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GAS CHROMATOGRAPHIC DETERMINATION OF THE PRODUCTS OF DEGRADATION OF POLYETHYLENE OVER A SILICA–ALUMINA CATALYST

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SUMMARY

The degradation products of polyethylene, especially a liquid fraction, formed over a silica–alumina catalyst were analyzed by glass capillary column gas chromatography. The liquid fraction contains large amounts of the same isoalkanes and aromatics as are present in the gasoline fraction of petroleum. Most of the isoalkanes are monobranched with a methyl group at the 2- or 3-position. The aromatics consist mainly of those with one or more methyl groups and are produced highly selectively at carbon numbers higher than 7. The degradation products are distributed in a narrow range of carbon number compared with those obtained by thermal degradation. The relative yield of C_3–C_5 fractions was greater than 70 wt. % at the initial stage of the reaction. Isomerization, aromatization and hydrogen transfer reactions seem to play an important rôle in the secondary degradation of the primary products of polyethylene.

INTRODUCTION

The catalytic degradation of polyethylene over solid acid catalysts occurs predominantly by the successive scission of carbon–carbon bonds to produce many gaseous, liquid and solid hydrocarbons having lower molecular weights than that of polyethylene. The reactivity of hydrocarbons is generally accepted to increase with their carbon number[1] and is dependent upon the type of hydrocarbons, *i.e.*, linear, branched, cyclic, saturated or unsaturated. The primary products with high molecular weights undergo a secondary degradation which must be very effective in determining the final distribution of products. We have reported the catalytic gasification of polyethylene over X-type zeolite and silica–alumina catalysts[2,3]. In these studies, however, the precise analysis of products was limited to gaseous hydrocarbons because of the difficulties of analyzing liquid fractions consisting of large numbers of components. The liquid fractions can be regarded as the intermediates in the formation of gaseous products, hence it is reasonable to expect that a survey of the compositions of liquid or solid products will provide a means for clarifying the mech-

anism of the catalytic degradation of polyethylene. Further, the survey will be important with regard to the recovery of plastic wastes as chemical resources or fuel.

The purpose of this study is to identify the degradation products of polyethylene, especially in liquid fractions, and to clarify the effect of secondary reactions on the degradation. From the results in the previous study[3], a silica–alumina catalyst was chosen because of its high activity in the degradation of polyethylene and its considerable resistance to deactivation by the accumulation of carbonaceous residues on the catalyst surface.

EXPERIMENTAL

Apparatus

The catalytic degradation was carried out in a fixed bed flow system at 452–526°C with a contact time, W/F, of 16.7–62.8 g catalyst · min/g PE; (weight of catalyst, $W = 3.0$ g, feed rate of polyethylene (PE), $F = 0.048$–0.180 g PE/min. The system consisted of three parts, melter, reactor and separator. The polyethylene sample was melted in the melter at 300°C under an atmosphere of nitrogen, and then introduced continuously over 3 h into the reactor at a constant feed rate. The reactor was packed with a silica–alumina catalyst. The degradation products were separated into gaseous and liquid fractions in the separator and analyzed by gas chromatography (GC). The details of the apparatus and the procedure have been described elsewhere[4]. The thermal degradation of polyethylene was carried out with the same apparatus at 575°C, 3.0 g of the catalyst being replaced by the same volume of glass beads (8.9 g, 3.5 mm diameter).

Materials

The polyethylene used was a commercial sample (UBEC 180N; Ube Industry, Tokyo, Japan) with a low density 0.90 g/cm³ and a molecular weight, $M_v = 1.3 \times 10^4$. The silica–alumina catalyst (13.5 wt. % Al_2O_3) was obtained from Nikki Chem. (Tokyo, Japan) and its surface area and acidity were 421 m²/g and 0.54 mmol/g ($H_0 \geqslant +3.3$), respectively. The catalyst was calcined before use in the air at 550°C for 3 h.

Analysis

The degradation products were analyzed by gas chromatography (Yanagimoto GCG-550 and G-180; Yanagimoto Seisakusho, Kyoto, Japan) and the peak areas were integrated with a Yanagimoto System-1100 integrator. Gaseous fractions were separated by packed columns with 10% squalane on 80–100 mesh Spherosil (4 m × 3 mm I.D.; Gasukuro Kogyo, Tokyo, Japan) and 60–80 mesh active carbon (1 m × 3 mm I.D.; Gasukuro Kogyo). A commercial glass capillary column (SCOT, 30 m × 0.28 mm I.D.; Gasukuro Kogyo) coated with OV-101 was used for the separation of liquid fractions. The retention indices of the products were compared with those of pure materials.

