

# The Effect of Polar Groups on the Dielectric Loss of Polyethylene

YUKIHIKO SATO and TAKAMASA YASHIRO, *Electrical Communication Laboratories, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki, Japan*

## Synopsis

The dielectric loss tangent for polyethylene with low dielectric loss was approximated by  $\tan \delta = C_f \sum (n\mu^2)$ , where  $n$  and  $\mu$  are the number and dipole moment of polar groups, respectively, and  $C_f$  is a parameter. The type and number of polar groups in the polyethylenes were mainly determined from infrared spectra obtained with a Fourier transform spectrometer. It was found that the contribution of hydroxyl and carbonyl groups to  $\tan \delta$  was significantly large, but the contribution of double bond groups was less significant. The  $\tan \delta$  was observed to decrease with a decrease of methyl group density although the overall contribution of methyl groups to  $\tan \delta$  was small. This suggests that  $\tan \delta$  is closely related to the secondary structure of polyethylenes, thus indicating the methyl groups seem to play an important role in the secondary structure.

## INTRODUCTION

Although polyethylenes are commonly considered to be "nonpolar" polymers, they have very low dielectric losses because they contain few polar groups such as methyl groups, hydroxyl groups, carbonyl groups, and olefinic bonds, which arise in the process of polymerization and formation. The loss increases gradually with frequency over the range of 1 MHz–1 GHz and is due to  $\gamma$ -dispersion, which is considered to be maximal in the vicinity of 1 GHz. This fact is very important in the case of low dielectric loss materials suitable for the inner insulation of a submarine coaxial cable.

Carbonyl groups are the usual polar groups generally considered to contribute to the dielectric loss, but quantitative measurements of the loss is difficult because of the small concentration of such groups. However, Fourier transform infrared spectroscopy now makes possible quantitative studies of dielectric loss dependence on polar group concentration. In this paper, the extent of the polar groups and the dielectric loss in low-loss polyethylenes are measured, and the relations between them are discussed.

## THEORETICAL CONSIDERATION

The complex dielectric constant  $\epsilon^*$  is generally expressed in terms of the dielectric constant  $\epsilon'$  and of the dielectric loss factor  $\epsilon''$ , as follows:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (1)$$

Polar groups in plastics are considered to form a multiple relaxation system because each polar group will have various relaxation times. The dependence of  $\epsilon''$  on these relaxation systems may be expressed by the Cole-Cole rule as

$$\epsilon'' = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \cdot \frac{\sin (\beta\pi/2)}{\cosh \beta x + \cos (\beta\pi/2)} \quad (2)$$

where  $\epsilon_0$  and  $\epsilon_\infty$  are the limiting low- and high-frequency values, respectively;  $\beta$  is a parameter lying between 0 and 1 and is related to relaxation time dispersion (when  $\beta = 1$  the relaxation system reduces to the Debye type, that is, a single relaxation system); and  $x$  is given by  $x = \log(\omega\tau)$ , where  $\omega$  is circular frequency and  $\tau$  is the relaxation time. It is found from eq. (2) that  $\epsilon''$  has its maximum at the dispersion frequency. Therefore, the dielectric loss factor at the dispersion frequency,  $\epsilon''_{\max}$ , is expressed as

$$\epsilon''_{\max} = \frac{1}{2}(\epsilon_0 - \epsilon_\infty) \tan\left(\frac{\beta\pi}{4}\right) \quad (3)$$

According to eq. (3),  $\epsilon''_{\max}$  decreases with decrease in  $\beta$ . That is, the relaxation system of plastics may vary from a single relaxation spectrum to a multiple relaxation spectrum. Also, the magnitude of dielectric dispersion,  $\epsilon_0 - \epsilon_\infty$ , decreases with the decrease in  $\beta$ . Since the magnitude of  $\epsilon_0 - \epsilon_\infty$  is almost zero for low loss polyethylenes,  $\epsilon''$  is expected to be very small. As may be seen from the graphic expression of the Cole-Cole rule, the following relation may be established in an analogous manner:

$$\epsilon' \simeq \epsilon_\infty \simeq \epsilon_0 \quad (4)$$

Accordingly, the dielectric loss tangent  $\tan \delta$  for the polyethylenes may be expressed as follows:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \simeq \frac{\epsilon''}{\epsilon_0} \simeq \frac{\epsilon''}{\epsilon_\infty} \quad (5)$$

