA1	0.20	420
Silicalite	SL	0.00	220

2.2 Analytical method and the definition of the reaction rate

The gaseous product was analyzed by gas chromatography with a packed column, and the liquid product was analyzed by gas chromatography with a capillary column. Separately, specific gravity, viscosity, and bromine number were measured following JIS method to know the properties of the liquid product.

The mass rate of volatilization is defined as the slope of the cumulative curve of volatile (shown in Figure 1) divided by the amount of reactor content. The definition of the mass rate of volatilization and the rate of double bond formation are shown below. For details of the analysis method of products and the definition of degradation rate, refer to the previous paper [6, 7].

Mass rate of volatilization =

rate of volatilization [kg/h] / amount of reactor content [kg]

Rate of double bond formation =

double bond in volatiles [mole C=C/h] / amount of reactor content [kg]

2.3 Experimental setup

Figure 1 shows the experimental apparatus for the thermal degradation of polymers in the continuous operation mode. This apparatus is the same one as that used in the previous study [5]. The operation method is exactly the same too. The experiment was carried out with the amount of reactor content being set to 1.0 kg during all of the experimental runs.

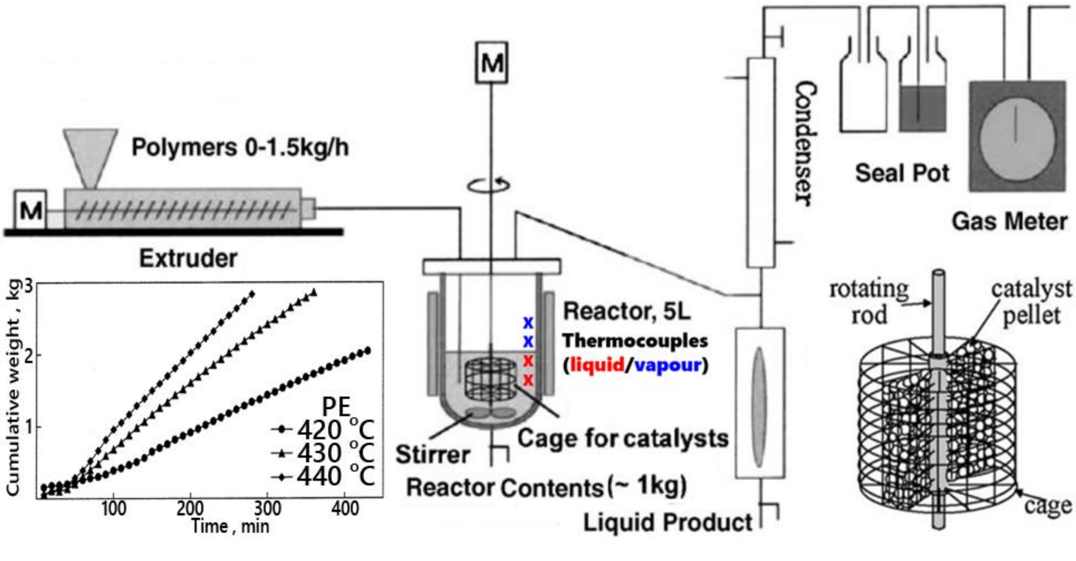


Fig. 1 Experimental set-up for thermal degradation of polymers in the presence of porous solid

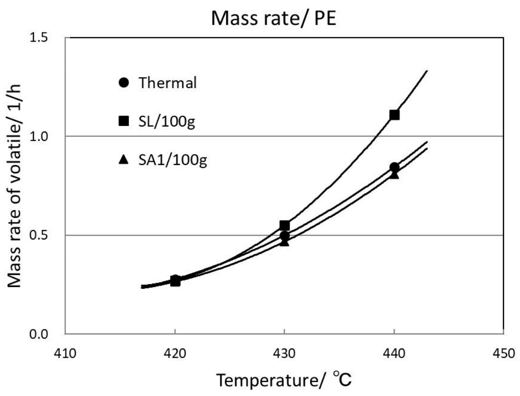
In 'Results and Discussion' described below, the results of the PP and PS experiments conducted in this study and the results of the PE experiment reported in the previous paper [5] are illustrated in parallel for comparison.

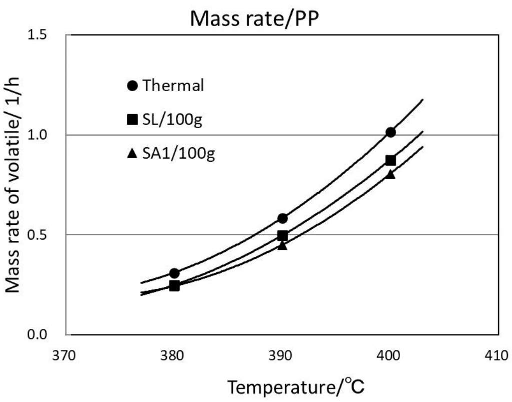
3. Results and Discussion

3.1 Rate of thermal degradation and activation energy

3.1.1 Mass rate of volatilization

Figure 2 shows the mass rates of PE, PP, and PS when SL, SA1 and Thermal (without catalyst) are applied, respectively. The mass rate depends not only on the reaction temperature, but also on the configuration of porous solids. For PE and PS, the mass rate with SL is the highest, followed by the case without catalyst, and the lowest with SA1. For PS, SL is almost twice as effective as SA1. On the other hand, for PP the mass rate of Thermal (without catalyst) is the highest, followed by the case with SL, and the lowest with SA1. Regarding PP, it is noteworthy that the effect of porous solid is limited, and the mass rate without catalyst is always higher than that in the case with catalyst.





