Effect of Branching of Polyolefin Backbone Chain on Catalytic Gasification Reaction

YUMIKO ISHIHARA,* HIDESABURO NAMBU, TADASHI IKEMURA, and TOMOYUKI TAKESUE, *Department of Industrial Chemistry,* College of Science and Technology, Nihon University, 1-8, Kandasurugadai, Chiyoda-ku, Tokyo 101, Japan

Synopsis

A basic study on the catalytic gasification of polyolefins such as PE and PP, which account for a major part of general waste plastics, was conducted in order to develop a technique for effective recycling of these wastes. In the case of PE, the gasification of PE is considered to consist of the following scheme: polymer → catalytically degraded polymer → catalytically degraded oligomer → liquid component → gas component. The gasification of PE does not occur directly from the polymer chains, but gaseous C_4 substances are selectively found from the liquid components with the highest branching frequency. The overall yield of C_4 components including isobutane was 74.5 and 60.5% molar for PE and PP. These liquid components (gasification precursors) have the branching frequencies. For example, a molecule with $\bar{M}_w$ of 400 contains about eight branches for every 30 methylenes. From the catalytic gasification of PE, PP, and PIB, the gas conversion rate is also found to increase with increasing frequency of the backbone branching. It is concluded that the branching frequency is the key factor governing the gas conversion rate of polyolefins.

INTRODUCTION

If an economical process can be developed to produce materials with high added value from waste plastics, it will help utilize waste plastics, which have been called "obstacles," and conserve energy. This will not only prevent environmental pollution by these waste plastics and reducing disposal refuse costs, but will also provide techniques that will be very useful from the standpoint of energy resource conservation.

Various studies have been carried out in an effort to utilize waste plastics effectively.[1-6] It has recently been revealed that gasification may be the most effective method for utilizing waste plastics. In most of these studies, however, gasification is carried out by thermal-decomposition type radical reactions which give products with complicated structures—mainly olefins. Such reaction products are likely to suffer oxidation or polycondensation during storage, reducing the possible value that might be added to them as commercial products. Furthermore, a high temperature (above 700°C) is required in order to yield reaction products with simple composition.

This, however, reduces the durability of the equipment and increases the energy costs for the decomposition process. Thus, it is difficult to develop a practical system using this type of reaction.

Some researchers have used catalytic gasification to avoid the problems of the thermal gasification reaction.[7,8] These studies, however, were designed

only to determine the composition of the gas and not to identify efficient gasification processes.

In the present study, placing emphasis on the latter issue, we analyzed the conversion of intermediates into gaseous substances, which is the most important reaction in the gasification process, in order to identify key factors that can efficiently accelerate gasification.

Results show that for some polymers, including PE and PP, accelerated isomerization of the intermediates backbones can greatly enhance conversion of intermediates into gaseous substances. The use of such isomerization reactions is essential in developing an efficient gasification process.

EXPERIMENTAL

Sample and Catalyzer

The sample used were polyethylene (hereafter referred to as PE, $\overline{M}_n = 3.1 \times 10^4$, Hizex 2100P manufactured by Mitsui Petrochemical Industries Co., Ltd.), polypropylene (PP, $\overline{M}_n = 1.5 \times 10^4$, Sanyokasei Co., Ltd.) and poly-isobutylene (PIB, $\overline{M}_n = 2.3 \times 10^4$, Nippon Oil Co., Ltd.).

A silica–alumina catalyzer with a 13 wt % alumina content (N631L, Nikki Chemical Co., Ltd.) was used after being burnt for 3 h in dry air at 540°C. The catalyzer was in the form of grains with a mesh of > 100.

