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The Catalytic Degradation Reaction of Polypropylene with Silica-Alumina

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A detailed analysis was carried out on the catalytic degradation of polypropylene with silica-alumina, using a glass tube reactor (25$\phi\times$150 mm) at 180 to 300 °C and a N_2 flow rate of 120 ml min^{-1} over a period of 5 to 120 minutes. The ratio of C/S was from 0.1 to 6.0. The molecular weight of PP decreased slightly at about 160 °C by cationic degradation, but the decrease started at about 200 °C by radical degradation (without catalyst). The main chain of PP was remarkable weakened by the catalytic degradation with silica-alumina. Analysis of degradation products by ^{13}C NMR, FD-MS and variation in chain scission number clearly indicated the catalytic degradation of PP to occur in two stages. The first stage at low temperature is initiated by the addition of a proton released from the catalyst to weak links in the main chain. The second stage at high temperature occurs by attack a low-molecular-weight carbonium ion of the saturated degraded oligomer. These ions are closely involved in the production of irregular structural oligomers and their redegradation.

The degradation reaction of polymer is important for the synthesis of materials by polymeric reactions starting from a high polymer and studying the molecular design of functional, heat-resistant polymers and the stabilization of a general-purpose polymers.

Many studies in this area, especially on pyrolytic radical reactions, have been reported. However, only a few studies have been carried out cationic and anionic degradation reactions of polymers in the presence of a catalyst. A study using an oligomer fraction produced by degradation of polypropylene (briefly "PP") as a lubricating oil has been conducted.[1] The catalytic degradation of PP,[2,3] and reactions of nylon, polyisobutylene (briefly "PIB"), and polystyrene (briefly "PS")[4–6] have been recently studied. Gasification reactions are studied to determine the yields and composition of volatile matter while PP, PIB, nylon, and PS reactions are investigated to clarify main chain skeleton reactions as polymeric reactions.

The authors found unusual polymeric reactions of the latter type to take place. For instance, a unique polyindan[6] can be produced at high yield in the catalytic reaction of PS with aluminum chloride and the multibranched ethylene oligomer is produced in the catalytic reaction of polyethylene (briefly "PE") with silica-alumina.[7]

The above cationic degradations are remarkably different from conventional pyrolytic radical reactions. It is not possible to synthesis the polyindan and the multibranched oligomer mentioned above either by a radical reaction nor by ordinary monomer polymerization. The cationic and anionic degradation reactions of polymers may thus possibly hold promise for the synthesis of new materials. And considerable research should be directed to the basic cationic and anionic degradation reactions of polymers as pyrolytic radical reaction. The authors consequently conducted fundamental research on the cationic degradation reactions of polymers and the catalytic degradation of general-purpose polymers.

Experimental

The sample used for this study was prepared by pulverizing a commercially available isotactic PP (Biscol 330P manufactured by Sanyo Kasei; isotacticity; 90%; and $\overline{M}_n$ (by viscosity method)=16000), to 60 mesh or under, extracting in with heptane in a Soxlet extractor, for 6 hours and drying at 40 °C for 72 hours under vacuum.

The catalyst was prepared by pulverizing a commercially available silica-alumina catalyst (N-631L manufactured by Nikki Chemical; alumina content: 13 wt%) to a 100 mesh or less sintering it at 540 °C for 3 hours and then drying it in a flow of dried air. The activity of the catalyst was measured by butylamine titration.[8,9]

Experimental Operation and Procedure. A Pyrex glass tube reactor (outer diameter: 25 mm and length: 150 mm) connected to traps for recovering gaseous and liquid products as shown in Fig. 1 was used.