On the other hand,  $\epsilon_0 - \epsilon_\infty$  is expressed from the concept of Onsager's reaction field as follows:

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi}{3kT} \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3}\right)^2 N\mu^2 \quad (6)$$

where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $N$  is the number of polar groups per unit volume, and  $\mu^2$  is the mean-square value of the dipole moment of polar groups. In the case of polyethylene,  $N$  may be expressed as follows:

$$N = \frac{d}{M} N_A \frac{M}{14 \times 1000} n \quad (7)$$

where  $d$  is the density of the polyethylene,  $M$  is its molecular weight,  $N_A$  is Avogadro's number, and  $n$  is the number of polar groups per 1000 carbon atoms of main-chain polyethylene. We term  $n$  the "polar group density." By use of eqs. (2), (5), (6), and (7),  $\tan \delta$  for low-loss polyethylenes may be expressed as follows:

$$\begin{aligned} \tan \delta &\simeq \frac{\epsilon''}{\epsilon_0} \\ &\simeq \frac{2\pi}{kT} \cdot \frac{1}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_0 + 2}{3}\right)^2 \frac{dN_A}{14 \times 10^3} \frac{\sin(\beta\pi/2)}{\cosh \beta x + \cos(\beta\pi/2)} n\mu^2 \end{aligned} \quad (8)$$

By use of a parameter defined by the following equation,

$$C_f \equiv \frac{2\pi}{kT} \frac{1}{2\epsilon_0 + \epsilon_\infty} \left(\frac{\epsilon_0 + 2}{3}\right)^2 \frac{dN_A}{14 \times 10^3} \frac{\sin(\beta\pi/2)}{\cosh \beta x + \cos(\beta\pi/2)} \quad (9)$$

$\tan \delta$  can be expressed as follows:

$$\tan \delta = C_f n \mu^2$$

According to eq. (10),  $\tan \delta$  for the polyethylenes is proportional to the polar group density and mean square value of the dipole moment. Also, as seen from eq. (9),  $C_f$  increases with frequency to its maximum value at the dispersion frequency.

If it is permissible to extend the interpretation of eq. (10) to a multicomponent system,  $\tan \delta$  for polyethylenes containing various polar groups may be expressed as

$$\tan \delta = \sum_i (C_{fi} n_i \mu_i^2) \quad (11)$$

where  $C_{fi}$  may change with each type of polar group, but is most sensitive to  $\beta$  and  $\tau$ . If  $\beta$  is a parameter giving the degree of dispersion in a total system containing various polar groups and  $\tau$  does not change much between polar groups,  $C_{fi}$  may be assumed to be a constant independent of the type and density of polar groups. Consequently,  $\tan \delta$  for polyethylenes may be expressed as

$$\tan \delta = C_f \sum_i (n_i \mu_i^2) \quad (12)$$

That is, the contribution of polar groups to  $\tan \delta$  can be obtained from the polar group density and the dipole moment of the polar groups, or  $C_f$  can be obtained from  $\tan \delta$ ,  $n$ , and  $\mu$ .

## EXPERIMENTAL

### Polyethylene

The polyethylenes used in this work had low dielectric losses and were polymerized under different conditions. The specimens are listed in Table I. There are four low-density (samples 1-4) and eight high-density polyethylenes (samples 5-12). These samples were made into films about 0.15 mm thick for infrared spectral measurements and about 1 mm thick for dielectric measurements by hot pressing powder or pellets of the polyethylenes at 160°C for 1 min.

### Infrared Spectrum

The infrared spectra of the samples were obtained with a Shimadzu grating infrared spectrophotometer Model IR-27G and a JEOR Fourier transform spectrometer Model JIR-03F. Liquid cells approximately 25 and 50  $\mu\text{m}$  thick with KBr windows were used to measure the low molecular weight standard compounds for the calibration curves. Standard compounds in solid form at room temperature were heated above their melting points before measurement.