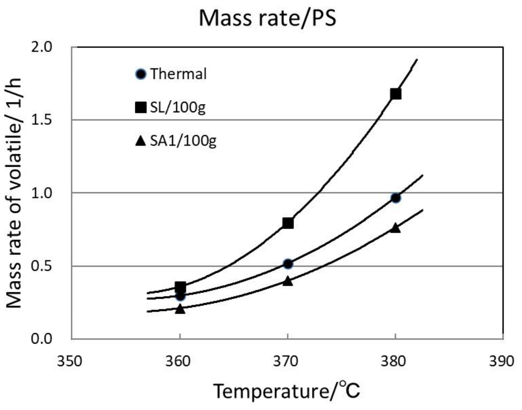


Fig. 2 Mass rate of volatilization of PE, PP and PS

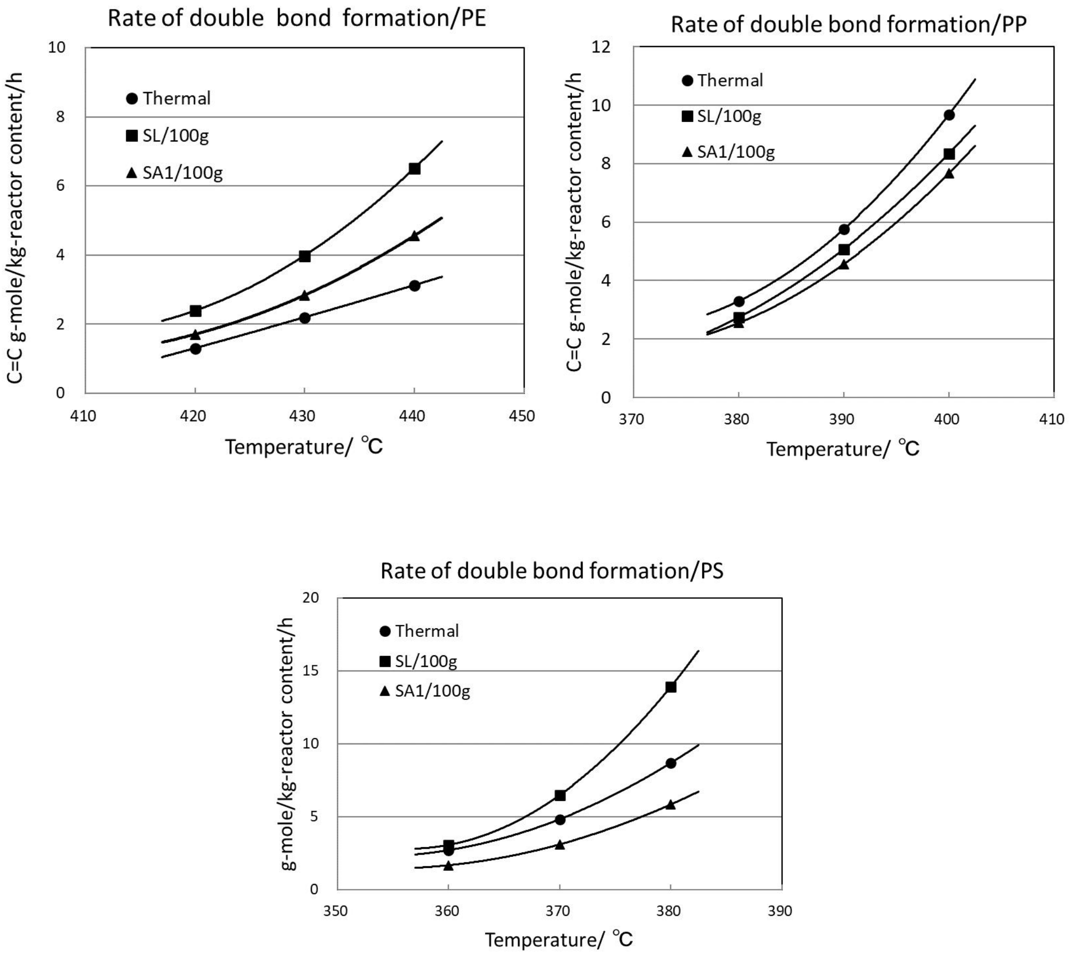


Fig. 3 Rate of double bond formation of PE, PP and PS

Figure 3 shows the rates of double bond formation of PE, PP and PS with SL, SA1 and Thermal (without catalyst), respectively. Similar to the mass rate, the rate of double bond formation depends not only on the reaction temperature, but also on the configuration of the porous solid.

For PE, the double bond formation rate with SL is the highest, followed by with SA1, and Thermal (without catalyst) the lowest. On the other hand, for PP the rate of double bond formation of Thermal (without catalyst) is the highest, followed by the case with SL, and the lowest with SA1. That is, for PP the rate of double bond formation without catalyst is larger than those of the cases with catalysts. It seems that in the thermal degradation of PP, the effect of porous solid, SL and SA1 is limited for the chain-end scission. For PS, similar to the mass rate, the rate of double bond formation with SL is the highest, followed by Thermal (without catalyst), and the lowest with SA1.

