

A Study on Hydroxyl Groups in Polyethylene

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Synopsis

The possibility of the presence of hydroxyl groups in polyethylene molecular chains has been investigated in observations of infrared spectra of O—H and C—O stretching vibrations in olefinic molecular chains. *n*-Paraffins and fresh medium-pressure process polyethylenes containing the primary alcohols were used as a model of polyethylene containing hydroxyl groups in the molecular chains. The characteristic wavenumber of the hydroxyl groups slightly contained in the polyethylene in the region 3600–3200 cm^{-1} becomes constant over about 10 of carbon-atom number of the alcohols, approximately 3336 cm^{-1} . The wavenumber does not agree with $\sim 3370 \text{ cm}^{-1}$, which has been hitherto assigned to hydroxyl groups in polyethylene molecular chains. Although the absorption due to the hydroxyl groups must appear in the region of C—O stretching band in the vicinity of 1050 cm^{-1} if the absorption around 3370 cm^{-1} is due to the hydroxyl groups, the absorption has not been observed. Changes in infrared spectra of polyethylene absorbing water as much as 10 ppm corresponding to the water absorbing capacity are not observed in comparison with those of extremely dried polyethylene. It is concluded that the absorption at 3370 cm^{-1} in polyethylene is not due to the hydroxyl groups and that the groups are not contained at least in fresh polyethylene.

INTRODUCTION

On a development of low dielectric loss material in the microwave range, it is very important to decrease polar groups in the material. Especially the direction of the investigation for decreasing dielectric loss in the material turns largely on the presence of hydroxyl groups because each of them has large permanent dipole moment. Characteristic infrared absorptions of hydroxyl groups in high molecular polymers have not been as clear as those in low molecular compounds.^{1–4} It is thought that the hydroxyl groups in polyethylene molecular chains are contained in conventional polyethylene on the basis of the presence of an absorption around 3370 cm^{-1} .^{5–8} However, as long as the presence of the hydroxyl groups are judged from changes in dielectric losses of polyethylenes in the region of 500 MHz at room temperature, the hydroxyl groups do not seem to be contained in polyethylene molecular chains.

In this study, the possibility of the presence of hydroxyl groups in polyethylene molecular chains has been investigated on observations of infrared spectra of O—H and C—O stretching vibrations in olefinic molecular chains.

EXPERIMENTAL

High-, medium-, and low-pressure process polyethylene (HPPE, MPPE, and LPPE), *n*-paraffins, and *n*-alcohols with various molecular chain lengths were mainly used as specimens. The specimens of polyethylenes were made into films ~ 0.15 mm thick for infrared spectral measurements by hot pressing at 160°C

for 1 min. The measurements of characteristic absorptions of *n*-alcohols in the infrared region were carried out by use of films made by hot pressing powder of a polyethylene in which *n*-alcohols were added. The infrared spectra of *n*-paraffins were obtained from those in liquid at temperatures a few degrees above the melting points. The infrared spectra of specimens were obtained with a Shimadzu grating infrared spectrophotometer Model IR-27G and a JEOR Fourier transform spectrometer Model JIR-03F. The densities of the specimens were measured at 23°C with a density-gradient tube in which an isopropyl alcohol-water mixture was filled.

RESULTS AND DISCUSSION

The reasons why Cross et al.⁵ assigned the absorption band in the vicinity of 3600 cm^{-1} to the free hydroxyl groups in the infrared spectra of polyethylenes are as follows: (1) the absorption band of 3600 cm^{-1} is not observed in paraffins and olefins, (2) ethylene and catalyst used in polymerization of polyethylene are contained a very small amount of oxygen, and (3) the intensity of the absorption varies depending on grades of polyethylene. However, it is clear that paraffins have the absorptions similar in the infrared spectra between 3600 and 3200 cm^{-1} to those of polyethylenes, if measured accurately. Figure 1(A) shows infrared spectra in the region 4000–3200 cm^{-1} of a MPPE (Marlex 50) and *n*-paraffins with various molecular chain lengths. In the region 3600–3200 cm^{-1} the absorptions of 3434 and 3370 cm^{-1} are not only observed in the polyethylene but in *n*-paraffins. Williams and Mosher,⁷ on the basis of whose report Luongo⁶ assigned the absorption band of 3380 cm^{-1} to the hydroxyl groups, have described characteristic absorptions of alkyl alcohols of which the molecular structure is expressed in the molecular formulas of $\text{CH}_3(\text{CH}_2)_n\text{OH}$ ($n = 1 \sim 9$) and $\text{CH}_3(\text{CH}_2)_n\text{CH}(\text{OH})\text{CH}_3$ ($n = 1 \sim 5$). With increasing molecular chains of alkyl alcohols, the wavenumber of $\text{CH}_3(\text{CH}_2)_n\text{OH}$ seems to approach $\sim 3330 \text{ cm}^{-1}$ from the higher wavenumber side, and the wavenumber of $\text{CH}_3(\text{CH}_2)_n\text{CH}(\text{OH})\text{CH}_3$ to scatter in the range between 3380 and 3350 cm^{-1} . These facts are a poor basis for an assignment of the absorptions of 3434 and/or 3370 cm^{-1} in polyethylene to the hydroxyl groups in polyethylene molecular chains. The absorptions of 3434 and 3370 cm^{-1} are observed in any polyethylene used in this study. The intensity of each absorption in MPPE and LPPE is almost the same as that in HPPE.