The intensities of the infrared absorption bands for standard compounds having strong absorption bands were obtained by diluting the compounds with *n*-pentadecane or *n*-hexadecane since these diluents hardly show any absorption at the characteristic absorption bands of carbonyl and vinyl groups.

TABLE I  
 Polyethylene Samples

Sample		Density	$\epsilon^a$	$MI$	$\bar{M} \times 10^{-4},^b$	Additives	
Type	No.						
LDPE	{	1	0.923	2.28	0.11	4.0	unknown
		2	0.923	2.28	0.12	3.9	unknown
		3	0.928	2.29	0.20	3.8	unknown
		4	0.929	2.29	0.14	3.9	unknown
HDPE	{	5	0.951	2.34	5.0	5.2	unknown
		6	0.950	2.34	5.0	5.2	unknown
		7	0.945	2.33	0.30	9.7	nothing
		8	0.952	2.34	0.34	9.4	nothing
		9	0.955	2.35	1.31	7.0	nothing
		10	0.948	2.33	0.28	9.8	unknown
		11	0.933	2.30	0.17	11.	unknown
		12	0.934	2.30	0.25	10.	nothing

<sup>a</sup> Calculated from  $\epsilon = 2.276 + 2.01(d - 0.9200)$ ,<sup>1</sup> where  $\epsilon$  is the dielectric constant and  $d$  is density.

<sup>b</sup> Calculated from  $^2\bar{M}_n = (0.654 \log MI - 3.33) \times 10^4$  for LDPE and from  $^3\bar{M}_v = (4.07 - 0.22 \log MI) \times 10^4$  for HDPE, where  $\bar{M}_n$  is number-averaged molecular weight and  $\bar{M}_v$  is viscosity-average molecular weight.

### Calibration Curves

The types of polar groups contained in the polyethylenes used in this work were determined from the infrared spectra. The polar groups so identified were mainly carbonyl, hydroxyl, vinyl, vinylidene, *trans*-vinylene, and methyl. The absorption coefficient for each polar group density was obtained by use of standard compounds. Details are discussed below.

**Carbonyl Group.** Although various types of carbonyl groups might be contained in polyethylenes,<sup>4</sup> ketonic and aldehydic types were these mainly observed in the polyethylenes used.

(a) *Ketonic Type:* Standard compounds the ketonic-type groups were *n*-amyl ethyl ketone,  $\text{CH}_3(\text{CH}_2)_4\text{CO}(\text{CH}_2)\text{CH}_3$ ; *n*-octyl ethyl ketone,  $\text{CH}_3(\text{CH}_2)_7\text{CO}(\text{CH}_2)\text{CH}_3$ ; and di-*n*-butyl ketone,  $\text{CH}_3(\text{CH}_2)_3\text{CO}(\text{CH}_2)_3\text{CH}_3$ . The characteristic absorption assigned to the carbonyl groups in these compounds appeared to wave number  $1722 \text{ cm}^{-1}$ . This absorption was assumed to correspond to the absorption at  $1719 \text{ cm}^{-1}$  in the polyethylenes. The characteristic absorption assigned to the carbonyl groups was very strong and required dilution in *n*-hexadecane.

(b) *Aldehydic Type:* Standard compounds of the aldehydic-type groups used were *n*-heptyl aldehyde,  $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ ; *n*-octyl aldehyde,  $\text{CH}_3(\text{CH}_2)_6\text{CHO}$ ; *n*-nonyl aldehyde,  $\text{CH}_3(\text{CH}_2)_7\text{CHO}$ ; *n*-decyl aldehyde,  $\text{CH}_3(\text{CH}_2)_8\text{CHO}$ ; and dodecyl aldehyde,  $\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$ . The absorption assigned to the carbonyl groups in these compounds appeared at  $1730 \text{ cm}^{-1}$ , the same value found for the polyethylenes. Also, *n*-pentadecane was used as a diluent as necessary.