3.1.3 Activation energy for thermal degradation of PE, PP and PS

Figure 4 show the activation energies for thermal degradation of PE, PP and PS based on the mass rate of volatilization and the rate of double bond formation respectively. The activation energy when using silicalite is always the maximum for each polymer.

As mentioned previously, the catalytic effect exhibited by the porous solid is based on the configuration derived from pore size, distribution and specific surface area. And the random scissions mainly proceed by the radical transfer mechanism in bulk liquid (reactor content), because the long-chain polymers have less access to the inner surface of the porous solid. As shown in Figure 5, in the thermal decomposition (without catalyst), the one end of macromolecule chain is anchored by bulk liquid, but in the presence of the porous solid, the anchoring effect due to the configuration of the porous solid promotes the chain-end breakage.

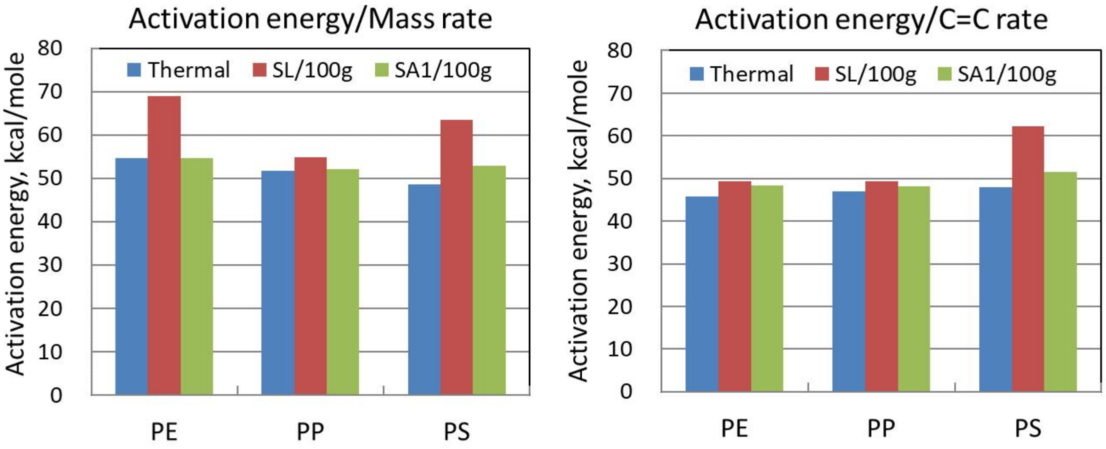


Fig. 4 Activation energy for the mass rate of volatilization and the rate of double bond formation

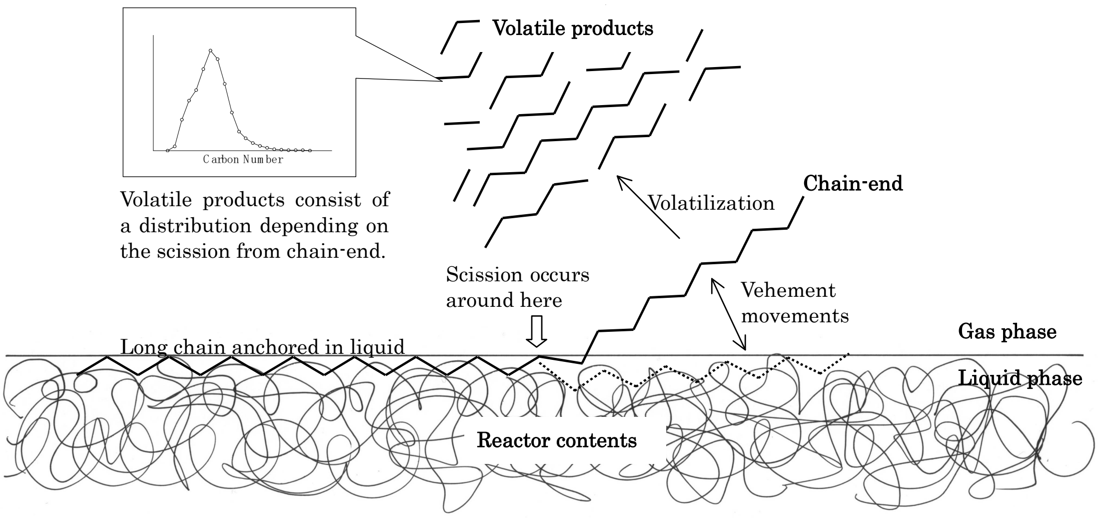


Fig. 5 Mechanism of the chain-end scission of polymer generating volatile products at gas-liquid interface proposed by K. Murata [8]

Figures 2, 3 and 4 show that SL (silicalite) favors the chain-end scission of macromolecule contributing to the anchoring effect for the chain-end scission. However, SA1 (silica-alumina) seems to have little anchoring effect for breaking the chain-end of macromolecules. And the catalyst investigated in this study has little effect on the thermal degradation of PP. It indicates that the effect of the catalyst varies depending on the configuration of macromolecule.