Reaction Apparatus and Measuring Method

As shown in Figure 1, the apparatus used consisted of a Pyrex reaction tube (inside diameter 23 mm and length 240 mm) equipped with bypass lines to which traps for gas and volatile liquid products are connected. A mixture containing 2 g of the sample and 2 g of the catalyzer was stirred and put into the reaction tube, which was then heated at 160–320°C in nitrogen atmosphere (N_2, 120 mL/min). The reaction products were collected in the traps provided outside the system to separate the gas product, the liquid products, and the components of oligomers or molecules larger than oligomers which remain in the reaction tube. The residues in the reaction tube were separated from the catalizer by extraction with heated xylene. The xylene solution was
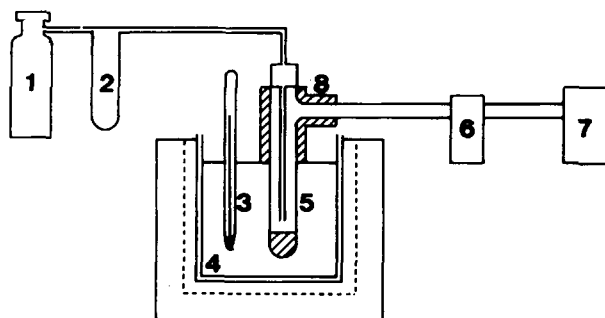

Fig. 1.   Apparatus for the catalytic degradation: (1) N_2 cylinder; (2) manometer; (3) thermometer; (4) metal bath; (5) reactor; (6) trap for liquid fraction; (7) trap for gaseous product; (8) asbestos.

poured into an excess volume of methanol to isolate the reprecipitable compo-
nents (hereafter referred to as degraded polymer chains) from the nonreprecip-
itable components (degraded oligomers), which were then collected separately.

Analysis Method

To analyze the reaction products recovered, the limiting viscosity method
($[\eta] = 5.10 \times 10^{-4} M_n^{0.725}$)[9] and the freezing point depression method were
used to determine the molecular weight of the reprecipitable and nonreprecip-
itable materials, respectively. Qualitative and quantitative analysis of the
branches were performed by ^{1}H-NMR (JEOL, Ltd., JNM-FX100) and [13]C-
NMR (JEOL, Ltd., JNM-GX270).

To prevent oxidation during measurement at high temperatures, each
sample ^{1}H- or ^{13}C-NMR was dissolved in a solvent and subjected to repeated
freezing and deairing to ensure adequate nitrogen replacement before sealing
the NMR tube.

RESULTS AND DISCUSSION

Mass Balance in the Catalytic Decomposition of PE and PP

PE and PP are typical polyolefins and represent the two main components
of general waste plastics. Thus, it is necessary to analyze, in detail, the
pathway of their conversion into gas.

Figure 2 shows the mass balance for the solid, grease, liquid, and gas
fractions that were produced from PE decomposed at 280°C for 10–120 min in
the presence of a silica–alumina catalyzer (a low-price, recyclable catalyzer
widely used in industry). The polymer chains length rapidly decreases (up to
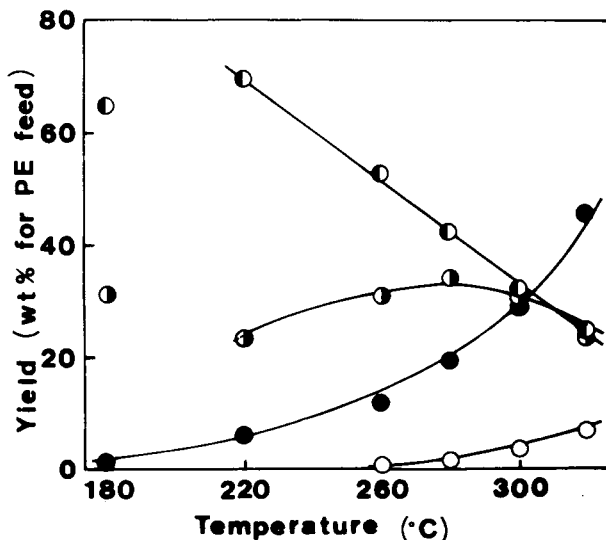40 min) due to catalytic degradation while a sharp increase occurs in the levels

Fig. 2.   Mass balance of the catalytic decomposition products from PE: time 60 min; C/S = 1;
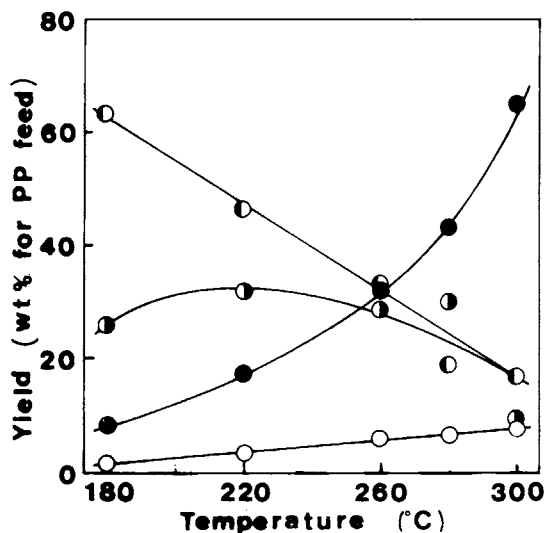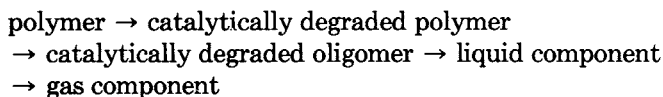(○) gas; (●) liquid; (◑) degraded oligomer; (◐) degraded polymer.

Fig. 3. Mass balance of the catalytic decomposition products from PP: time 60 min; C/S = 1; (○) gas; (●) liquid; (◑) degraded oligomer; (◐) degraded polymer.

of oligomers and liquid components. The yield of catalytically degraded polymer chains becomes moderate after 50 min and the yield of the liquid components greatly increases after 60 min. This increase corresponds to the decrease in the number of oligomers, indicating that the liquid components are formed from further decomposed oligomer components.

Gas is formed in these liquid components in the final stage of the catalytic decomposition of PE.[10] Thus, the gasification of PE is considered to consist of the following molecular weight reduction stages:

polymer → catalytically degraded polymer
→ catalytically degraded oligomer → liquid component
→ gas component

In the gasification process of PE, gas is not produced directly from the catalytically degraded polymer chains but is formed from the liquid components formed by the further decomposition of degraded polymer chains and oligomers. This indicates that the key stage in the gasification process is what concentrates the liquid components. It seems reasonable here to divide the gasification reaction into two processes, i.e., molecular weight reduction of PE and gasification of the liquid components, and consider them separately.

It may be of interest to compare the catalytic gasification of PE with that of PP, another typical polyolefin, under the same reaction conditions. Figure 3 illustrates the experimental results for PP, which correspond to those in Figure 2 for PE. Figures 2 and 3 indicate that PP and PE show similar behavior during gasification.

The above observations suggest that, during decomposition of PP, gas is formed from liquid components by a similar process to that shown above for

PE: Polymer chains first decrease due to catalytic degradation while oligomers increase, followed by decomposition of the oligomers into liquid components.

The yield of the gasification precursors, or the liquid components, of PE at 280°C (60 min) is about 20 wt % (Fig. 2) while that of PP is about 43 wt % (Fig. 3) under identical conditions. It is obvious from these results that PP is gasified at a higher rate than PE, and the gasification rate of PP is twice that of PE which corresponds to the difference in yields for the liquid components. As discussed later, the difference in gasification rates between PE and PP can be attributed to the difference in the chemical structures of the gasification precursors of these polymers.

In both cases, the liquid components consist of saturated hydrocarbons resulting from hydrogenation during the catalytic reaction. In relation to this, no signals from the olefins were detected in ^{1}H-NMR measurement of the catalytically degraded polymer chains and oligomers produced by the molecular weight reduction process, indicating that they were also saturated. While all polymer chains degraded by the thermal-decomposition type radical reaction have an olefinic group at chain end of their backbones,[11, 12] all of the oligomers formed from the catalytic reaction are saturated hydrocarbons. Investigations have shown that the latter oligomers are more resistant to oxidation and polycondensation than the products of thermal-decomposition type radical reactions. Also catalytic decomposition reactions at very low temperature yield products with a long storage life. Thus, it can be concluded that the use of the catalytic reaction is more advantageous for the decomposition of polymers than the radical reaction.

Composition of Gaseous Products Formed from PE and PP

Table I lists the results of the analysis of the gases resulting from catalytic decomposition of PE and PP. For both PE and PP, the resultant gas consisted mainly of isobutane. The overall yield of C_4 components including isobutane for PE and PP was 74.5 and 60.5% molar, respectively, revealing that C_4 components represent a major portion of the gaseous product. Furthermore, the yield of C_4 olefins is the second or third highest of the gasification products. Observation of the formation of isobutane, the major product, suggests that it results from the hydrogenation of these olefins.

The conversion rate was 70.0% weight and the yield of the major products were 23.0 and 25.0% molar for C_3 and C_4 compounds, respectively when catalytic gasification of PE was conducted using the same catalyzer in the flow reactor (fixed bed) system at a reaction temperature of 430°C.[13] Uemichi et al. reported a gas conversion rate of 71.2% weight with an isobutane yield of 18.9% weight.[14] The overall yield of gaseous C_4 products including isobutene was 27% molar when an ion-exchange zeolite catalyzer was used.[8]

In all cases, with catalytic gasification a high gas conversion rate was achieved at reaction temperature below 500°C while, with thermal-decomposition gasification, the gas conversion rate was about 7.0% weight and C_1–C_3 substances, ethylene in particular, represent the major portion of the products.[13]

During catalytic gasification, the olefin component of isobutene is immediately hydrogenated to isobutane. This reaction depends on the physical

TABLE I
Composition of Gaseous Products

Sample yield (mol % for gaseous products)	PE[a]	PP[b]	PE[c]
		(catalytic)	(thermal)
Methane	0.00	0.11	8.90
Ethane	0.46	0.11	0.00
Ethylene	0.00	0.00	40.80
Propane	7.88	0.54	9.00
Propylene	9.50	6.84	12.60
iso-Butane	54.85	40.39	1.30
n-Butane	5.97	0.53	6.40
1-Butene	0.00	0.12	11.40
iso-Butene	8.94	15.46	—
trance-2-Butene	4.76	4.15	1.00
iso-Pentane	5.88	30.88	—
n-Pentane	1.85	0.65	2.10
Gaseous yield (wt %)	2.30	8.10	7.00

[a,b] temp 280°C; time 60 min; C/S = 1.
[c] flow; temp 430°C.

conditions of the system and the reaction time. The resultant olefin gas will be completely hydrogenated into paraffin gas after sufficient residence time. As a result, carbon is deposited on the catalyzer, reducing catalytic activity.

However, this may not be a serious problem as carbon function as an energy source (fuel) when the catalyzer is burned during recycling.

It can be concluded from the above investigation that, in the catalytic reaction of polymers, all gaseous components are formed through decomposition and molecular weight reduction processes and the final gasification is closely associated with the structures of low-molecular weight ethylene oligomers, which appear to act as precursors for gasification.

Another study is reported below which determined effects of polymer molecular weight reduction on the formation of final gaseous components.

Molecular Weight Reduction and Gas Conversion Rate of PE and PP

Figure 4 illustrates the changes in gas conversion rate during molecular weight reduction of PE and PP. The gas conversion rate tends to increase linearly with decreasing polymer molecular weight. Gasification would not occur if the molecular weight is not decreased. This supports the above-mentioned observation (Fig. 2), showing that gas is produced from low-molecular weight oligomers or liquid components.

Similar relations are seen with PE and PP. It is obvious from Figure 4, where observations for the two polymers are listed together, that the gas conversion rate of PP is much higher than that of PE. As discussed in mass balance, PP is gasified much more rapidly than PE, but, in both polymers, final gasification occurs from oligomers or liquid components. This suggests that the chemical structure of the oligomer components, especially the
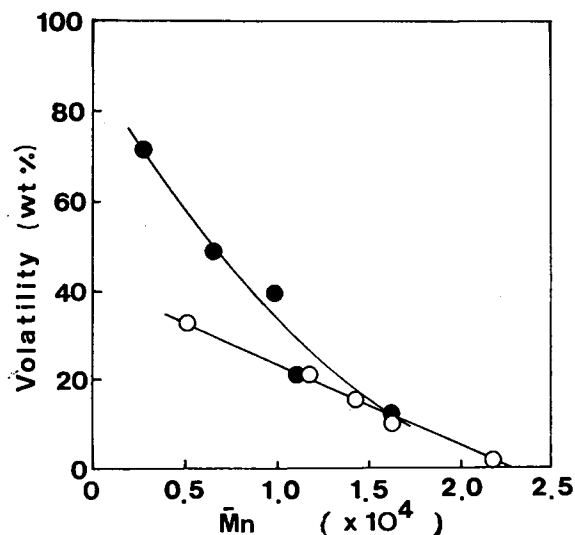
Fig. 4.   Effect of number of average molecular weight ($\overline{M}_n$) and volatilities: (○) PE; (●) PP.

branching frequency, is the key factor in determining the gasification rate. Some studies revealed that catalytically degraded PE backbone chains (oligomers) had a highly increased branching frequency compared to the chemical structure of the original PE chains.[15] To make further assumptions, it is necessary to clarify the relation between branching frequency and molecular weight reduction during the catalytic decomposition of PE.

Relation between Branching Frequency and Molecular Weight Reduction of PE

The oligomers resulting from the catalytic decomposition of PE contain a large number of short branches, most of which are C_6 or less in length. The branching frequencies of oligomers formed from catalytically degraded PE can be elucidated using the ^{13}C-NMR spectrum shown in Figure 5. The major types include short linear chains ranging from methyl to penthyl and branched alkyl chains such as 2-ethylhexyl, 2-ethylpentyl, and 2-ethylbutyl.[15] The results are at variance with the fact that thermal decomposition of PE leads solely to the formation of long branches.[11]

Figure 6 illustrates the relation between molecular weight reduction and the branching frequency of catalytically degraded polymer chains and oligomers. The concentration of the methyl group on the vertical axis represents the overall concentration of branches including short ones in the catalytically degraded molecules examined. The methyl groups at each end of the backbone are excluded. It can be seen from Figure 6 that the number of side chains increases linearly with decreasing PE molecular weight, indicating that catalytically degraded products with smaller molecular weights have higher branching frequencies. The maximum frequency is 74 per 1000 carbon atoms in these catalytically degraded polymers. Probably, the branching concentration of liquid components that form gaseous products is higher than that for oligomers. For example, a molecule with a $\overline{M}_w$ of 400 contains about eight
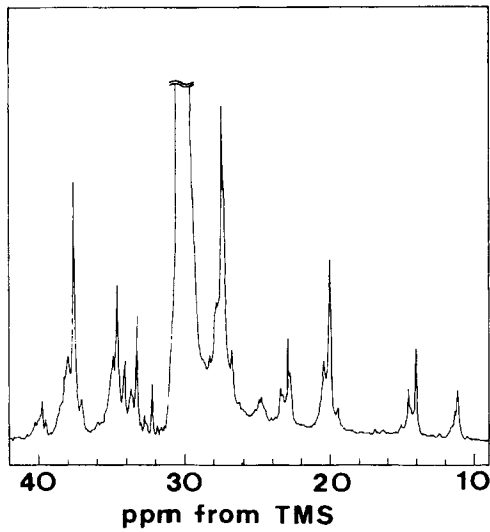
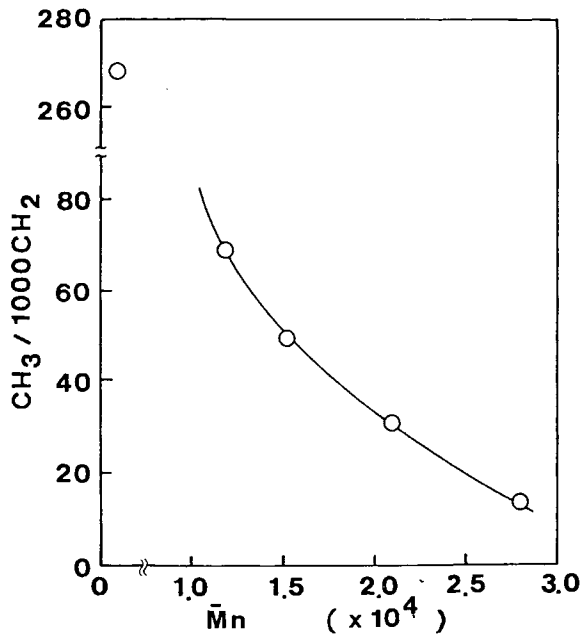Fig. 5. ^{13}C-NMR spectrum of the catalytically degraded PE oligomer.

Fig. 6.   Relations of the degree of molecular weight reduction and the branching concentration in the catalytically degraded products from PE.

branches for every 30 methylenes, as shown in Figure 6. This indicates that, in the case of PE, gaseous products are formed from these oligomers and liquid components with high branching frequencies.

In conclusion, the gasification of PE does not occur directly from the polymer chains, but gaseous C_4 substances are selectively formed from the most severely degraded components, i.e., the components with the highest branching frequency.
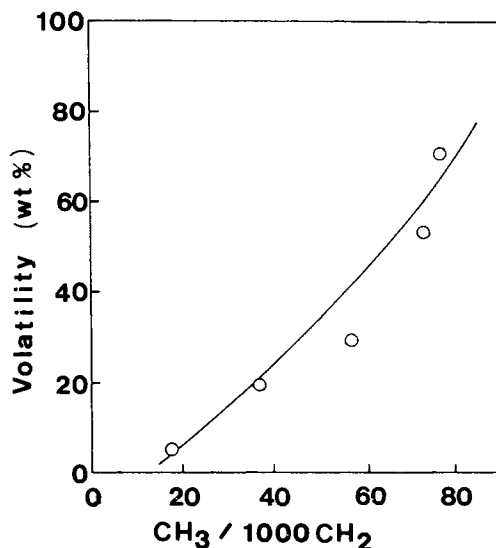
Fig. 7.   Relationship between $CH_3/1000CH_2$ and volatility.

As previously pointed out, Figure 4 shows that the gas conversion rate is increased to molecular weight reduction. These results indicate that the branching frequency increases with decreasing molecular weight. The effects of branching frequency on gas conversion rate are discussed below in terms of a parameter that represents both of these relations.

Relation between PE Gas Conversion Rate and Branching Frequency

Figure 7 illustrates relation between the gas conversion rate and branching frequency at various stages of the molecular weight reduction process. There is a linear relationship where the gas conversion rate increases with increasing branching frequency. This supports the results in Figure 4, which suggest that PP oligomers with higher branching frequencies than PE oligomers also have a higher gas conversion rate. Thus, gasification is directly governed by the branching frequency of the low-molecular weight oligomer components (precursors for gasification).

With PE, for instance, it appears that the gasification of polymer molecules is closely associated with the isomerization of the backbone chain during the molecular weight reduction process of the polymer molecules. The branching frequency corresponds to the key factor controlling gas conversion rate.

Comparison of the Gas Conversion Rates of PE, PP and PIB

As stated above, it became clear that the frequency of branching in the backbone chain of low-molecular-weight ethylene oligomers (gasification precursors) is directly related to the gas conversion rate of PE. The gas conversion rate of PE increased with the increasing concentration of branches in the main chains.

This suggests that the gas conversion rate of PIB, which has a much higher branching frequency than PE or PP, should also be a higher gas conversion rate.
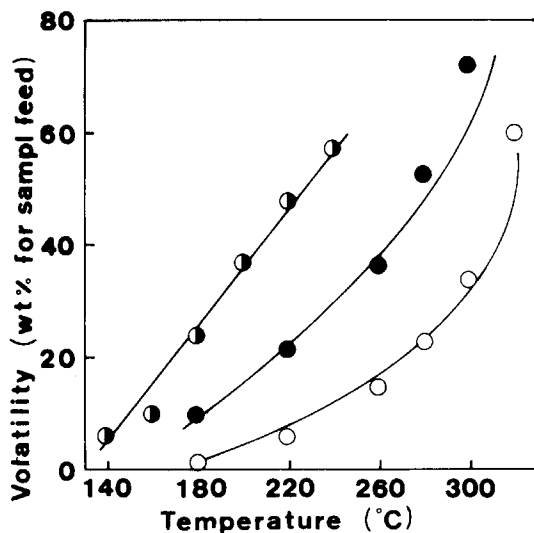
Fig. 8. Effect of reaction temperature on volatility of each polymer by the catalytic degradation: time 60 min; (○) PE; (●) PP; (◐) PIB.

Thus, observations of the catalytic gasification of PE, PP, and PIB carried out under identical conditions were evoluted in order to confirm the phenomena seen in the gasification of PE and to determine whether these phenomena are common to all polyolefins.

Figure 8 compares the gas conversion rates of PE, PP, and PIB under identical reaction conditions. The gas conversion rate is also found to increase with increasing frequency of branching from the backbone chains, suggesting that the above phenomena are commonly seen in all polyolefins during gasification. It is concluded from the results that the branching frequency is the key factor governing the gas conversion rate of polyolefins.
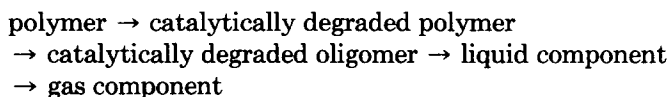
It is obvious from all these results that catalytic gasification of polyolefins can be performed very efficiently by carrying out reactions that accelerate reduction in polymer molecular weight (β-scission of backbone) and the isomerization (increase in branching frequency) of low-molecular-weight gasification precursors. For PE, which represents the greatest part of general waste plastics, technology—particularly to control the isomerization of gasification precursors—should be established in order develop an efficient gasification process. Such technology will provide the basis for high-performance practical gasification process.

At present, however, there is no evidence that reasonably explains the increasing reaction mechanism of the branching frequency in backbones.

CONCLUSION

A basic study on catalytic gasification of polyolefins such as PE and PP was conducted in order to develop a technique for effective recycling of these

wastes. The gasification of PE is considered to consist of the following scheme:

polymer → catalytically degraded polymer
→ catalytically degraded oligomer → liquid component
→ gas component

The gasification of PE does not occur directly from the polymer chains, but gaseous C_4 substances are selectively found from the liquid components with the highest branching frequency. The overall yield of C_4 components including isobutane was 74.5 and 60.5% molar for PE and PP. These liquid components (gasification precursors) have the branching frequencies. For example, a molecule with $\bar{M}_w$ of 400 contains about eight branches for every 30 methylenes. From the catalytic gasification of PE, PP, and PIB, the gas conversion rate is also found to increase with increasing frequency of the backbone branching. It is concluded that the branching frequency is the key factor governing the gas conversion rate of polyolefins.

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