**Hydroxyl Group.** Cross et al.<sup>5</sup> found that the absorption of the hydroxyl groups appears near  $3360 \text{ cm}^{-1}$ . Luong<sup>4</sup> found the hydroxyl absorption at  $3380$  or  $3388 \text{ cm}^{-1}$ . Anderson's<sup>6</sup> value was  $3340 \text{ cm}^{-1}$ . The absorption assigned to the hydroxyl groups appeared at  $3370 \text{ cm}^{-1}$  for the polyethylenes. The standard compounds were *n*-tetradecanol,  $\text{CH}_3(\text{CH}_2)_{13}\text{OH}$ ; and 1-octadecanol,  $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$ .

**Vinyl Group.** 1-Decene,  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}_2$ ; 1-tridecene,  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}_2$ ; 1-hexadecene,  $\text{CH}_3(\text{CH}_2)_{13}\text{CH}=\text{CH}_2$ ; and 1-octadecene,  $\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$ , were used as vinyl group standards. The characteristic absorptions assigned to the groups appeared at  $909\text{ cm}^{-1}$  and were in agreement with the absorption in the polyethylenes. *n*-Hexadecane was used as a diluent because of the strong absorptions.

**Vinylidene Group.** 2-Ethyl-1-butene,  $\text{CH}_3(\text{CH}_2)\text{C}(\text{C}_2\text{H}_5)=\text{CH}_2$ ; 2-ethyl-1-hexene,  $\text{CH}_3(\text{CH}_2)_3\text{C}(\text{C}_2\text{H}_5)=\text{CH}_2$ ; and 2-methyl-1-heptene,  $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{CH}_3)=\text{CH}_2$ , were used as standards. The absorptions assigned to the vinylidene groups appeared at  $888\text{ cm}^{-1}$  in 2-ethyl-1-butene and 2-ethyl-1-hexene, and at  $886\text{ cm}^{-1}$  in 2-methyl-1-heptene. These absorptions were assumed to correspond to the absorption of  $888\text{ cm}^{-1}$  in the polyethylenes. *n*-Hexadecane was used as a diluent.

**trans-Vinylene Group.** *trans*-3-Nonene,  $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)\text{CH}_3$ ; and *trans*-4-nonene,  $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$ , were used as standards. The characteristic absorption found for *trans*-vinylene in these compounds appeared at  $966\text{ cm}^{-1}$  and was assumed to correspond to the absorption of  $965\text{ cm}^{-1}$  in the polyethylenes.

**Methyl Group.** The intensity of the absorption was calculated from the absorption of  $1378\text{ cm}^{-1}$  based on  $1303\text{ cm}^{-1}$  with the same procedure used by Shirayama.<sup>7</sup> The standard compounds used are listed in Table II.

### Dielectric Loss Measurements

The dielectric losses of the polyethylenes were measured at frequencies of 10, 50, and 500 MHz by the previously published method.<sup>8</sup> The measurements were made at  $20^\circ\text{C}$  in an atmosphere of 60% R.H.

### RESULTS AND DISCUSSION

The calibration curves for the polar groups are shown in Figure 1. Table III shows the polar group density for each specimen calculated from these calibration curves. From these calculations it was generally found that the density of carbonyl groups in high-density polyethylenes is greater than in low-density polyethylenes. The polar group density of the aldehydic type is greater than the ketonic type for all specimens. This indicates that most of the carbonyl groups in polyethylenes are located at the end of the polymer chains. The density of

TABLE II  
Standard Compounds for Methyl Groups

<i>n</i> -Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$
<i>n</i> -Docosane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$
<i>n</i> -Tetradecane	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$
<i>n</i> -Pentadecane	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$
<i>n</i> -Hexadecane	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$
<i>n</i> -Octadecane	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$
<i>n</i> -Eicosane	$\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3$
<i>n</i> -Docosane	$\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$
<i>n</i> -Tetracosane	$\text{CH}_3(\text{CH}_2)_{22}\text{CH}_3$
<i>n</i> -Octacosane	$\text{CH}_3(\text{CH}_2)_{26}\text{CH}_3$
<i>n</i> -Dotriacontane	$\text{CH}_3(\text{CH}_2)_{30}\text{CH}_3$