3.2 Product

3.2.1 Gaseous product

Figures 6, 7 and 8 show the gas yield, the carbon number distribution and the average molecular weight of the gaseous product during the thermal degradation of PE, PP and PS in the presence of SL, SA1 and Thermal (without catalyst), respectively.

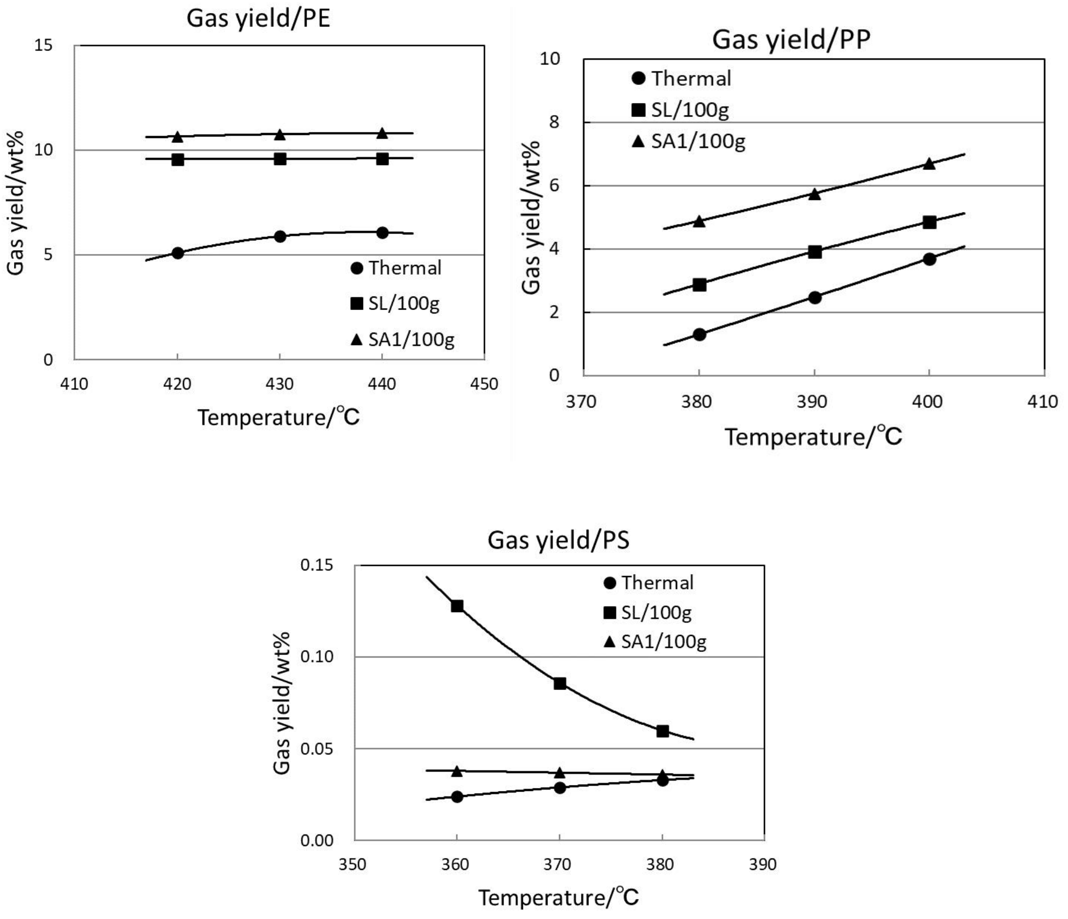
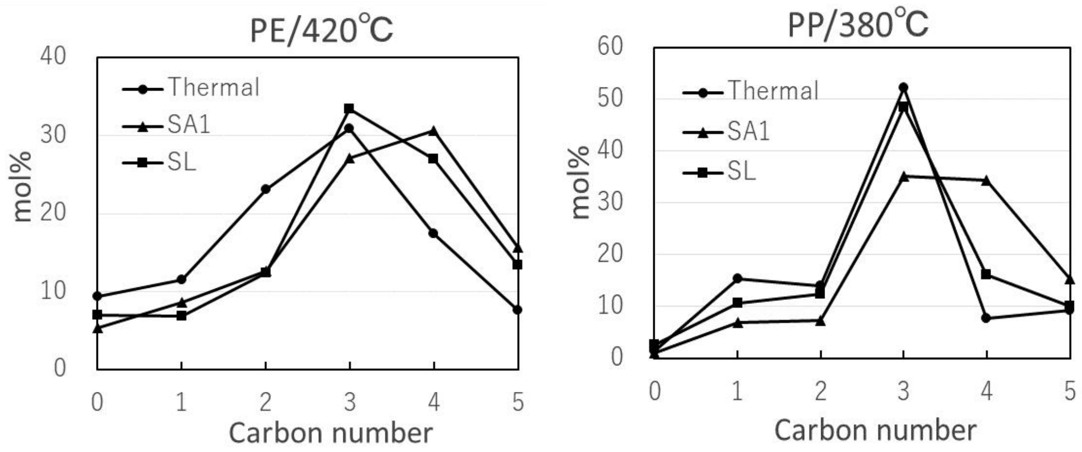