Hydrogenation of alkenes and selective absorption of alkenes and aromatics were carried out as supplementary techniques for the identification of the liquid fractions. The hydrogenation was carried out at 230°C by the use of a catalytic column (10 cm × 3 mm I.D.) packed with 2% Pd + 5% OV-101 on 60–80 mesh Diasolid (Nippon Kuromato Kogyo, Tokyo, Japan) which was connected just before a splitter. The

absorption was carried out according to the method of Hasegawa *et al.*[5] using a precut column (10 cm × 3 mm I.D.) packed with 30% mercury perchlorate on a support (Gasukuro Kogyo) at room temperature.

RESULTS AND DISCUSSION

Distribution of degradation products

The identification of the products in the gaseous fractions is easily achieved by GC, whereas the number of possible isomers is so large in the liquid fractions that the chromatographic separation is incomplete. This can be solved to some extent by the use of a high-resolution capillary column in combination with a hydrogenation catalyst or an absorbent column.

Fig. 1a shows a representative chromatogram of liquid products, which is expressed as the relative peak area against retention time. About twenty peaks with less than 0.1 area % were omitted. The chromatogram contained 58 peaks, while gaseous fractions consisted of twelve components of hydrogen and eleven hydrocarbons of carbon number less than 5 (see Table I where "butenes" contains four isomers). Consequently, 70 components were separated by GC. When the liquid products were passed through the mercury perchlorate column, the alkenes and aromatics were selectively absorbed[5] and the resulting chromatogram in Fig. 1b consisted of *n*-alkanes and isoalkanes. On the other hand, aromatics were distinguished from alkenes by hydrogenation; all aromatics except for naphthalenes were not hydrogenated, while alkenes were transformed to corresponding alkanes[6]. Thus, the degradation
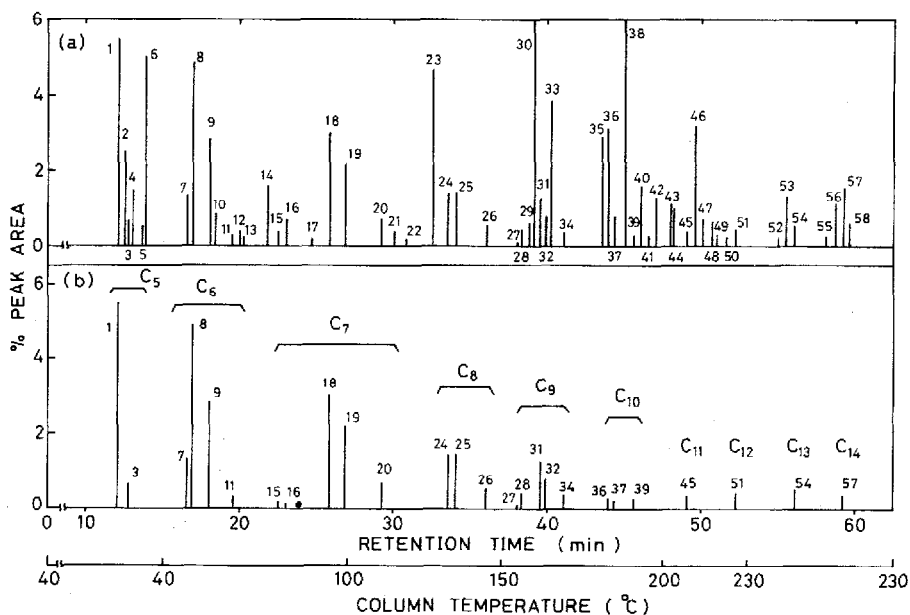

Fig. 1. Chromatogram of liquid products formed over a silica–alumina catalyst at 502°C and polyethylene feed rate, *F* = 0.090 g PE/min. a, Without absorbent column; b, with absorbent column. Peak numbers correspond to those in Table I.

products were classified into five groups: hydrogen, *n*-alkanes, isoalkanes, alkenes and aromatics. Methylcyclopentane and cyclohexane were placed in the isoalkane group, because they were formed only in limited amount.