On radical polymerization, such as HPPE and γ -radiation polymerization of ethylene in the presence of methanol, introduction of hydroxyl groups into polyethylene molecular chains may be possible; on catalytic polymerization, such as the medium- and low-pressure polymerizations of ethylene, impurities such as oxygen, water, and alcohol are catalyst poisons and even a small amount of these impurities markedly decreases polymer conversion because the impurities cause the loss of activity in the catalyst. It can be assumed that a part of the catalyst acts as an agent for the removal of catalyst poison and that the residue of the catalyst, which is exhausted for the removal of the poison, acts as an effective catalyst for the polymerization of ethylene; there is little possibility for hydroxyl groups to be contained in the molecular chains of fresh polyethylenes produced by the medium- and the low-pressure process. Granted that hydroxyl groups appear in polyethylene molecular chains though it is very difficult to

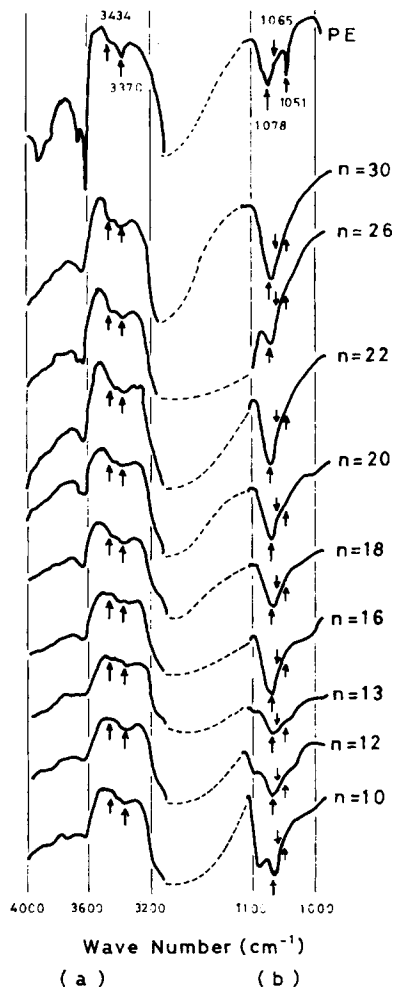


Fig. 1. Infrared spectra of polyethylene and n -paraffins $[\text{CH}_3(\text{CH}_2)_n\text{CH}_3]$ in the ranges 4000–3200 and 1100–1000 cm^{-1} .

consider such productions, those will be the primary hydroxyl groups considering the polymerization mechanism of LPPE and MPPE, and the amount of the groups in the polyethylenes will be extremely small because those act as the catalyst poisons. The behaviors of such hydroxyl groups are analogous to those in MPPE and/or LPPE containing a very small amount of high molecular n -alcohols.

Figure 2 shows wavenumber dependences of O—H stretching band of n -alcohols in a MPPE on the molecular chain length. The wavenumber assigned to the hydroxyl groups decreases with increasing the chain length and becomes constant over about 10 of carbon-atom number in the molecular chains, depending upon the concentration of the n -alcohol in the polyethylene. Figure 3 shows a wavenumber dependence of the O—H stretching band of an n -alcohol $[\text{CH}_3(\text{CH}_2)_{21}\text{OH}]$, of which the characteristic wavenumber does not depend upon the chain length on the concentration in a MPPE.