Fig. 6 Gas yield of PE, PP and PS



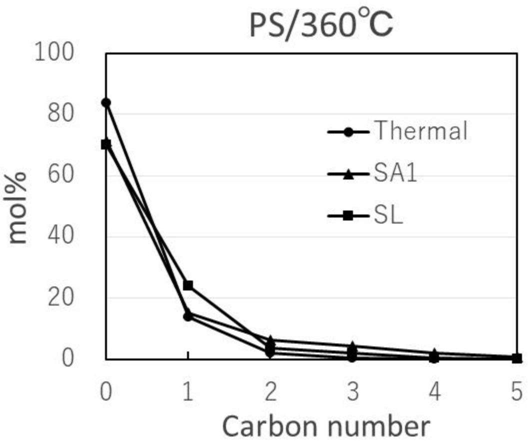


Fig. 7 Carbon number distribution of the gaseous product

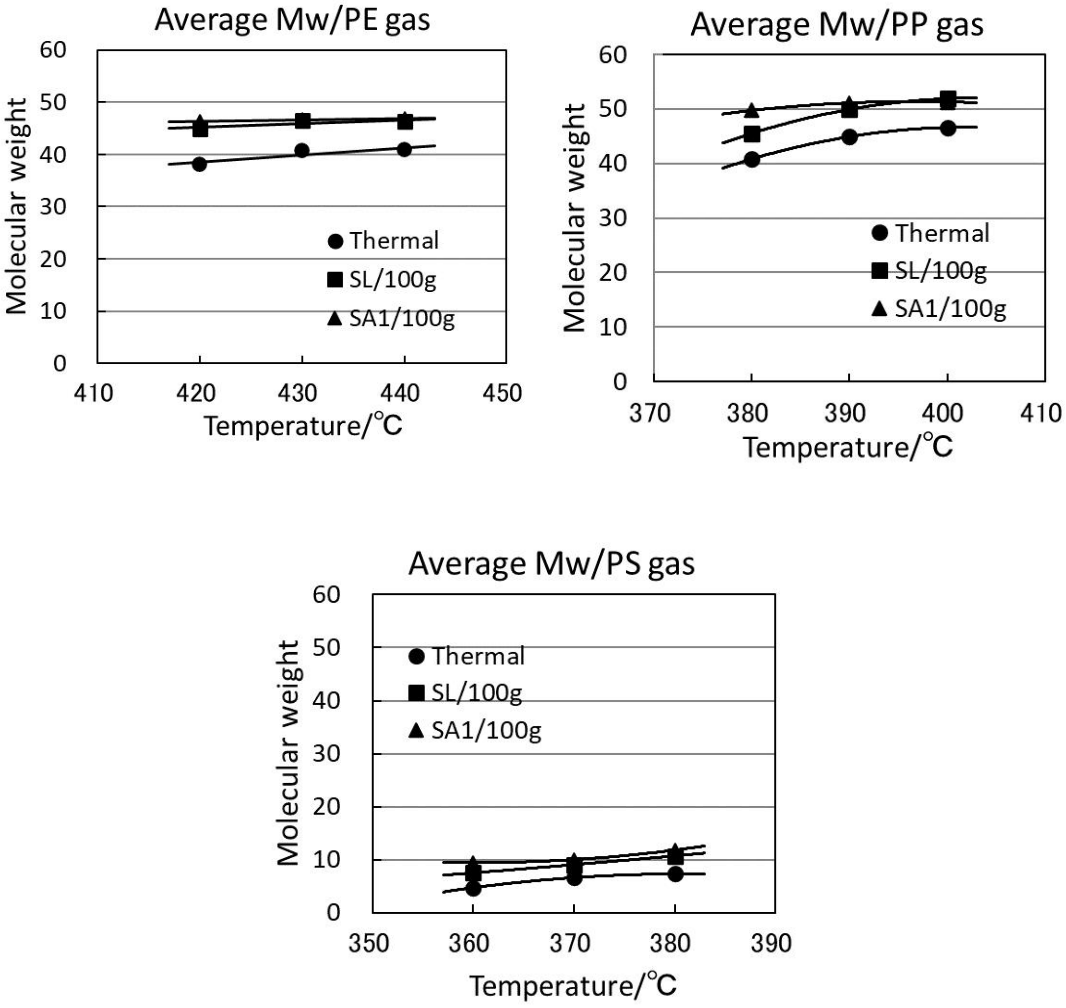


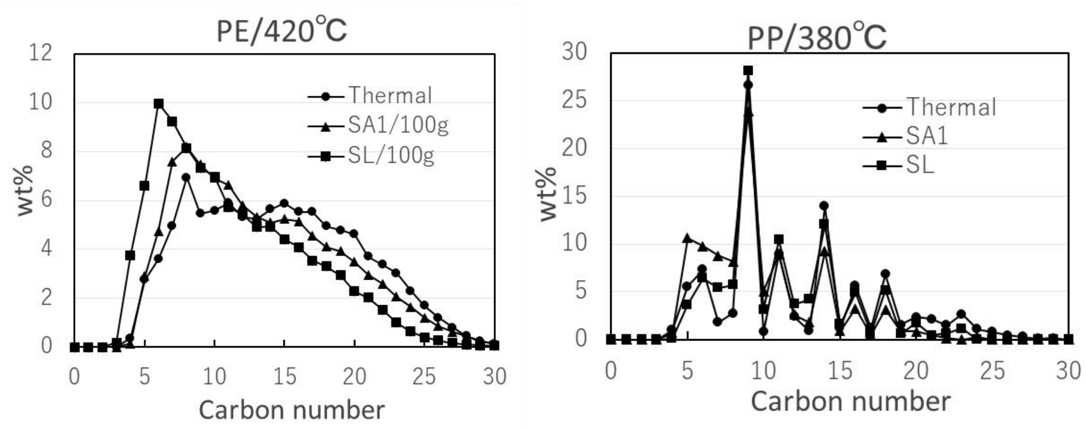
Fig. 8 Average molecular weight of the gaseous product

As shown in Figure 6, the gas yield is larger in the case of thermal decomposition with catalyst than Thermal (without catalyst). In particular, the gas yield with SA1 is the largest for PE and PP. And for PS the gas yield with SL is much larger than the others and decreases with temperature.