The experimental procedure was as follows: 2 g each of the sample and the catalyst were mixed by stirring at different temperatures and timings and 0.6 to 2 g of the sample and 0.2 to 4 g of the catalyst were mixed by stirring with different concentrations of the catalyst. The mixture was put in a

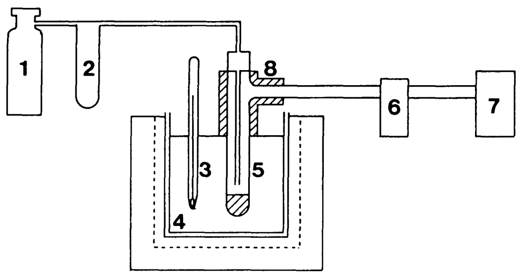


Fig. 1. Apparatus for the catalytic degradation: (1) N_2 cylinder, (2) manometer, (3) thermometer, (4) metal bath, (5) reactor, (6) trap for liquid fraction, (7) trap for gaseous product, (8) asbestos.

reactor; the reaction a value was maintained from 180 to 300 °C in an oil or metal bath; nitrogen was passed through the reactor at a flow rate of 120 ml min^{-1} for 5 to 120 minutes and the ratio of catalyst to sample (C/S) was varied from 0.1 to 6.

Analytical Method. A gas-liquid chromatograph (GC-8A of Shimadzu) was used.

The gaseous product was qualitatively analyzed by a comparison with the retention time of the standard gas and quantitatively analyzed by the absolute calibration curve method.[10]

A FT-IR spectrometer (Fourier transform infrared spectrophotometer of Nihon Denshi) was used. The range of wavelength for measurement was from 4000 to 400 cm^{-1}.

Parameter of the starting PP sample were determined by the Fourier transform infrared spectroscopic method.

Field desorption- (FD-) and field ionization-mass spectrometers (FI-MS) (RMU-7M of Hitachi) were used. The molecular weight distribution of the oligomer was determined by FD-MS. The molecular weight of low- and high-boiling fractions in the liquid product were determined by FI- and FD-MS, respectively.

The measuring conditions are shown in Table 1.

^{1}H and ^{13}C NMR (JUM FX-100 of Nihon Denshi) were used. The resonance frequencies of ^{1}H and ^{13}C NMR were 99.6 and 25.05 MHz, respectively.

The PP sample dissolved in 1,2,4-trichlorobenzene, benzene-*d* as the internally locking agent of the magnetic field and a small amount of hexamethyldisiloxane (HMDS) as the internal standard material were introduced into a 5 mm-NMR tube which was then deaereated by freezing, followed by a complete substitution with nitrogen and sealing. The oligomer dissolved in chloroform-*d* and a small amount of tetramethylsilane (TMS) as the internal standard material were put in a 5 mm-NMR tube.

Table 1. Operational Conditions for FD- and FI-MS

	FD-MS	FI-MS
Sample	Oligomer, Liquid	Liquid
Total scan No.	79	64
Data format	3	3
Sampling period	25 μs	25 μs
Rescan duration	1.2 s	1.2 s
Threshold	100	100
Acquiring range	0—10000 min	0—10000 min
Cathode voltage	−3 kV	−3 kV
Emitter current	0—30 mA (3 mA min^{-1})	0 mA
Disk	87%	86%

Table 2. Chemical Shift Parameters of Lindeman–Adams

S	*Bs*	*M*	*Asm*	*γs*	*Δs*
1	6.80	2	9.56	−2.99	0.49
		3	17.83		
		4	25.48		
2	15.34	2	9.75	−2.69	0.25
		3	16.70		
		4	21.43		
3	23.46	2	6.60	−2.07	0
		3	11.14		
		4	14.70		
4	27.77	2	2.26	+0.68	0
		3	3.96		
		4	7.35		

The measuring conditions of ^{1}H and ^{13}C NMR are the same as in the previous paper.[10]

Method for the Assignment of ^{13}C NMR Signal. The addition rules of Grant–Paul,[11] Randall,[12] and Lindeman–Adams[13] are generally used for assigning ^{13}C NMR signals. In particular, the addition rule Grant–Paul is used for the ^{13}C NMR signal of PP. Nishioka et al.[14] calculated the average values of standard deviations in the structures with ethyl to hexyl or higher side chains.

In contrast, the addition rule of Lindeman–Adams has the following advantages: the standard deviation from the Lindeman–Adams method is intermediate between the values obtained from these three methods and the calculated value of a quaternary carbon atom can be obtained. Accordingly, in the present study, the addition rule of Lindeman–Adams was used mainly. For comparison, both these addition rules were used.

