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Identification of Normal Paraffins and Olefins from Thermal Decomposition Products of Polyethylene

Takeaki A. Iida, Kenichi Honda, and Hiroshi Nozaki
Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106

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Straight-chain components of the high boiling fractions of thermal decomposition products of low-density polyethylene were obtained through urea adduct formation, and analyzed by chromatographic separation methods. They were found to be a mixture of approximately 60 wt% of paraffins (C_{10} to C_{30}), 35 wt% of terminal olefins (C_{10} to C_{26}), and 5 wt% of nonterminal olefins (C_{10} to C_{26}) with predominantly 2-alkenes. A silica gel–silver nitrate mixture was found to be useful for chromatographic separation of hydrocarbon components.

Thermal decomposition products of polyethylene are a complex mixture of saturated and unsaturated hydrocarbons. It is important to know the types of these compounds as well as to determine the structures of individual hydrocarbons, not only for elucidation of the mechanism of thermal decomposition of polyethylene, but also for regeneration of polyethylene as an industrial raw materials.

Thermal decomposition products of polyethylene have been determined by many investigators. Kambe and Shibasaki[1] analyzed the thermal decomposition products of polyethylene by gas chromatography and identified several paraffins and olefins with carbon numbers from C_5 to C_9. Tsuchiya and Sumi[2] made a comprehensive analysis of the volatile thermal decomposition products by gas chromatography. They discussed the mechanism of the decomposition by assuming intramolecular transfer of free radicals. The result was valuable for identification of the thermal decomposition products consisting of low boiling fractions of hydrocarbons from C_1 to C_6. Madorsky[3] determined thermal decomposition products of polyethylene by mass spectrometry. Moiseev[4] used gas chromatography for the separation of decomposition products of low boiling fractions, and explained the formation of volatile thermal decomposition products by assuming intramolecular transfer of radicals or isomerization. However, high boiling fractions which constitute a major portion of decomposition products have not been so extensively investigated. The present work deals with the identification of straight-chain hydrocarbons of thermal decomposition products of low-density polyethylene obtained through urea adduct formation. Emphasis was placed on the separation and identification of an olefin mixture.

Experimental

Materials used. Commercial low-density polyethylene was used; its properties are given in Table 1.

Table 1. Properties of low-density polyethylene

Appearance: white, translucent, solid
Density: 0.923 g/cm^3
Softening point: 97°C
Crystalline melting point: 102°C
Molecular weight: about 56000

Thermal Decomposition. The apparatus is illustrated in Fig. 1. A universal-joint Pyrex Claisen-flask containing 10 g of sample was prepared. Nitrogen gas was introduced into the flask in order to prevent the oxidation of polyethylene and decomposition products. The sample was decomposed for 120 min at 420°C. The high boiling fractions, which constitute 75 wt% of thermal decomposition products, were collected in a flask (5, Fig. 1), heated with a water bath at 80 °C. The mixture of saturated and olefinic hydrocarbons was used as a starting material.

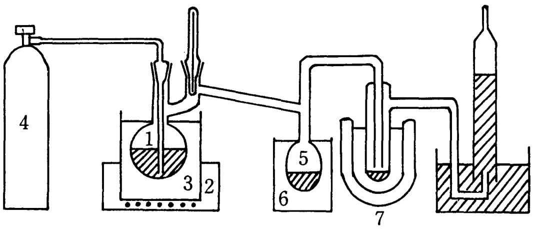

Fig. 1. Apparatus for the thermal decomposition of polyethylene.
1 Polyethylene sample, 2 Electric furnace, 3 KNO_3–$NaNO_2$–$NaNO_3$ salt bath, 4 N_2 gas, 5 High boiling fraction, 6 Water bath, 7 Liquid nitrogen trap.

Analysis. *(1) Reagents*: Silica gel impregnated with silver nitrate for elution column chromatography was prepared by thoroughly mixing 40 grams of silica gel (Wakogel, C-100) and 8 g of 50% aqueous silver nitrate, followed by drying in the dark at 120 °C for 4 hr.[5] Thin-layer plates of silica gel–silver nitrate were prepared by spraying the usual 250-micron layer of silica gel (Wakogel, B-10) with 20% aqueous silver nitrate, followed by reactivation at 110°C for 10—15 min. A *n*-hexane–benzene mixture (20 to 1) was used as a developing solvent system. Spots were detected by spraying 60% sulfuric acid and heating at 100 to 150°C.

(2) Apparatus: For gas-liquid chromatography (glc) on a preparative scale, a Beckman Megachrom instrument with 2 m columns in parallel was used. The column packing was 7% methyl silicone polymer (SE-30) coated on 40- to 60-mesh Microsorb F. The temperature range was 193—203 °C. For analytical glc, a Shimadzu Model GC-4APE1 instrument was used in conjunction with a hydrogen flame detector. Dual column, 4 mm in diameter and 2 m in length packed with

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[1] H. Kambe and Y. Shibasaki, *J. Soc. Polym. Sci. Jap.*, **20**, 641 (1963).

[2] Y. Tsuchiya and K. Sumi, *J. Polym. Sci., A-1*, **6**, 415 (1968).

[3] S. L. Madorsky, "Thermal Degradation of Organic Polymers," Interscience, N. Y. p. 93 (1964).

[4] V. D. Moiseev, *Soviet Plastics*, (*English Transl. Dec.* 1963), *Dec.*, 6 (1964).

[5] H. Wagner, J. D. Goetschel, and P. Lesch, *Helv. Chim. Acta*, **46**, 2986 (1963).

1.5% OV-17 on silanized Shimalite W, were generally used with a temperature program of 4 °C per minute. Nitrogen was used as carrier gas. Infrared spectra were obtained by Hitach-Perkin Elmer Model 210 Spectrophotometers.

(3) Procedure: The thermal decomposition product of the high boiling fraction was resolved into straight-chain and branched-chain hydrocarbons through a urea complex formation technique. The infrared spectra of these straight-chain hydrocarbons were first obtained. Analytical glc of this sample was obtained with the use of OV-17 column. Tlc as well as elution column chromatography (silica gel–silver nitrate) were carried out to separate paraffin, terminal olefin and nonterminal olefins. The amounts of paraffin, terminal olefin and nonterminal olefin were determined by direct weighing of the concentrates. Each peak separated by the analytical glc and consisting of hydrocarbon of the same carbon number was fractionated by preparative scale glc with the use of SE-30 column. The double bond distribution in nonterminal olefin was estimated by ozonolysis of the fractioned hydrocarbon followed by glc analysis of the derived carboxylic acid methyl esters.

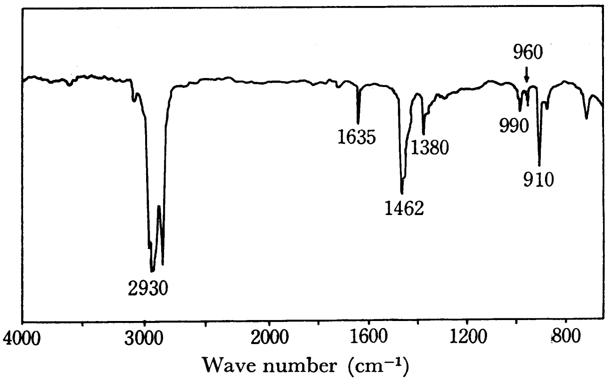

Fig. 2. Infrared spectrum of straight-chain paraffin and olefin from the thermal decomposition products of polyethylene.

Results and Discussion

The yield of urea adduct formation of straight-chain paraffin and olefin mixture was about 25 wt% of the high boiling fractions. Infrared spectra of the straight-chain hydrocarbons are shown in Fig. 2. The spectra at 2930 and 1462 cm^{-1} correspond to stretching band and deformation band of C–H bond, respectively. Methyls are observed at 1380 cm^{-1}, terminal olefins at 910 and 990 cm^{-1} (deformation bands) and 1635 cm^{-1} (stretching band) and nonterminal olefin (*trans*) at 960 cm^{-1} (deformation band). Thus, it can be said that the hydrocarbon mixture consists of paraffins, terminal olefins and nonterminal olefins. Analytical glc of the straight-chain paraffin and olefin mixture added with authentic specimens of *n*-paraffins of $C_{16}H_{34}$, $C_{20}H_{42}$, $C_{26}H_{54}$ is shown in Fig. 3. We see that carbon numbers are distributed from C_{10} to C_{30} through a maximum at around C_{16}. It is also noted that each peak from C_{11} to C_{26} shows two resolved peaks. Since there is the possibility of separation of olefin and paraffin of the same carbon numbers on the glc of OV-17 column, the two peaks probably represent olefin and paraffin of the same carbon numbers.

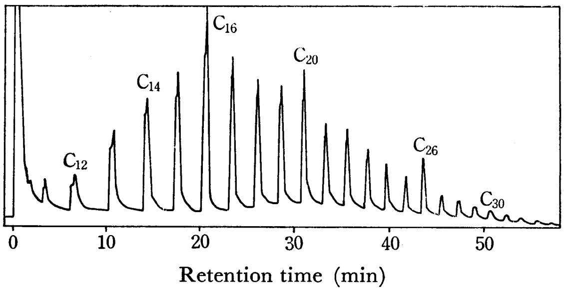

Fig. 3. Gas chromatogram of straight-chain hydrocarbons from the decomposition products of polyethylene.