As shown in Figure 7, for PE and PP, C_3 components are major, and for PS hydrogen is major. The average molecular weight of gaseous product with Thermal (without catalyst) is always the lowest and that with SA1 is always the highest, as shown in Figure 8. SA1 seems to favor the gasification of macromolecules.

3.2.2 Liquid product

Figure 9 shows the carbon number distributions (based on NPgram) of the liquid product derived from PE, PP and PS in the presence of SL, SA and Thermal (without catalyst), respectively. See reference [6] for NPgram. And Figure 10 shows the average carbon number of the liquid product calculated based on the carbon number distributions shown in Figure 9. Figures 9 and 10 show that the distribution of liquid products is narrowed due to the anchoring effect of SL comparing with Thermal (without catalyst).



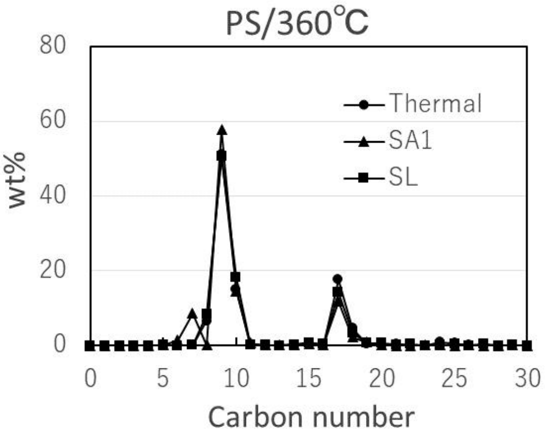


Fig. 9 Carbon number distribution of the liquid product

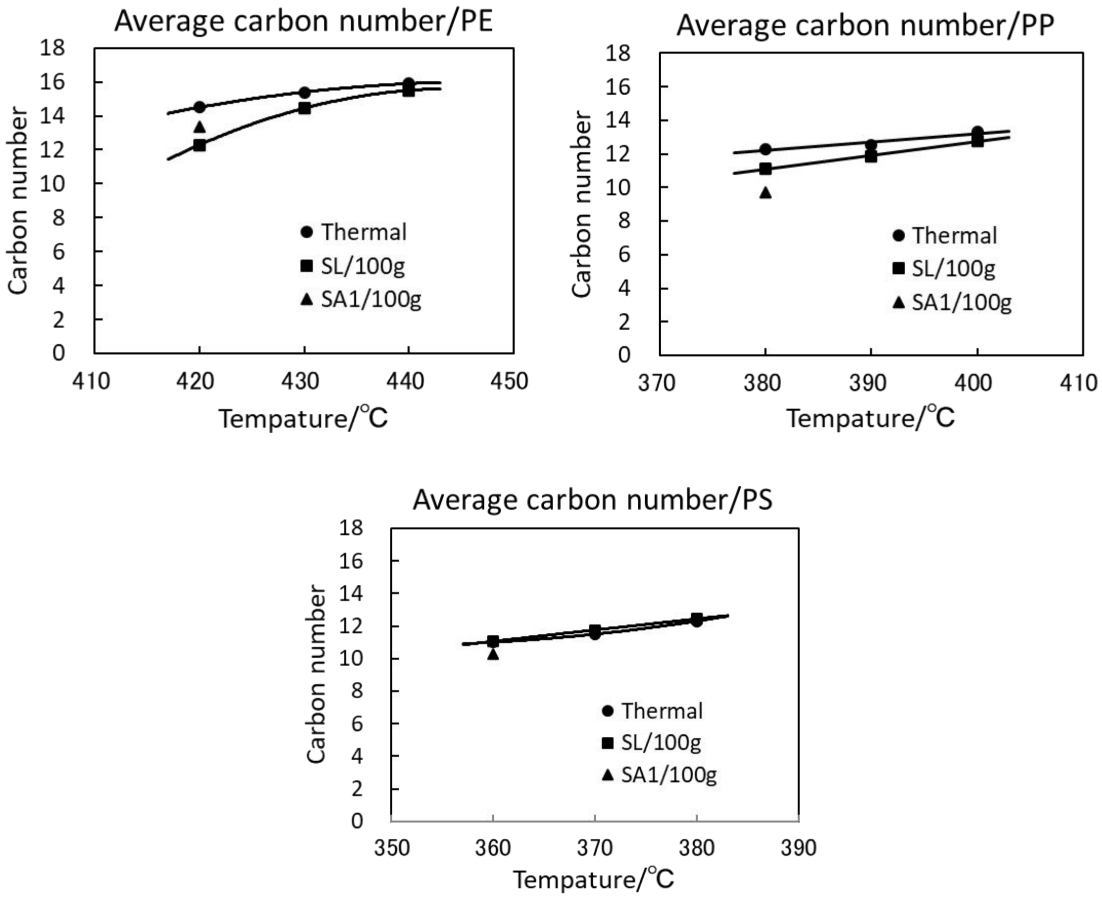


Fig. 10 Average carbon number of the liquid product

Figure 11, 12 and 13 show the bromine number, the specific gravity and the viscosity of the liquid products derived from PE, PP and PS, respectively. They clearly show the catalytic effect of silicalite for the properties of the products during the thermal degradation of PE, PP and PS.