The chromatogram of the alkanes mainly consisted of two isoalkane and one *n*-alkane peaks for each carbon number fraction, as shown in Fig. 1b. The two isoalkanes were assigned to monobranched alkanes with a methyl group at the 2- or 3-position on the basis of a relation between boiling point and retention index. .Peaks 1, 8, 18, 24, 31 and 36 were identified as 2-methylalkanes and 9, 19, 25, 32 and 37 were 3-methylalkanes, while peaks 3, 11, 20, 26, 34, 39, 45, 51, 54 and 57 corresponded to *n*-alkanes. The identification of alkenes was more difficult than that of isoalkanes because of many possible isomers. However, the main components were ascertained as *n*-alkenes and monomethyl-branched alkenes on the basis of the chromatogram of the hydrogenated liquid products. The identified components are listed in Table I together with their relative amounts at the initial stage, *i.e.*, 5 min after starting the reaction. Toluene, xylenes and trimethylbenzenes were the main aromatics. Alkyl groups bonded to a benzene ring were limited to methyl and ethyl, and no aromatics with groups larger than propyl were found. Unknown compounds would be limited to C_9 and/or C_{10} aromatics from their retention indices and by hydrogenation and absorption methods. As shown in the table, most of the liquid components are the same as those contained in the gasoline fraction of petroleum[7].

Fig. 2 shows the molar percentages of four groups in each carbon number fraction at the initial stage of the reaction. Isoalkanes were produced preferentially in the C_4–C_7 fractions. Aromatics were formed highly selectively in the higher carbon number region, but only small amounts of alkenes. These results indicate that isomerization and aromatization are the important secondary reactions. The formation of aromatics is especially of interest. They are formed through alkene and/or alkane intermediates since polyethylene has no ring structure. Three moles of H_2 are expected to be eliminated from the monoalkene intermediate when 1 mol of aromatics is formed, and similarly 4 mol of H_2 from the alkane intermediate. However, the degradation products contained no more than 7 mol % hydrogen, so that the hydrogen eliminated in the aromatization processes transferred in part to unsaturated acceptor molecules, *i.e.*, a hydrogen transfer reaction occurred. Therefore, a portion of the hydrogen required to form the saturated hydrocarbons was supplied through the formation of aromatics. Hydrogen transfer reactions in the coking process would also contribute to the formation of saturated hydrocarbons.

In Fig. 3 the distribution of products obtained by catalytic degradation is compared with that obtained by thermal degradation. The thermal degradation was carried out at a higher temperature than that of the catalytic degradation, thus making it possible to analyze wax-like products at lower viscosity. The thermal degradation products consisted of linear *n*-alkanes, monoalkenes and alkadienes, the molar ratio of which was 24:69:7. The chromatogram of the liquid fractions obtained by thermal degradation was different from that upon catalytic degradation and consisted of several triplets corresponding to the three components as reported previously[8]. Branched and aromatic hydrocarbons were extremely minor products. The identification of these products was based on the extensive chromatographic data in the literature[8–10], in addition to use of the analytical techniques described above. It is evident from Fig. 3 that the silica alumina catalyst remarkably accelerates the degra-

TABLE I

COMPOSITION OF DEGRADATION PRODUCTS FORMED OVER SILICA–ALUMINA

tr = Trace amount of less than 0.05 mol %.