The addition rule is expressed as follows:

$$\delta c(K) = B_s + \sum^{4} D_{\mathrm{M}} A_{\mathrm{SM}} + \gamma_{\mathrm{S}} N_3 + \Delta S N_4$$

where B, A, γ, and Δ=the respective additive parameters for the α-, β-, γ-, and δ-positions of C-k, s=number of carbon atoms directly bonding to C-k, D_{M}=total M carbon atoms bonding to C-k, and Nk3 (Nk4)=number of carbon atoms three (four) bonds away from C-k, that is, the γ-carbon atom (δ-carbon atom).

The parameters used in the addition rules are shown in Table 2.

Results and Discussion

Variation in the Number of Chain Scission of Polypropylene. Variation in the molecular weight of the main of PP was measured to examine its catalytic degradation reaction when using a silica–alumina catalyst.

The results are shown in Fig. 2. Decreasing molecular weight in the thermal degradation with non catalyst was observed at 200 °C. But, in the degradation of PP with the catalyst, the molecular weight sharply decreased from 16000 to 10000 at lower temperature in the experiment on variation in reaction temperature (open symbol). It slowly decreased from 10000 to 7500 at higher temperature. These trends are more pronounced for variation in time (closed symbol). The decrease in molecular weight at the early stage (lower temperature) of the catalytic degradation reaction thus appears to differ from that at the late stage (higher temperature).

The results are expressed as change in the number of main-chain scissions by rearranging the above results is shown in Table 3. The number of chain scissions was 0.45 from 180 to 220 °C, and 0.3 to 0.38 from 220 to 280 °C. Thus, the molecular weight decreased more sharply at the early stage. The number of chain scissions was 0.44 in the period from zero to 40

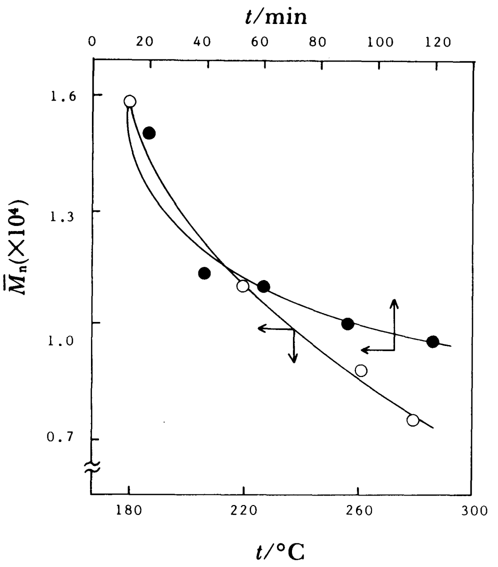


Fig. 2. Changes in the molecular weight ($\overline{M}_n$) of the degraded polymer. ○: temp., ●: time.

Table 3. The Number of Main-Chain Scission of Catalytic Degraded Polymer

t/°C	180	220	260	280	
Number of main-chain-scission	0	0.45	0.75	1.13	
t/min	20	40	60	90	120
Number of main-chain-scission	0.06	0.44	0.48	0.56	0.60

Reaction conditions; time=60 min, C/S=1
Reaction conditions; temp=220 °C, C/S=1.

minutes, and 0.14, only a third of the former in the period from 40 to 120 minutes. Chain scission thus takes place, more rapidly at the early stage than late stage. The molecular weight decreasing reaction at the early stage differed from that at the late stage.

The molecular weight decreasing reaction of PS was similar to the above reaction.

The molecular weight of PS decreased rapidly at the early stage and slowly at the late stage.[15] This rapid decrease is attributed to a low activation energy reaction caused by weak links in the main chain.[16] Since these weak links are more distinct in the main chain of PP than in that of PS, the initial reaction is possibly initiated by low activation energy in the same manner as in PS. It is thus likely, that the rapid decrease in molecular weight is caused by weak links in the same way as in PS. The weak links in the sample of this study are illustrated in Fig. 9.

These two molecular weight decreasing reactions were analyzed in terms of change in degraded product composition.

Yields of Degradation Products vs. Reaction Conditions. Figure 3 shows variation in the yields of the four main fractions, gas, liquid, grease (oligomer), and wax (low polymer). Another important product was carbon deposited on the catalyst.

The yield of wax (low polymer) linearly decreased with increase in reaction temperature, while that of the liquid sharply increases.