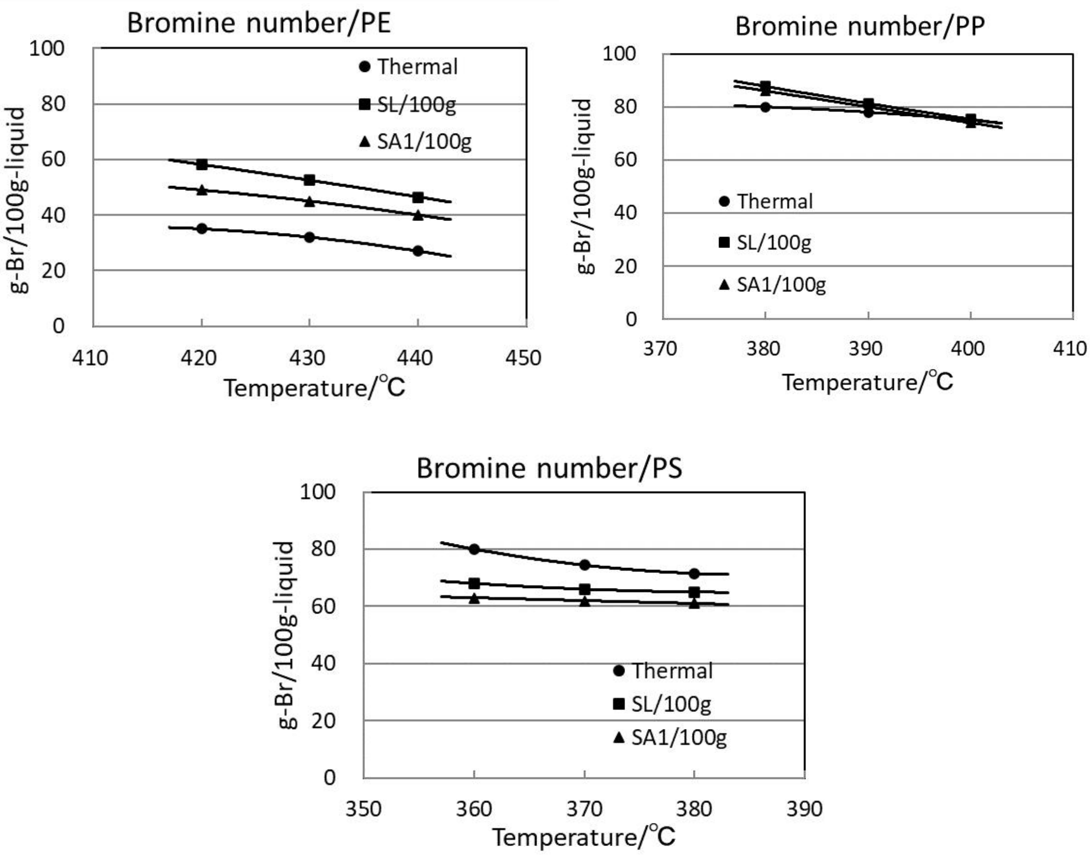
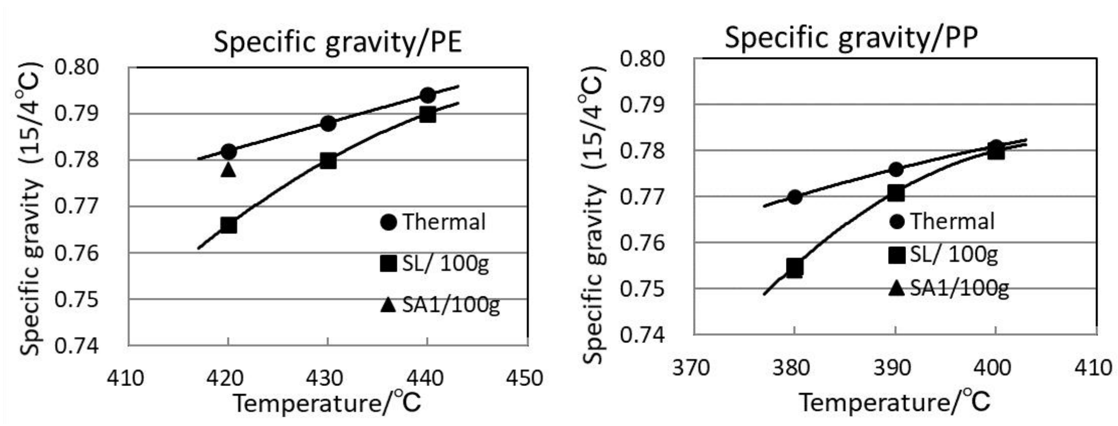