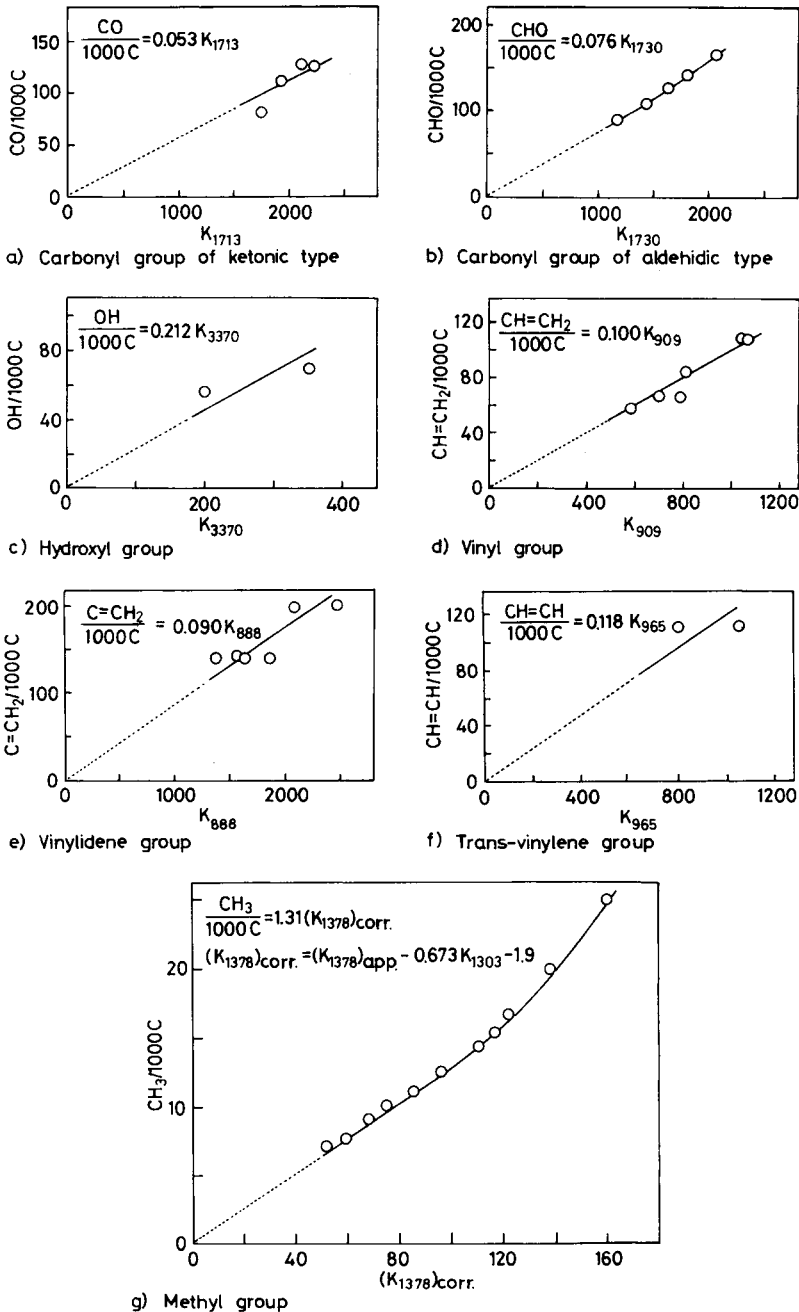


Fig. 1. Calibration curves for the polar groups in polyethylene.

the hydroxyl groups is about 10 times that of the carbonyl groups, and the density of the hydroxyl groups in the low-density polyethylenes is almost the same as in the high-density polyethylenes, no matter what the polymerization method. This fact may suggest that the hydroxyl groups in polyethylenes are mainly caused by very small amounts of impurities such as water and oxygen gas in the ethylene gas used for both polymerization methods.