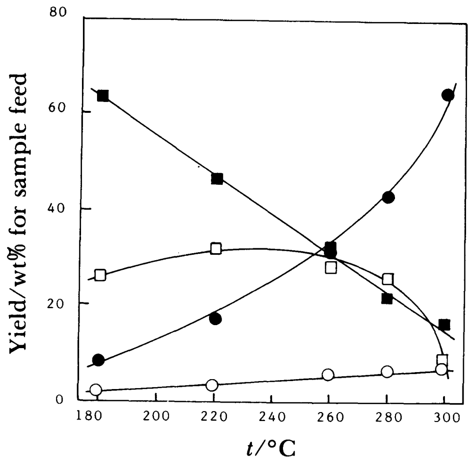


Fig. 3. Catalytic degradation product yield from PP. ○: gas, ●: liquid, □: oligomer, ■: polymer. Reaction conditions: 60 min, C/S=1.

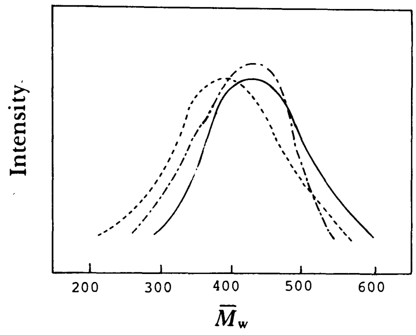


Fig. 4. $\overline{M}_w$ distribution of the propylene oligomer (liquid fraction) formed by catalytic degradation of PP. —: 220 °C, ------: 260 °C, ------: 280 °C. Reaction conditions: 60 min, C/S=1.

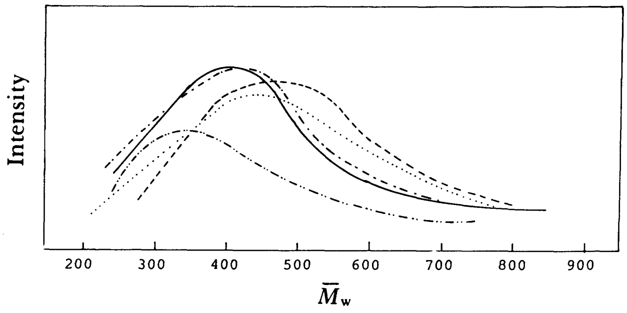


Fig. 5. $\overline{M}_w$ distribution of the propylene oligomer (grease fraction) formed by catalytic degradation of PP. ------: 180 °C, —: 220 °C, ------: 260 °C, ······: 280 °C, ------: 300 °C. Reaction conditions: 60 min, C/S=1.

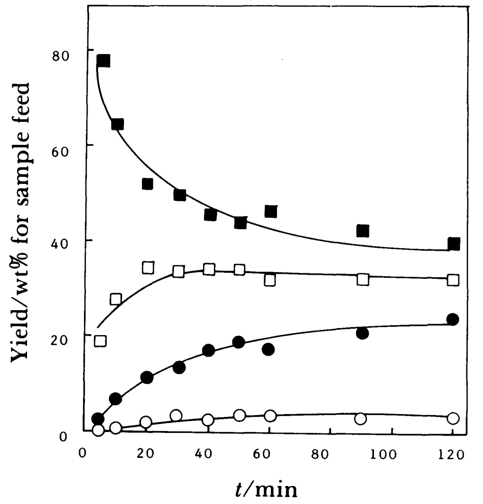


Fig. 6. Catalytic degradation product yield from PP. ○: gas, ●: liquid, □: oligomer, ■: polymer. Reaction conditions: 220 °C, C/S=1.

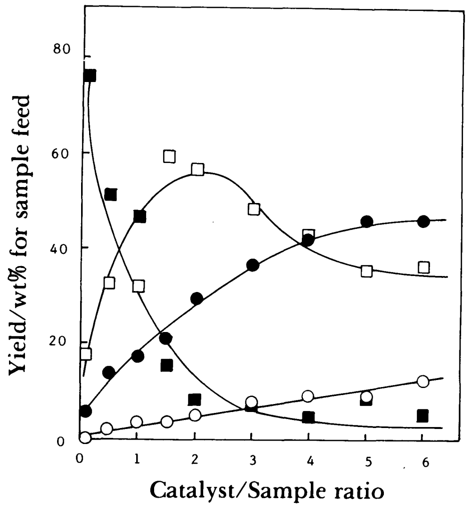


Fig. 7. Catalytic degradation product yield from PP. ○: gas, ●: liquid, □: oligomer, ■: polymer. Reaction conditions: 220 °C, 60 min.

The results of FD-MS in Figs. 4 and 5 indicate the molecular weight distributions of the liquid and oligomer (mixture of grease and wax) fractions produced at 280 °C from 200 to 600, mainly at 360 and from 200 to 900, mainly at 450. Figure 4 shows the fraction (shown as····) produced at higher temperature to have a lower molecular weight, while that (shown as——) produced at lower temperatures, a higher molecular weight. Since the exhaust fume temperature in the higher temperature reaction system was high, the high boiling heavier fraction (oligomer) formed could flow out of the system. Phenomena such as reflux and redegradation way occur in the lower temperature reaction system, since the heavier fraction can hardly flow out. The molecular weight of the higher temperature reaction product should thus be higher than that of the lower temperature reaction product. This however, is the reverse of the above theory and at variance with the concept based on the boiling point of the reaction product in the reaction system.

This variance, however, may be resolved by considering that the oligomer redegradation to proceed at high temperature and the recombination–addition reactions of low-boiling products formed to occur during reflux in the long residence time at low temperature. Consequently, the molecular weights of the products become higher than those of products formed at high temperature. The molecules of a degradation product from an oligomer are smaller than those of the oligomer itself, and thus they move more easily toward the catalyst, should be more readily degraded and recombined. Evidence for this view is shown in Figs. 7 and 8.

The above results show PP to hardly be depolymerized in the catalytic degradation reaction, but to be degraded through random scission. The yield of the component (propylene) produced by the depolymerization of PP was only 0.35 wt% the total yield.

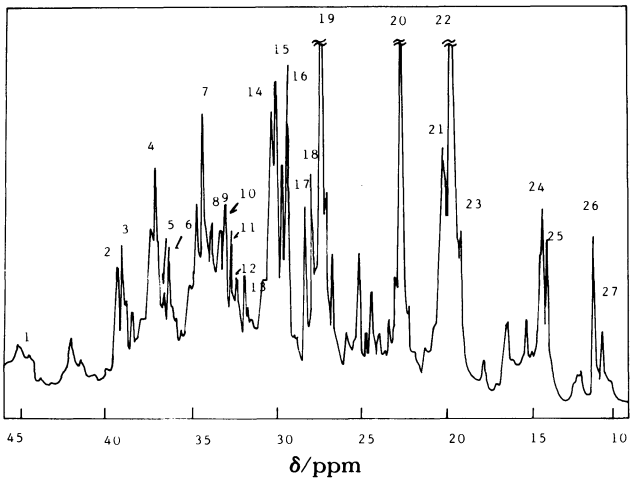


Fig. 8. ^{13}C NMR spectrum of the propylene oligomer (grease fraction). Reaction conditions: 220 °C, 60 min, C/S=1.

The decrease in molecular weight of the main chain dominates at the early stage of the reaction mentioned above, while volatile matter is vigorously produced at the late stage. The catalytic degradation of PP was confirmed to occur in two stages remarkably different from each other. This reaction is similar to that of PS degradation. However, most of the reaction products in the latter half of the reaction of PS are olefinic monomers derived from depolymerization, while those of PP comprise a low-boiling liquid mixture of saturated hydrocarbons containing recombination and addition products as was shown by NMR analysis (in the later section).

The relationships among the four main fractions and reaction time are shown in Fig. 6. They were all essentially the same the composition of each reaction product attained equilibrium during the catalytic degradation reaction. Each product thus appears to be formed in a simple reaction process. This, however, should be considered in relation to the catalyst concentration.

Variation in Degradation Products with Catalyst Concentration. The effect of the concentration of the catalyst was examined to elucidate the relationship between its activity and degradation. The results are shown in Fig. 7. The oligomer was degraded more than the liquid at a high concentration of catalyst (C/S=3) and the yield of polymer remarkably decreased as C/S exceeded 2 and the decrease was approximately 5.1 wt% at C/S of 4. The degradation reaction thus depends mainly the reaction temperature and catalytic concentration.