Component	Peak number in Fig. 1	452°C		502°C		526°C		Ident. method*
		mol %	wt. %	mol %	wt. %	mol %	wt. %	
Hydrogen		4.0	0.1	7.1	0.3	6.9	0.3	i
n-Alkanes								
Methane		2.4	0.6	6.5	2.0	7.4	2.4	i
Ethane		1.2	0.7	1.5	0.8	2.0	1.2	i
Propane		6.6	4.8	7.6	6.4	9.3	8.3	i
Butane		2.6	2.5	2.5	2.8	2.8	3.3	i
Pentane	3	0.6	0.7	1.1	1.5	0.9	1.3	ii
Hexane	11	0.2	0.3	0.3	0.4	0.3	0.4	ii
Heptane	20	0.1	0.2	0.1	0.3	0.1	0.1	ii
Octane	26	0.1	0.1	0.1	0.1	0.1	0.1	ii
Nonane	34	0.1	0.1	0.1	0.1	0.1	0.1	ii
Decane	39	tr		tr		tr		ii
Others	45,51,54,57	0.1	0.1	0.1	0.2	tr		ii
Total		14.0	10.2	19.7	14.6	23.0	17.2	
Isoalkanes								
Isobutane		20.0	18.9	13.4	14.9	13.1	15.3	i
Isopentane	1	12.7	14.9	8.0	11.0	7.5	10.9	ii
Isohexanes	7,8,9	5.1	7.1	3.1	5.2	1.7	2.9	ii, iii
Isoheptanes	15,16,18,19	2.3	3.8	1.0	1.8	0.4	0.8	ii, iii
Isooctanes	24,25	1.3	2.4	0.4	0.9	0.2	0.4	iii
Isononanes	27,28,31,32	0.7	1.4	0.3	0.6	0.1	0.3	iii
Isodecanes	36,37	0.4	0.9	0.1	0.3	tr		iii
Others		0.4	1.1	tr		tr		iii
Total		42.9	50.5	26.4	34.7	23.0	30.6	
Alkenes								
Ethylene		1.4	0.6	2.8	1.5	3.6	2.0	i
Propylene		15.5	10.6	19.1	15.4	19.1	16.2	i
Butenes		10.8	9.9	13.8	14.7	14.4	16.3	i
Pentenes	2,4,5,6	4.1	4.7	3.8	5.0	4.2	5.8	ii, iii
Hexenes	10,12,13,14	1.7	2.3	0.8	1.2	1.1	1.8	iii
Others	15,16,21,22	0.7	1.2	tr		0.1	0.3	iii
Total		34.2	29.3	40.3	37.8	42.5	42.4	
Aromatics								
Benzene	17	tr		tr		0.1	0.1	ii
Toluene	23	0.4	0.6	0.8	1.4	0.7	1.3	ii
Ethylbenzene	29	0.1	0.1	0.1	0.2	0.1	0.2	ii
Xylenes	30,33	1.5	2.7	1.9	3.9	1.6	3.4	ii
Ethyltoluenes	35,37	0.4	0.7	0.4	0.8	0.2	0.5	iii
Trimethylbenzenes	36,38,40	1.4	2.8	1.4	3.1	0.9	2.2	ii
Unknown	41–49,52	0.8	1.7	0.8	1.9	0.3	0.9	
Naphthalene	50	0.1	0.2	tr		tr		ii
Methylnaphthalenes	53,54	0.1	0.3	0.2	0.4	0.1	0.3	ii
Dimethylnaphthalenes	55,56,57,58	0.2	0.6	0.3	0.8	0.2	0.4	ii
Total		5.0	9.7	5.9	12.5	4.2	9.3	
Contact time (g catalyst · min/g PE)		28.7		34.3		30.7		
Yield of products (wt. %)		71.2		72.5		75.4		

* Identification method of each component: i, by comparison with standard retention time; ii, co-injection with standard materials; iii, extrapolation of a linear relation between boiling point and retention index.
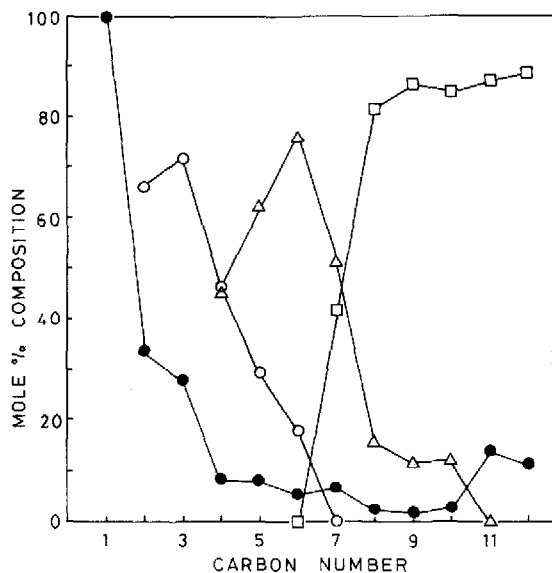
Fig. 2. Composition of four groups in each carbon number fraction obtained by catalytic degradation at 502°C and F = 0.090 g PE/min. ●, *n*-alkanes; △, isoalkanes; ○, alkenes; □, aromatics.

dation of polyethylene and the relative yield of C_3-C_5 fractions is greater than 70%. In contrast, the thermal degradation products were distributed over a wide range of carbon numbers even at a high reaction temperature.