TABLE III  
 Number of Polar Groups per 1000 Main-Chain Carbon Atoms in Polyethylene

Sample Type	Sample No.	Carbonyl		Hydroxyl	Vinyl	Double bond groups		Methyl
		Ketonic	Aldehydic			Vinylidene	<i>trans</i> -Vinylene	
LDPE	1	0.029	0.050	0.275	0.254	0.241	0.041	36.8
	2	0.039	0.065	0.291	0.111	0.315	0.567	36.5
	3	0.019	0.057	0.368	0.032	0.797	0.031	26.0
	4	0.090	0.123	0.246	0.096	0.156	0.028	24.3
HDPE	5	0.014	0.026	0.238	1.73	0.107	0.012	2.7
	6	0.012	0.028	0.306	1.24	0.056	0.009	0.0
	7	0.011	0.036	0.332	0.861	0.107	0.026	3.1
	8	0.005	0.018	0.762	0.697	0.259	0.078	8.0
	9	0.100	0.146	0.332	0.886	0.154	0.098	5.7
	10	0.025	0.053	0.330	0.776	0.104	0.0	5.5
	11	0.027	0.115	0.264	0.674	0.143	0.017	15.1
	12	0.029	0.046	0.351	0.659	0.162	0.0	13.9





6	50	28	20.9	6.8	15.4	65.9	11.3	0.5	0.1	0.0
	500	44	32.8							
7	10	20	13.8							
	50	29	20.0	5.6	18.4	66.3	7.3	0.9	0.2	1.4
	500	45	31.1							
	10	30	11.8							
8	50	41	16.1	1.4	5.2	86.4	3.4	1.2	0.4	2.0
	500	59	23.2							
	10	24	8.06							
	50	37	12.4	24.9	36.3	32.3	3.7	0.6	1.1	1.2
9	500	56	18.8							
	10	27	16.1							
	50	39	23.3	11.1	23.4	57.0	5.7	0.8	0.0	2.1
	500	59	35.2							
10	10	52	25.8							
	50	76	37.7	10.1	42.2	37.9	4.1	0.9	0.1	4.8
	500	82	40.7							
	10	22	12.5							
11	50	50	28.5	12.1	19.3	57.8	4.6	1.1	0.0	5.1
	500	58	33.0							

<sup>a</sup> Dipole moments  $\mu$  ( $\times 10^{-18}$ ) used were 2.72 for ketone,<sup>9</sup> 2.72 for aldehyde,<sup>9</sup> 1.70 for hydroxyl,<sup>10</sup> 0.35 for benzyl,<sup>11</sup> 0.35 for vinylidene,<sup>11</sup> 0.35 for *trans*-vinylene,<sup>11</sup> and 0.08 for methyl groups.<sup>12</sup>

The density of the vinyl groups in high-density polyethylenes is greater than in the low-density polyethylenes in general. It may be seen that the density of the vinyl groups in low dielectric-loss polyethylenes such as samples 5 and 6 is considerable greater than in low-density polyethylenes. This seems to indicate a difference between the polymerization methods. The densities of the vinylidene groups and of the *trans*-vinylene groups in the high- and low-density polyethylenes are almost the same. The density of the *trans*-vinylene groups is the lowest among those of the polar groups containing double bonds. The density of methyl groups in the high-density polyethylenes is less than in the low-density polyethylenes, as is generally known. Although some of the high-density polyethylenes contained many methyl groups in comparison with the other high-density polyethylenes, these high-density polyethylenes may be copolymers made from ethylene and a small amount of  $\alpha$ -olefin such as propylene, due to the manufacturing method of generally available high-density polyethylenes.

The dielectric loss tangents for the polyethylenes used are shown in Table IV. Generally speaking, it is found that the dielectric losses for the high-density polyethylenes are smaller than those for the low-density polyethylenes. The commercial polyethylenes with low dielectric loss contain a small amount of thermal stabilizers (less than 0.1 wt-%). Although the stabilizers may affect the loss, there are some excellent stabilizers such as 2,6-di-*t*-butyl-*p*-cresol (commercial name Antage BHT) and 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxy-benzyl)benzene (commercial name Ionox 330). The influence of the stabilizer content on  $\tan \delta$  was investigated by use of Antage BHT. As seen from Figure 2, the stabilizer has little influence on  $\tan \delta$ . Thus, the polyethylenes which are assumed to contain the stabilizer are not influenced by the stabilizer since its effect is within experimental error. If  $\tan \delta$  is insensitive to the small amount of water in polyethylenes, it may be concluded that  $\tan \delta$  is primarily due to polar groups.