Fig. 11 Bromine number of the liquid product



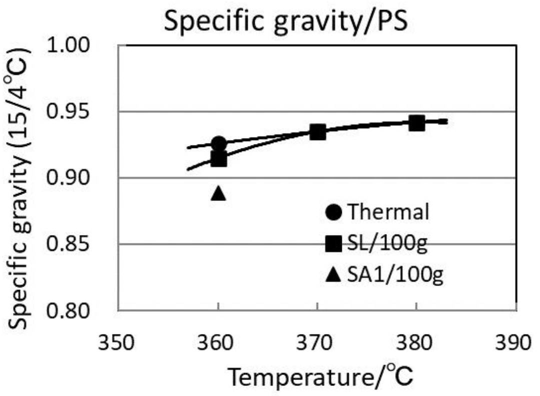


Fig. 12 Specific gravity of the liquid product

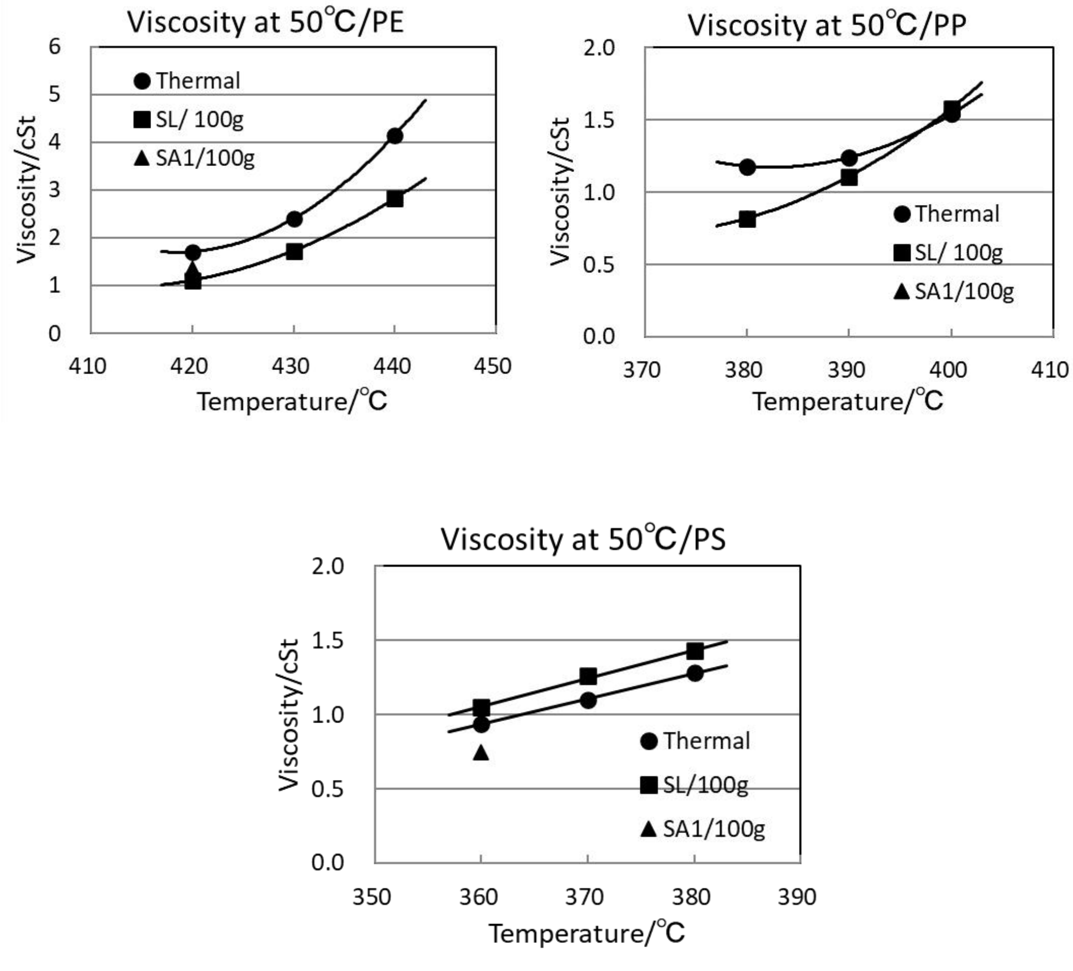


Fig. 13 Viscosity of the liquid product

4. Conclusion

- It was confirmed that silicalite, a non-acidic porous solid, affects the thermal degradation behavior of polypropylene and polystyrene as well as polyethylene, respectively.
- The catalytic effect of the porous solid on polypropylene are limited compared to the effects on polyethylene and polystyrene. The catalytic effect on the thermal degradation behavior of macromolecule depends not only on the configuration of the porous solid but also on that of macromolecule.
- Silicalite favors the chain-end scission of macromolecule contributing to the anchoring effect for the chain-end scission. However, silica-alumina seems to have little anchoring effect for breaking the chain-end of macromolecules.
- The experimental fact that silicalite, a porous solid having no acid site, has similar catalytic effect as silica-alumina, a porous solid having acid site, indicates that the catalytic degradation of polymer occurs without involving active centers on the catalyst surface. The catalytic effect exhibited by porous solids is based on the configuration derived from pore size, pore distribution and specific surface area.

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