As shown in Fig. 3, the distribution of the catalytic degradation products shifted to higher carbon numbers with increasing reaction time. Even after 3 h, however, the products were distributed over a narrower range of carbon number than those obtained by thermal degradation. The shift reflects a decrease in catalytic activity,
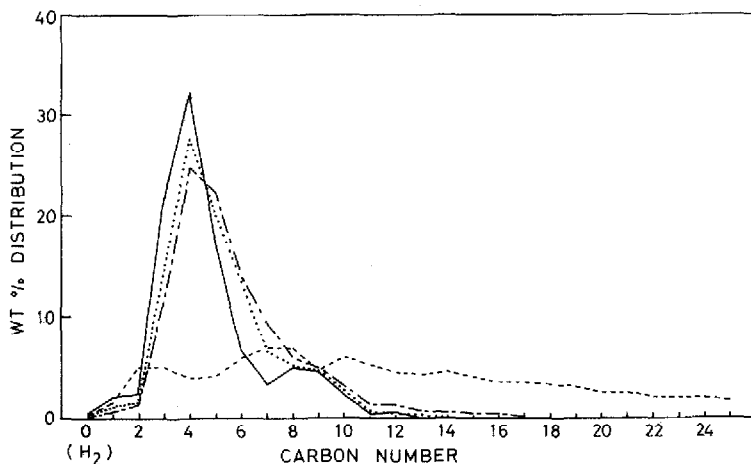

Fig. 3. Product distribution as a function of carbon number in catalytic and thermal degradations. Conditions: over silica–alumina at 502°C and F = 0.090 g PE/min; reaction time = 5 (—), 110 (· · ·) and 180 min. (– · –);   , over glass beads at 575°C and F = 0.140 g PE/min.

caused by the accumulation of coke. The product composition also varied with re-
action time and after 3 h the degradation products consisted of 3 mol % of hydrogen,
12% of n-alkanes, 13% of isoalkanes, 67% of alkenes and 5% of aromatics.

Effect of contact time on product composition

Fig. 4. shows the effect of contact time on the product distribution. The relative
yield of C_1–C_4 fractions increased with contact time, because longer contact time
promoted the secondary degradation of primary products. The dependencies of con-
tact time on the total amount of each group and on the formation of the main
components in each group are shown in Figs. 5a and 6, respectively. It is evident that
the increase in the amount of n-alkanes with contact time is primarily attributed to
methane and propane. Further, only isobutane among isoalkanes increased, although
the total amount of isoalkanes decreased slightly (Figs. 5a and 6). Fig. 5b shows the
effects of contact time on the ratios of isoalkanes/n-alkanes in the C_4–C_{10} fraction
where both groups coexist and of aromatics/aliphatics (alkanes + alkenes) in the frac-
tions of carbon number greater than 6. The aromatics/aliphatics ratio increased with
contact time, indicating a larger decrerase in the formation of aliphatics than that of
aromatics. The decrease of the aliphatics suggests their further degradation to smaller
fractions, reflecting the increase in C_1–C_4 formation. On the other hand, the secon-
dary degradation of aromatics seems unlikely to occur for the following reasons. No
cleavage of the benzene ring would occur because of its great stability. The extent of
dealkylation on solid acid catalysts generally depends on the relative ease of for-
mation of alkyl carbonium ions[11]. Since methyl carbonium ions are very difficult to
form, most of the aromatics produced essentially would not undergo decomposition.
These considerations are supported by the result that the composition of the aro-
matics changed very little with contact time. The catalytic degradation of polyethyl-
ene proceeds through a carbonium ion mechanism[3], in which isoalkanes containing
one or more tertiary carbon atoms undergo secondary degradation much more
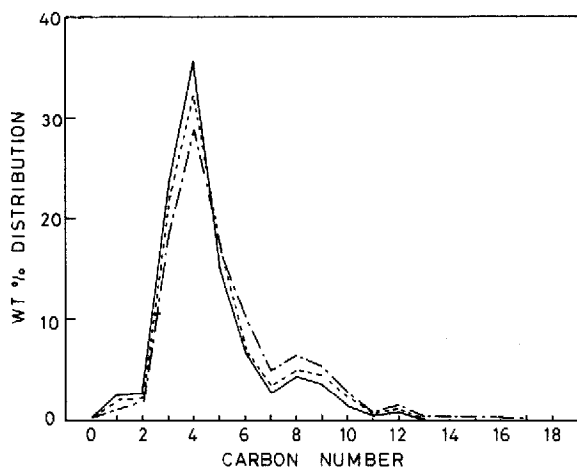readily than n-alkanes. The high reactivity of isoalkanes results in the decrease in

Fig. 4. Effect of contact time on product distribution at 502°C. W/F = 62.7 (—), 34.3 (– – –) and 16.7 g
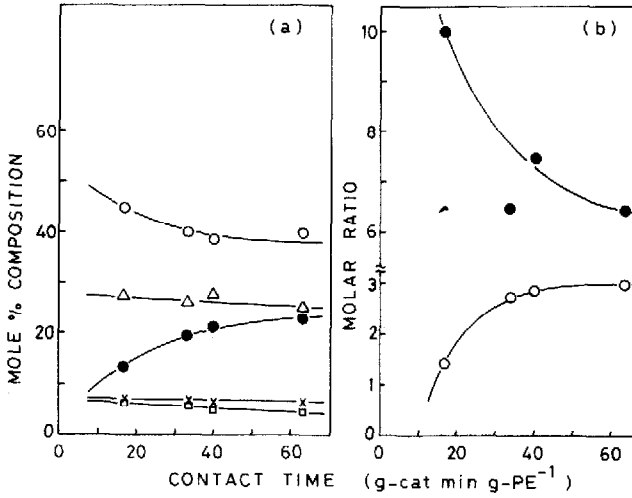catalyst · min/g PE (– · –).

Fig. 5. Effect of contact time on product composition at 502°C. a, Total amount of each group; ●, *n*-alkanes; △, isoalkanes; ○, alkenes; □, aromatics; ×, hydrogen. b, Molar ratio; ●, isoalkanes/*n*-alkanes (C_4–C_{10}); ○, aromatics/aliphatics ($\geqslant C_7$).
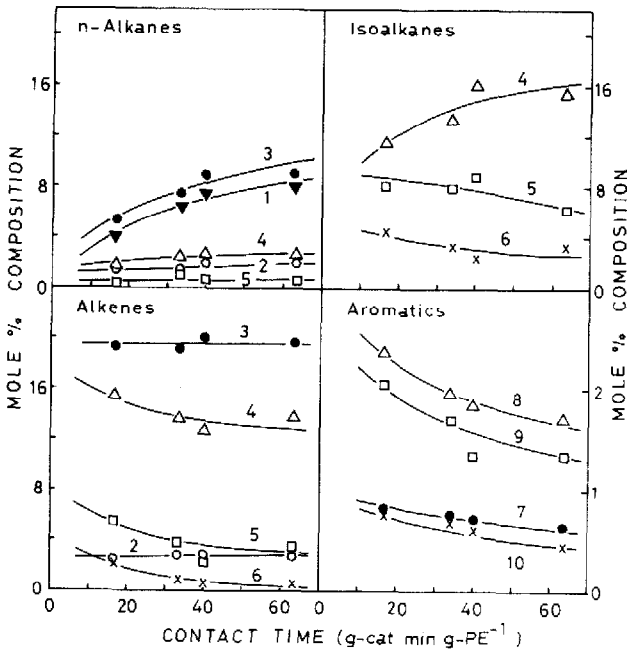

Fig. 6. Effect of contact time on the formation of the main components in four groups. The numbers on the curves indicate the carbon number of each component.

isoalkanes/n-alkanes ratio with increasing contact time. The smallest fragment expected from the carbonium ion mechanism is C_3 in linear hydrocarbons or iso-C_4 in branched hydrocarbons. So, it is reasonable to conclude that propane and isobutane are formed in increasing amount with increasing contact time, as shown in Fig. 6.

CONCLUSION

The degradation products of polyethylene formed over a silica–alumina catalyst were distributed in a narrow range of carbon numbers. The relative yield of C_3–C_5 was greater than 70 wt. % at the initial stage of the reaction. The liquid fraction contained large amounts of the same isoalkanes and aromatics as those contained in the gasoline fraction of petroleum. From the viewpoint of recovery of plastic wastes, the narrow distribution of the products and the formation of a gasoline fraction seem to be significant results.

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