On the basis of these assumptions, the relation between  $\tan \delta$  and the polar groups was estimated. Table IV shows the rates of contribution of each polar group to  $\tan \delta$ , which are calculated [eq. (12)] by use of the polar group densities in Table III and the published values<sup>9-12</sup> of the dipole moments. Also, the values of the parameter  $C_f$  for the polyethylenes polymerized under different conditions were calculated from eq. (12) by use of the loss, the polar group densities, and the dipole moments. As seen from Table IV, the contribution of the hydroxyl groups to the dielectric loss is very large, although the dipole moment of the hydroxyl groups is smaller than that of the carbonyl groups. It has been assumed that the contribution of the carbonyl groups to the loss is the largest among the polar groups in the polyethylenes. The effect of the double bond groups is not as great as expected because their polar group density is small. The vinyl polar groups have the most and the *trans*-vinylene groups have the least effect on  $\tan \delta$  of all the double bond groups. The rate of contribution of the methyl groups to the loss is comparatively small even though these groups are present in the greatest amount.

The parameter  $C_f$  increases with frequency within the limits of the frequencies measured, as expected from eq. (9). The  $\gamma$ -dispersion frequency of polyethylenes is considered to be near 1 GHz. But  $C_f$  calculated from eq. (12) decreases with the decrease in the dielectric loss. Figure 3 shows an example of the relation

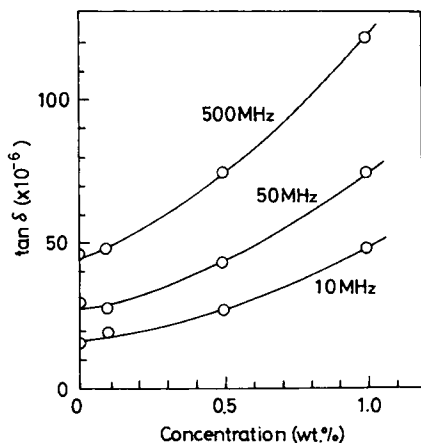


Fig. 2. Dependence of a thermal stabilizer on  $\tan \delta$ . Thermal stabilizer, 2,6-di-*t*-butyl-*p*-cresol; base polymer, sample no. 7.

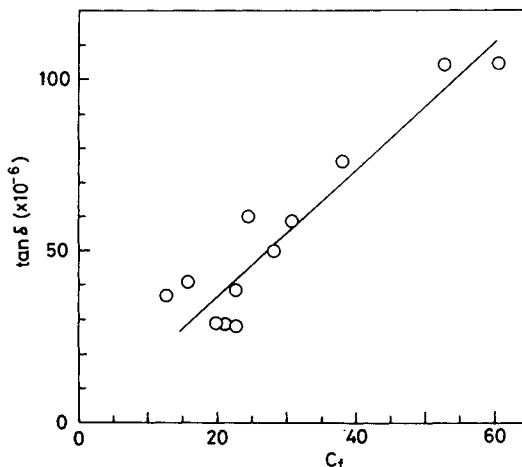


Fig. 3. Relation between  $C_f$  and  $\tan \delta$  at 50 MHz.

between  $C_f$  and  $\tan \delta$ . The theory which relates  $\tan \delta$  to  $C_f$  implicitly assumed a homogeneous isotropic dielectric medium, and the calibrations were carried out under this assumption. We tested this assumption by comparing the value of  $\beta$  computed from  $C_f$  via eq. (9) with values for general thermoplastics. Our computed values ( $\beta \approx 0.01$ ) are much smaller than the general thermoplastic values. If the polyethylenes used in this work have  $\beta$  values similar to those of general thermoplastics, values of  $n$  and/or  $\mu$  for the polyethylenes must be smaller than those used in the above computations. The computed values of  $\beta$  make the homogeneous isotropic assumption questionable.

The absorption bands of the infrared spectra used to calculate the polar group density are independent of the degree of crystallinity in the polyethylenes. Thus, the polar group density is assumed to be composed of both crystalline and amorphous regions in the polyethylenes. The polar groups in the crystalline region cannot be as readily oriented as those in the amorphous region since  $\gamma$ -dispersion for polyethylenes is due to orientation of polar groups. Also, the polar groups in the amorphous region in solid polyethylenes cannot move as easy as

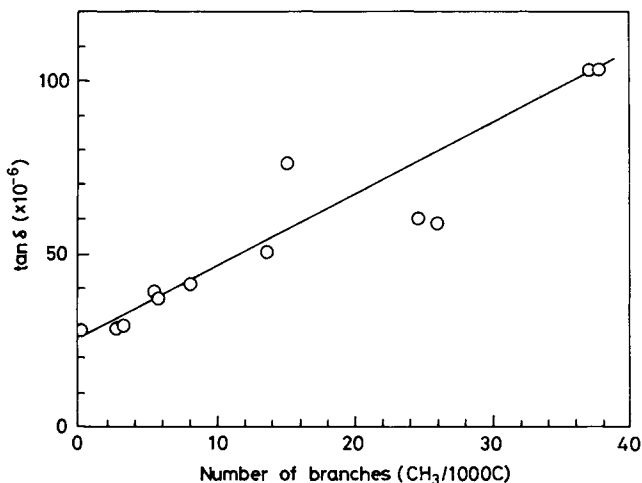


Fig. 4. Relation between dielectric loss at 50 MHz and methyl group density.

the groups contained in similar low molecular weight compounds in the gaseous or liquid phases. If the values of  $n$  and  $\mu$  are determined after consideration of the influence of factors such as the effect of the amorphous region, defects in the crystalline region, and hindrance of rotation of the dipoles, the values of  $n_i$  and  $\mu_i$  in eq. (12) will be less than those used in the computation. Thus, the values of  $\beta$ , for thermoplastics and polyethylenes will be in agreement. This suggests that  $\tan \delta$  will be closely related to the secondary structure of the polyethylenes.

One of the most important factors changing the secondary structure is branching. The methyl group density may be regarded as a parameter of the branching in polyethylenes because most endgroups located at branches are assumed to be methyl groups. Thus, the relation between methyl group density and  $\tan \delta$  was investigated. As seen from Figure 4,  $\tan \delta$  depends linearly on the methyl group density. This dependence appears to be larger than the rate of the contribution of the methyl groups to the loss shown in Table III. Therefore, methyl groups may play a more important role in changing the secondary structure than in changing the dipole moment. More investigations are necessary to verify this possibility.

## CONCLUSIONS

Endeavors to decrease the dielectric loss of polyethylenes in the very high frequency (VHF) region have mainly been in the direction of decreasing polar groups such as methyl and carbonyl groups in polyethylenes. Little attention has been devoted to the secondary structure of polyethylenes. This investigation indicates that the polyethylene structure may be as important as the polar groups. It is concluded that one of the ways to decrease the dielectric loss for polyethylenes in the future will be to decrease hydroxyl and carbonyl groups. Reduction of secondary structure may also reduce the dielectric loss.

The authors would like to thank the Japan Electron Optics Laboratory Co. Ltd. for the Fourier transform infrared spectrometer and the Showa Yuka k.k., the Nissan Chemical Industries Ltd., the Ube Industries Ltd., and the Nippon Unicar Co. Ltd. for polyethylenes.

### References

1. v. H. Lanza and D. B. Herrman, *J. Polym. Sci.*, **28**, 622 (1958).
2. C. A. Sperati, W. A. Frantu, and H. W. Starkweather, *J. Am. Chem. Soc.*, **75**, 6127 (1953).
3. T. Ota, A. Takahashi, and K. Nakayama, *Polyethylene*, Nikkan Kogyo Press, Tokyo, 1962, p. 130.
4. J. P. Luong, *J. Polym. Sci.*, **42**, 139 (1960).
5. L. H. Cross, R. B. Richards, and H. A. