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Oligoethylenes in High Pressure Polyethylenes I Identification of Homologues

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Summary

Low molecular weight components which were present in commercial polyethylene resins in minor amounts were analyzed in detail by gaschromatography (GC) and mass spectroscopy (MS). More than forty oligoethylenic homologues were identified, which were consisted of a variety of alkanes, alkenes, cycloalkanes, aromatics, alkanones, alkanol and esters.

Introduction

Commercial high pressure polyethylene has been known to contain low molecular weight components, though not much in quantity. They have been generally assumed to be the products of low polymerization degrees, but the exact constitution has scarcely been elucidated before.

In this study the structures of low molecular weight components separated from commercial resins were elucidated by GC and MS. Low molecular weight components were found to be consisted of a large number of oligoethylenic homologues. Up to the present, more than forty homologues have been indentified.

Experimental

Commercial samples (100-200g) of high pressure polyethylene were extracted with chloroform (800 ml) in a Soxhlet extractor. The extract was separated into acetone-soluble and acetone-insoluble parts. The acetone-soluble part, which was sometimes freed from higher molecular weight fraction by GPC, was then subjected to GC or GC-MS analysis.

Details of GC and GC-MS analyses will be published later. Only important points are mentioned here.

GC : OV-101 coated open tubular glass capillary column 40m, temperature programmed at 3°C/min from 150°C to 270°C.

MS : Equipment JEOL D-300 directly coupled with GC and

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capable of either electron-impact ionization (EI) or chemical ionization (CI).

An example of GC chart is shown in Fig.1, where peaks attached with numbers are assigned to n-alkanes having the numbers of carbon atoms as shown.

It can be seen that peaks similar in both peak height and relative position to the neighbouring n-alkanes appear repeatedly, and GC-MS analyses have shown unambiguously that the majority of the peaks belongs to one of the oligoethylenic homologues, which are represented by a general formula, $X-(CH_2)_n-Y$.

The identification of each homologue or compound was generally not easy. Adopted procedures and criteria for the identification were as follows.

GC : If retention times of an oligoethylene and two neighbouring n-alkanes are t, t_n, and t_{n+1}, then the relative retention time (RRT) of the oligoethylene may be defined as follows.

$$RRT = \left(\frac{t - t_n}{t_{n+1} - t_n} + n \right) \times 100$$

where n was chosen as the number of carbon atoms of the neighbouring n-alkane with lower molecular weight

As our GC-condition was programmed linearly to temperature, RRT thus determined was assumed equivalent to "retention index" defined for an isothermal GC. (KOVATS, 1958 ; ETTRE, 1964)

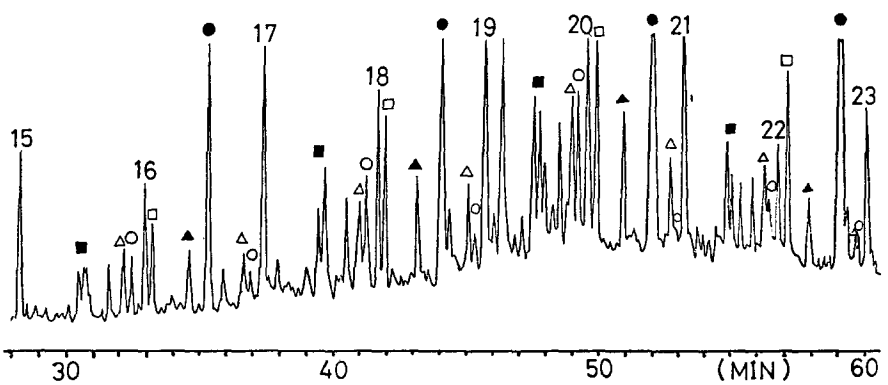


Fig.1 An Example of Gaschromatogram

Numbered peaks are n-alkanes containing indicated carbon atoms, ● alkylcyclopentane, ○ n-1-alkene, ■ 4-ethylalkane et al., □ 5,5-diethylalkane, ▲ 5-ethylalkane, △ 2-ethyl-1-alkene.

GC-MS : GC-MS analyses were carried out in two ways using two modes of ionization, EI and CI.

In identifying oligoethylene structure based on the analytical data, it was highly desirable to have the reliable information or supposition concerning the polymerization conditions of the resin from which the oligoethylene was separeted. Oligoethylene homologues were found to be classified into two groups : the first group appeared only in particular resins, while the second was common among almost all the resins examined. The former seemed closely related to the specific polymerization condition, especially the use of specific chain tranfer agents or comonomers. This finding and the consideration of reasonable chain transfer mechanisms did greatly aid the identification of each oligoethylene.

Identification criteria are tabulated in Table 1. At least the minumum postulate must be satisfied, and the more the positive evidences are obtained, the more reliable the identification becomes.

Table 1	Homologue Identification Criteria	
	positive evidence	minimum postulate
GC : RRT	consistent with authentic sample	acceptable RRT-structure relationship
EI-MS : MS-pattern	consitent with authentic sample or authentic spectrum data (STENHAGEN 1974)	not conflicting with those expected on the fragmentation rule from the proposed structure (McLAFFERTY 1973)
CI-MS : QM^+ (quasi molecular ion)	QM^+ and MS-pattern consistent with authentic sample	only type classification possible : acyclic alkane M-1 acyclic alkene M+1 cyclic alkane M-1 aromatics M+1 oxygen-contg. M+1 (except alkanol)
Polymerization information and mechanism	unambiguous and well-established mechanism from the feed	speculative mechanism from the feed