Paraffin, terminal olefin and nonterminal olefins were completely separated from each other on tlc as well as by elution column chromatography. Among olefins, the terminal one was most strongly adsorbed; the more the double bond goes toward the center of the chain, the less it is adsorbed. Tlc (silica gel–silver nitrate) showed three spots, assigned by infrared spectra to be paraffin, nonterminal olefin, and terminal olefin in this order. The amounts of paraffin, terminal olefin and nonterminal olefin separated by elution column chromatography using silica gel–silver nitrate are given in Table 2.

TABLE 2. AMOUNTS OF PARAFFIN, NONTERMINAL OLEFIN, AND TERMINAL OLEFIN SEPARATED BY ELUTION COLUMN CHROMATOGRAPHY

Sample No.	Paraffin (wt%)	Nonterminal olefin (wt%)	Terminal olefin (wt%)	Tar (wt%)
1	62.7	5.7	30.6	1.0
2	65.1	5.5	28.2	1.1
3	52.6	5.6	40.9	1.0
4	56.7	5.2	37.2	0.9

Figure 4 shows the analytical glc of the normal paraffin concentrate separated by elution column chromatography (silica gel–silver nitrate) with *n*-$C_{16}H_{34}$ added as an authentic specimen. In this case the peak on C_{16} is not resolved. On the other hand, as shown in Fig. 5, the analytical glc of the terminal olefin concentrate with *n*-$C_{16}H_{34}$ added shows two resolved peaks on the C_{16} peak. It was found by the retention time of *n*-$C_{16}H_{34}$ that peak A corresponds to terminal olefin and peak B to paraffin of *n*-$C_{16}H_{34}$. It was also confirmed that nonterminal olefin and terminal olefin were not separated from each other

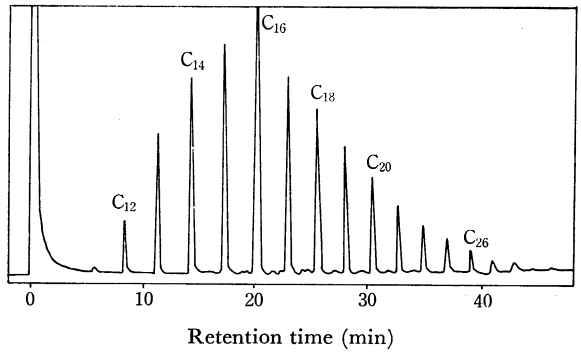

Fig. 4. Gas chromatogram of straight-chain paraffins from the thermal decomposition products of polyethylene.

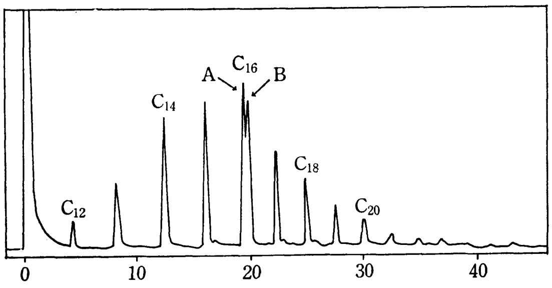

Fig. 5. Gas chromatogram of straight-chain terminal olefins from the thermal decomposition products of polyethylene.

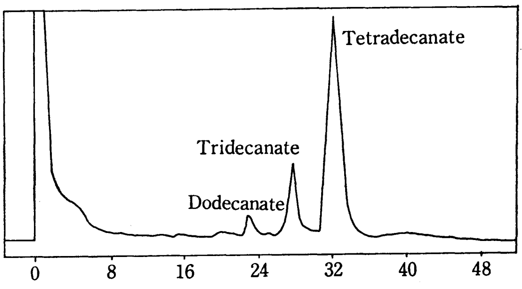

Fig. 6. Gas chromatogram of carboxylic acid methyl esters obtained from straight-chain C_{16} nonterminal olefins.

on the glc of OV-17 column. It is therefore considered that two resolved peaks correspond to olefin and paraffin of the same carbon numbers, respectively.

In order to determine the double bond distribution in nonterminal olefins, the ozonolysis of C_{16} nonterminal olefin concentrate fractionated by preparative scale glc was carried out and glc analysis of the derived carboxylic acid methyl esters was followed. The result is shown in Fig. 6. A noticeable fact about the straight-chain olefinic components is that double bond distribution is strongly favored toward the end of the chain. This supports the mechanism of the decomposition reaction on the assumption of intramolecular transfer of free radicals from the end of the chain to the center as proposed by Tsuchiya and Sumi.[2]

Many usages of this decomposition product are considered, a prospective one being the production of biodegradable detergents from terminal olefins.[6]

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6) C. L. Furrow, *Ind. Eng. Chem.*, **7**, 26 (1968); C. J. Norton, *J. Org. Chem.*, **33**, 4158 (1968).