With decreasing concentration, the wavenumber assigned to the hydroxyl

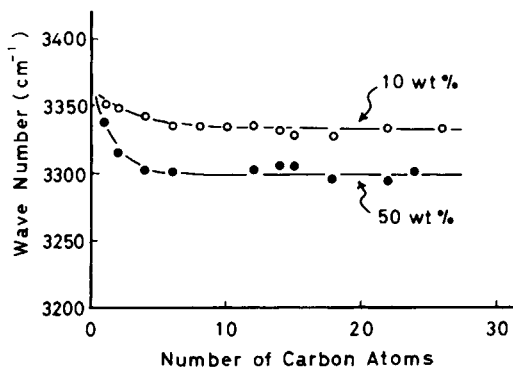


Fig. 2. Dependence of wavenumber of O—H stretching band of *n*-alcohols on the molecular chain length.

groups increases and then approaches a constant value, $\sim 3336 \text{ cm}^{-1}$, below the concentration of about 10 wt%. From those results, it is difficult to consider that the absorptions of 3434 and/or 3370 cm^{-1} are assigned to hydroxyl groups in polyethylene molecular chains.

It is generally known that the absorptions assigned to O—H stretching vibration of polymeric hydroxyl groups in alcohols are observed in the region $3400\text{--}3200 \text{ cm}^{-1}$, and that assigned to C—O stretching vibration in the region $1200\text{--}1000 \text{ cm}^{-1}$, especially the intensities of the absorptions assigned to the C—O stretching are strong and that of the primary hydroxyl groups are observed in the vicinity of 1050 cm^{-1} , that of the secondary in the vicinity of 1100 cm^{-1} , and that of the third in the vicinity of 1150 cm^{-1} . According to the idea described above, the absorptions assigned to hydroxyl groups might be observed in the region $1200\text{--}1000 \text{ cm}^{-1}$ even if the absorptions in the region $3400\text{--}3200 \text{ cm}^{-1}$ are not detected. Machi et al.⁹ have described that a part of the characteristic absorptions assigned to the primary hydroxyl groups in polyethylene molecular chains is observed in the vicinity of 1050 cm^{-1} in the examination of the infrared spectrum of polyethylene produced in the presence of methanol by γ -radiation polymerization. The characteristic absorptions in the region $1100\text{--}1000 \text{ cm}^{-1}$ of conventional polyethylenes appear at 1078 , 1065 , and 1051 cm^{-1} [top spectrum in Fig. 1(b)]. The absorptions of 1078 and 1065 cm^{-1} are assigned to the C—C

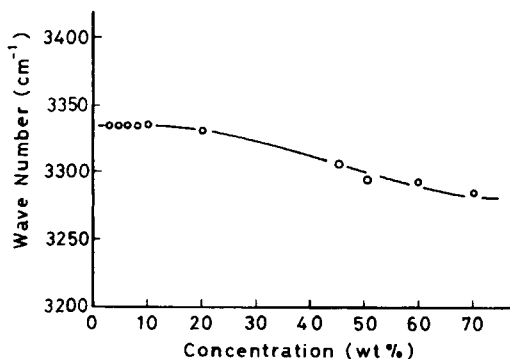


Fig. 3. Dependence of wavenumber of O—H stretching band of an *n*-alcohol $[\text{CH}_3(\text{CH}_2)_{21}\text{OH}]$ on the concentration in polyethylene.

stretching vibration of ethylene groups. The absorption at 1051 cm^{-1} is called a crystal band and the intensity of the absorption varies with the degree of crystallinity of polyethylene. If the absorption assigned to the hydroxyl groups in the molecular chains appears in the vicinity of 1050 cm^{-1} , it must be observed in the infrared spectra of paraffins that have similar absorptions in the region $3600\text{--}3200\text{ cm}^{-1}$ to that in polyethylene. The absorption, however, is not observed in the paraffins. Figure 1(b) shows the infrared spectra in the region $1100\text{--}1000\text{ cm}^{-1}$ of *n*-paraffins, which are melted because of elimination of the influence of the crystallinity on the spectra of the absorptions. As can be seen from the spectra, the absorption at $\sim 1050\text{ cm}^{-1}$ is not observed, although the absorptions in the region $3600\text{--}3200\text{ cm}^{-1}$ are observed.