Since the oligomer with high-molecular mobility comes into contact more easily with the catalyst than the polymer with low molecular mobility and the oligomer is more rapidly degraded than the polymer an at extremely high concentration of catalyst, the yield of the oligomer is likely to drop. The yield of the oligomer, however, was not so much reduced as that of the polymer. The yield of gas and liquid should increase since the degradation reaction is accelerated more with increase in the concentration of catalyst. The yield of the oligomer did not decrease as shown in Fig. 7. This is probably because the oligomer was produced not only by degradation of the polymer but also by recombination or addition reaction of low-molecular components such as gaseous and liquid fractions. These results are essentially the same as those shown in Fig. 4.

These recombination reactions were confirmed by the chemical structures of the degraded products and the reaction of a model compound, 1-pentadecene. Thus, most of the olefin groups of the model compound are recombined, leading to increased molecular weight.17) The reaction was quite different from the radical degradation reaction and characterized the cationic polymer degradation with the silica–alumina catalyst.

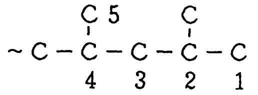
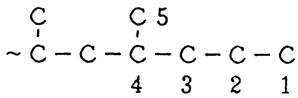
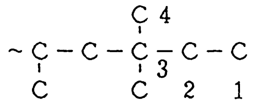
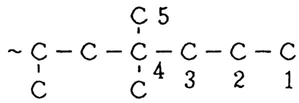
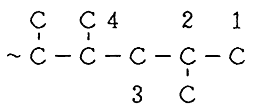
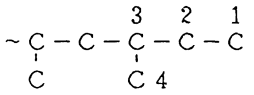
Table 4. Chemical Shift (ppm) Observed from ^{13}C NMR Spectrum of the Propylene Oligomer

Peak No.	δ	Peak No.	δ
1	44.56	15	29.77
2	39.39	16	29.41
3	39.10	17	28.36
4	37.16	18	28.00
5	36.69	19	27.42
6	36.40	20	22.66
7	34.40	21	20.31
8	33.93	22	19.73
9	33.41	23	19.26
10	33.11	24	14.44
11	32.76	25	14.15
12	32.53	26	11.39
13	32.00	27	10.92
14	30.41		

Reaction conditions; 220 °C, 60 min, C/S=1.

NMR Analysis of Degradation Products. Figure 8 illustrates the ^{13}C NMR spectrum of the oligomer

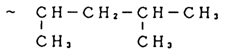
Table 5. Chemical Shifts Observed by ^{13}C NMR and Calculated

Branched species	Carbon No.	Calcd a) (ppm)	Peak No. b)
(a) 	1	22.62	6
	2	25.92	7
	3	46.55	1
	4	28.38	5
	5	20.63	8
(b) 	1	14.35	10
	2	19.96	9
	3	39.60	2
	4	30.45	3
	5	20.12	8
(c) 	1	7.88	27
	2	31.64	13
	3	33.65	9
	4	27.28	19
(d) 	1	14.84	24
	2	17.27	23
	3	44.33	1
	4	34.44	7
	5	27.77	19
(e) 	1	19.14	23
	2	32.53	12
	3	37.06	4
	4	16.64	24
(f) 	1	10.87	27
	2	29.85	15
	3	32.52	11
	4	19.63	22

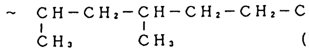
a) Chemical shifts calculated by Lindeman–Adams method. b) Peak No. in ^{13}C NMR spectrum of Fig. 8.

fraction produced at the late stage. The spectrum of the liquid fraction was nearly equal to that of the oligomer. The chemical structures of the products were assigned by calculation of the formulas.[11–13] The signals of the chain ends and chain skeletons of the main components are shown in Table 4. The relationship between the detailed structures and their signals are shown in Table 5.

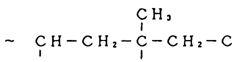
The chemial structures of the chain ends of the oligomer and liquid include the following six types:



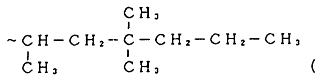
$\sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_3$ (a)



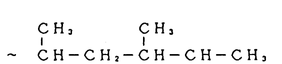
$\sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-CH_3$ (b)



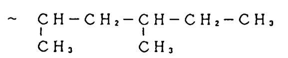
$\sim\underset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$ (c)



$\sim\underset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$ (d)

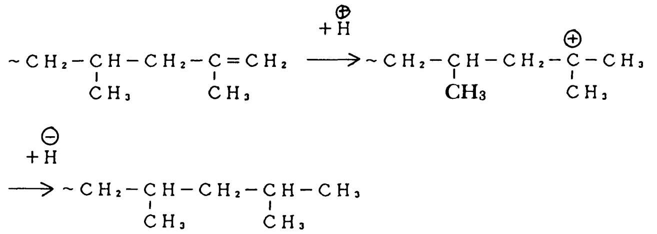


$\sim\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$ (e)

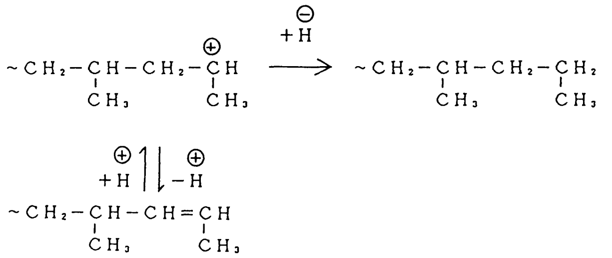


$\sim\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$ (f)

Thus, the formation of these chain ends can be resonably explained on the basis of the following reaction schemes:



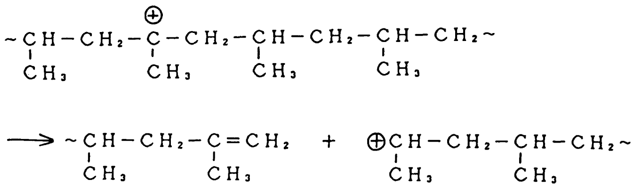
Scheme 1.



Scheme 2.

These chain end olefins with high affinity for protons are hydrogenated or saturated by the addition of a low-molecular-weight carbonium ion intermediate and the hydride ion $(\overset{\ominus}{H})$. The results of qualitative analysis indicated the chain ends of degradation products to be approximately hydrogenated. Moreover, the chain end of the degraded polymer includes only two types, (a) and (b), which are extremely simple compared to those of the oligomer and liquid. These two types of ends are also the main chain end structures of the oligomer fractions.

It is clear from the end structure of the main chain that main chain scission of the polymer is caused mainly by β-scission of the tertiary carbonium ion produced on the main chain according to the following scheme:



Scheme 3.

It was confirmed that the quaternary carbon atoms in (c) and (d) structures are produced in the oligomer and liquid fractions unlike those in the normal end structure. All these quaternary carbon atoms are found only in components produced in a high-temperature reaction. This proves that the oligomer and liquid fractions are produced by recombination of the low-molecular gaseous and liquid fractions. But they are not formed as internal carbon atoms in backbone chains and are located in the vicinity of the chain ends.

The concentration of quaternary carbon atoms seem high, considering the ratio of intensities of spectra. The chain end olefin ($>C=CH_2$ Scheme 1) is immediately attacked by a proton released from the catalyst or by a reaction intermediate possessing a tertiary carbonium ion formed from olefinic products consisting of the gaseous and liquid fractions.

The analytical results of the chemical structure of a catalytically degraded product of PP indicated the carbonium ion produced on the main chain to cause β-scission, and both the chain end olefin and the chain end high-molecular-weight carbonium ion to be saturated by hydrogenation or addition of activated low-molecular component.

The catalytic degradation reaction of PP occurs in two stages. The first stage is a low-temperature reaction initiated by the addition of a proton released from the catalyst to weak links in the main chain. The reaction should proceed using low activation energy. The formation of the carbonium ion on the main chain takes place at weak links in PP, which are the following functional groups included in the main chain.[18,19] These weak links in the starting sample in this study are shown by the FT-IR spectrum in Fig. 9. The functional groups confirmed in the sample are shown in the 1, 2, and 3 in figure. [1,2: $>C=O$, (1758, 1689 cm^{-1}), 3: olefin group, (1646 cm^{-1})]

These groups are easily attacked by protons, producing an on-chain a molecular weight decrease.

The second stage should be initiated by a higher activation energy than in the first stage reaction at high temperature. The chain ends of the oligomer

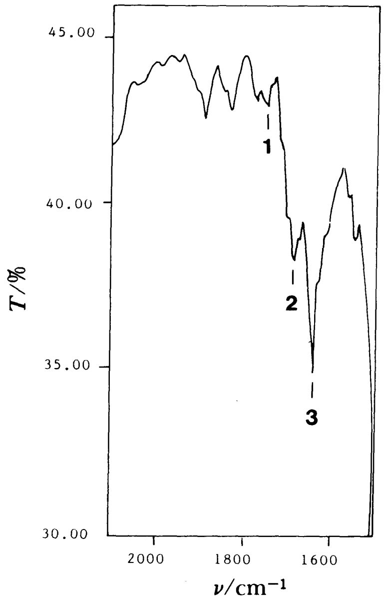


Fig. 9. FT-IR spectrum of the starting polypropylene

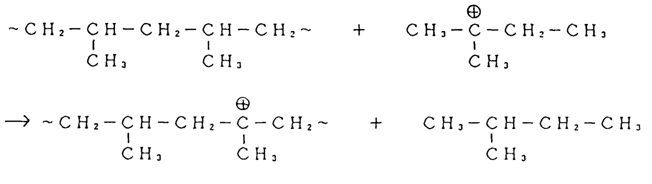
produced by the catalytic degradation reaction are saturated because the weak links (functional groups) were eliminated at the first stage of reaction. The oligomer is thus, chemically stable and contains no functional groups with affinity for a proton. The reaction which produces the on-chain carbonium ion causing the decrease in molecular weight of the saturated oligomer should require an extremely high activation energy. There is a wide difference in the activation energies required for producing the on-chain carbonium ion between the first and second stages of the reaction. Accordingly, the decreasing rate of molecular weight was determind in the two stages.

The results from variation in yields of the four fraction produced, FD-MS of liquid fraction and the determination of quaternary carbon atom by NMR indicate the lower molecular components including the liquid fraction to participate in the recombination reaction at low temperature but not the higher molecular weight components including the oligomer and polymer. The redegradation reaction of the chemically stable paraffinic oligomer is initiated by the intermolecular reaction with the intermediates of low-molecular-weight carbonium ion.

That is, in the reaction at high temperature, these ionic intermediates are formed by proton addition with olefinic gaseous and liquid products and also attack the on-chain tertiary carbon atoms of a saturated oligomer and degraded polymers. The activation energy of the reaction should be higher than that of the weak links.

These ionic intermediates are saturated by hydride ions extracted from the oligomer and polymer chains. Consequently, chain tertiary carbonium ions are again produced on the paraffinic oligomer and degraded polymers chains.

The intermolecular rearrangement of carbonium ions takes place on the surface of the catalyst. These reactions certainly require much higher activation energies than the addition reaction of protons to the weak links. The reaction of the intermolecular rearrangement of carbonium ion in the latter takes place as follows:



$$\sim CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2\sim \;+\; CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_2-CH_3$$
$$\longrightarrow \sim CH_2-\underset{CH_3}{CH}-CH_2-\overset{\oplus}{\underset{CH_3}{C}}-CH_2\sim \;+\; CH_3-\underset{CH_3}{CH}-CH_2-CH_3$$

Scheme 4.

The schematic process of the catalytic degradation of PP using a silica–alumina catalyst involves the production of the on-chain carbonium ion initiated by the addition of protons to the weak links at the early stage and production of on-chain carbonium ion by the intermolecular rearrangement reaction of the low-molecular-weight carbonium ionic intermediates with tertiary carbon atoms in paraffinic oligomers at the late stage. The carbonium ionic intermediates of the low-molecular-weight fractions produced recombine with the low-molecular-weight olefinic fractions to increase the concentration of the oligomer fraction. In particular, it is clear that the intermediate of the low-molecular-weight tertiary carbonium ion is equally involved in the production of oligomer fraction with irregular structures. These reactions are quite different from the pyrolytic radical reaction of PP in which recombination of volatile matter is not important.[20)]

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