Table 2 | Oligoethylenes in High Pressure Polyethylene

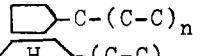
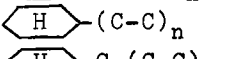
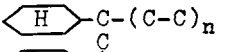
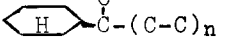
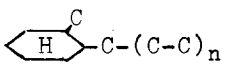
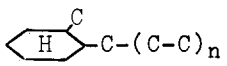
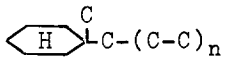
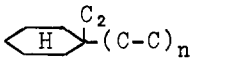
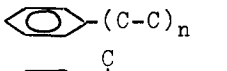
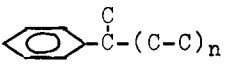
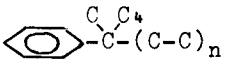
Oligoethylenes	numbers of carbon atoms (even or odd)	structures
alkanes(normal)	even	$C\text{-}C\text{-}(C\text{-}C)_n$
do.	odd	$C\text{-}C\text{-}C\text{-}(C\text{-}C)_n$
2-methylalkanes	odd	$C\text{-}\overset{\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
3-methylalkanes	even	$C_2\text{-}\overset{\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
5-methylalkanes	even	$C_4\text{-}\overset{\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
3-ethylalkanes	odd	$C_2\text{-}\overset{\overset{C_2}{\vert}}{C}\text{-}(C\text{-}C)_n$
4-ethylalkanes	even	$C_3\text{-}\overset{\overset{C_2}{\vert}}{C}\text{-}(C\text{-}C)_n$
5-ethylalkanes	odd	$C_4\text{-}\overset{\overset{C_2}{\vert}}{C}\text{-}(C\text{-}C)_n$
2,2-dimethylalkanes	even	$C\text{-}\overset{\overset{C}{\vert}\quad\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
5,5-diethylalkanes	odd	$C_4\text{-}\overset{\overset{C_2}{\vert}\quad\overset{C_2}{\vert}}{C}\text{-}(C\text{-}C)_n$
3-ethyl-3-methylalkanes	even	$C_2\text{-}\overset{\overset{C_2}{\vert}\quad\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
5-ethyl-5-methylalkanes	even	$C_4\text{-}\overset{\overset{C_2}{\vert}\quad\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
1-alkene (normal)	even	$C{=}C\text{-}(C\text{-}C)_n$
do.	odd	$C{=}C\text{-}C\text{-}(C\text{-}C)_n$
2-alkenes	even	$C\text{-}C{=}C\text{-}C\text{-}(C\text{-}C)_n$
2-methyl-1-alkenes	even	$C{=}\overset{\overset{C}{\vert}}{C}\text{-}C\text{-}(C\text{-}C)_n$
2-ethyl-1-alkenes	even	$C{=}\overset{\overset{C_2}{\vert}}{C}\text{-}(C\text{-}C)_n$
do.	odd	$C{=}\overset{\overset{C_2}{\vert}}{C}\text{-}C\text{-}(C\text{-}C)_n$
3-methyl-1-alkenes	even	$C{=}C\text{-}\overset{\overset{C}{\vert}}{C}\text{-}(C\text{-}C)_n$
alkylcyclopentanes	even	
alkylcyclohexanes	even	
do.	odd	
2-cyclohexylalkanes	even	

Table 2 (Continued)

1-alkyl-trans-2-methylcyclohexanes	even	
1-alkyl-cis-2-methylcyclohexanes	even	
1-alkyl-1-methylcyclohexanes	even	
1-alkyl-1-ethylcyclohexanes	even	
alkylbenzenes	even	
2-phenylalkanes	even	
5-methyl-5-phenylalkanes	even	

Results and Discussion

On the basis of the above-mentioned procedures, more than forty of oligoethylene homologues could be identified, which are tabulated in Tables 2 and 3. Table 2 shows various hydrocarbon oligomers and Table 3 various oxygen-containing oligomers. The oligomers shown are with a great diversity in structure : alkanes, alkenes, cycloalkanes, aromatics, alkanones, alkanol and esters.

Some of these oligoethylenes have never been reported on their existence in high pressure polyethylene. In fact, the presence of cycloalkanes in all commercial samples of high pressure polyethylene was quite unexpected.

These varieties of oligoethylenes in high pressure ethylene polymerization is very informative to the mechanism of polymerization, which will be considered in the succeeding paper.

Table 3 | Oligoethylenes in High Pressure Polyethylene

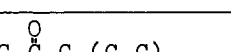
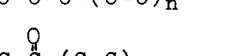
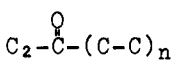
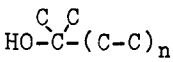
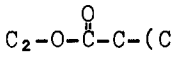
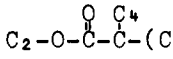
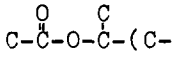
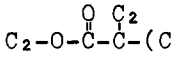
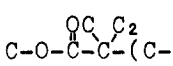
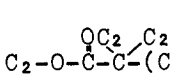
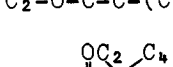
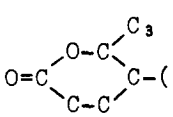
Oligoethylenes	numbers of carbon plus oxygen atoms (even or odd)	Structures
2-alkanones	even	
do.	odd	

Table 3 (Continued)

3-alkanones	even	
2-methyl-2-alkanols	even	
ethyl alkanoates	even	
ethyl 2-butylalkanoates	even	
1-methylalkyl acetates	even	
ethyl 2-ethylalkanoates	even	
methyl 2-ethyl-2-methylalkanoates	even	
ethyl 2,2-diethylalkanoates	even	
ethyl 2-butyl-2-ethylalkanoates	even	
4-alkyl-5-propyl-5-pentanolides	even	

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