For an estimation of changes in the infrared spectrum of polyethylene absorbing water, the infrared spectra in the region $3600\text{--}3200\text{ cm}^{-1}$ of *n*-pentadecane in which pure water was added were examined (Fig. 4). With increasing water in *n*-pentadecane, the absorption in the vicinity of 3434 cm^{-1} becomes broad and the intensity increases. However, the changes in the infrared spectra of polyethylene with the water absorption and drying treatments are not observed, as shown in Figure 5. The water absorbing capacity of conventional polyethylene is about 10 ppm at room temperature under atmospheric pressure; this fact indicates that the absorption in the vicinity of 3434 cm^{-1} of polyethylene does not change even if polyethylene absorbs water as much as 10 ppm. From these results, the absorption at 3434 cm^{-1} of conventional polyethylene is not considered to be that assigned to the absorption of water in polyethylene.

These facts suggest that the absorptions in the region $3600\text{--}3200\text{ cm}^{-1}$ are not those assigned to the hydroxyl groups in polyethylene molecular chains, but to vibrations due to more essential structure unit in polyethylene molecules such as those due to CH_2 groups and C—C stretching vibration in hydrocarbons. If the absorptions in the region $3600\text{--}3200\text{ cm}^{-1}$ are those assigned to the essential

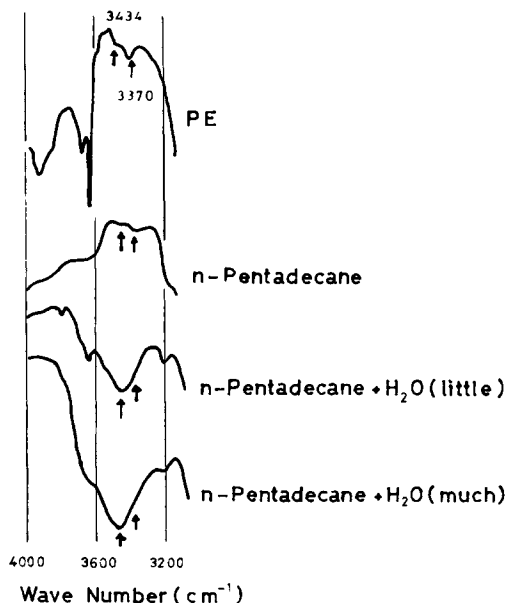


Fig. 4. Changes in infrared spectra of *n*-pentadecane added water.

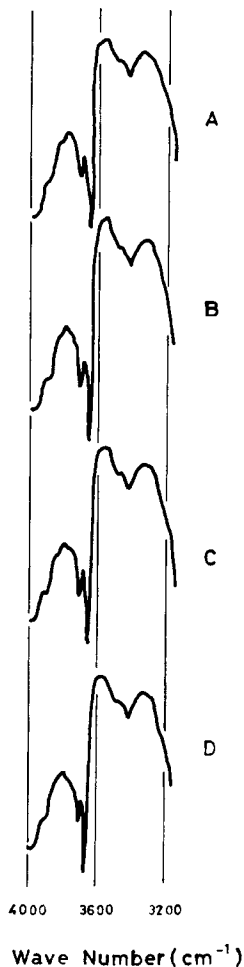


Fig. 5. Infrared spectra of polyethylene with drying and/or immersion-in-water treatments in the region $4000\text{--}3200\text{ cm}^{-1}$: (A) just after molding; (B) 23°C , 13 hr in water; (C) 80°C , 13 hr, 1 atm after (B); and (D) 80°C , 40 hr, 10^{-5} mm Hg after (C).

vibrations, those must have a certain relation of the extinction coefficients to those due to CH_2 groups and C—C stretching vibration in other absorption regions.

Comparable isolated absorptions among those essential vibrations in melted *n*-paraffins are observed at 1303 cm^{-1} assigned to CH_2 wagging vibration in the amorphous region and at 1078 cm^{-1} assigned to C—C stretching vibration in the amorphous region. Table I shows a comparison of the extinction coefficient at 3370 cm^{-1} with those at 1303 and 1078 cm^{-1} in melted *n*-paraffins. The ratios of those coefficients to 1303 and 1078 cm^{-1} are almost the constant, respectively. This fact leads to an idea that the absorption at 3370 cm^{-1} is assigned to that due to CH_2 group or C—C stretching vibration in the amorphous region.

The intensity of the absorption at 3434 cm^{-1} is weak and affected by the absorption at 3370 cm^{-1} . If the absorption at 3434 cm^{-1} , however, is assigned to the vibrations due to more essential structure unit in the molecules similarly to

TABLE I
Comparison of the Extinction Coefficient at 3370 cm^{-1} with those at 1301 and 1078 cm^{-1} in Melted *n*-Paraffins

Number of <i>n</i> in $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$	K_{3370}	K_{1303}	K_{1078}	K_{3370}/K_{1303}	K_{3370}/K_{1078}
30	1.34	22.9	7.88	0.058	0.17
26	1.20	21.2	8.09	0.057	0.14
22	1.29	22.3	8.34	0.058	0.16
20	1.19	20.7	7.67	0.058	0.16
18	1.16	20.3	7.23	0.057	0.16

the absorption at 3370 cm^{-1} , there must be a certain relation between the extinction coefficients of both absorptions. The relation was examined by use of polyethylenes in which changes in infrared spectra in the region 3600–3200 cm^{-1} with the absorption of water were negligible. Table II shows the ratios of both extinction coefficients in polyethylenes with various branching. The ratios are almost the constant, and this fact suggests that the absorption at 3434 cm^{-1} is ascribed to the essential motions due to the fundamental molecular structure of polyethylene such as C—C, CH, and CH_2 , although Nielsen et al.^{10,11} have assigned the absorption to ternary combination bands of CH_2 rocking, twisting, and wagging motions.

Although Luongo⁶ and Rugg et al.⁸ have described that with increasing oxidation of polyethylene the absorption at 3370 cm^{-1} increases and that the increase is ascribed to the increasing OH groups in polyethylene, if the absorption at 3370 cm^{-1} is not assigned to OH groups, how it is to be interpreted that the absorption in the vicinity of 3370 cm^{-1} increases with the oxidation? Figure 6 shows a change in the absorption in the vicinity of 3370 cm^{-1} with increasing 1-docosanol added in polyethylene. It is clear that with increasing content of OH groups the absorption at 3370 cm^{-1} does not increase, but that at 3336 cm^{-1} does. The detection of the difference in the wavenumber between the absorption at 3370 cm^{-1} and that appearing with increasing content of OH groups is possible with a Fourier transform infrared spectrometer, not with a grating infrared spectrometer. They are thought to mistake the increasing absorption in 3336 cm^{-1} to that at 3370 cm^{-1} because of poor resolutions of their infrared spectrometers.

TABLE II
Comparison of the Extinction Coefficient at 3434 cm^{-1} with that at 3370 cm^{-1} in Polyethylenes

Polyethylene grade	Density (g/cm^3)	K_{3434}	K_{3370}	K_{3434}/K_{3370}
1	0.915	0.712	1.24	0.57
2	0.921	0.713	1.28	0.56
3	0.926	0.647	1.12	0.58
4	0.930	0.711	1.25	0.57
5	0.938	0.801	1.42	0.57
6	0.949	0.880	1.58	0.56

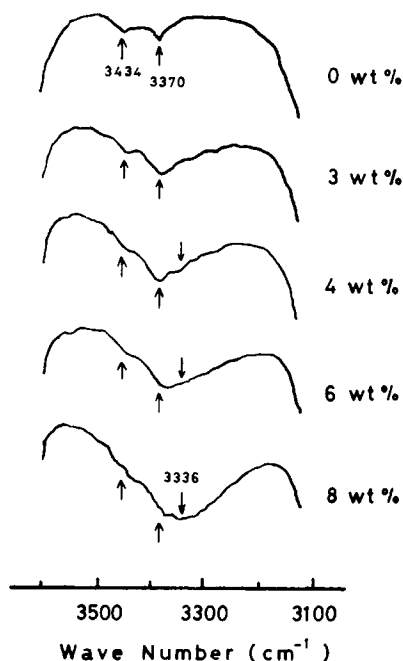


Fig. 6. Changes in infrared spectra of polyethylene in the vicinity of 3370 cm^{-1} with increasing 1-docosanol added in polyethylene.

CONCLUSIONS

From the facts described above, it may be concluded that the absorptions at 3434 and 3370 cm^{-1} of conventional polyethylenes, which have been hitherto thought to be due to hydroxyl groups, are not those due to the hydroxyl groups but those ascribed to the essential motions due to the fundamental molecular structure of polyethylene, and also that the hydroxyl groups in polyethylene molecular chains are not contained at least in the polyethylenes, which have almost the same intensities of absorptions at 3434 and 3370 cm^{-1} as those of fresh polyethylenes produced by the medium- or low-pressure process.

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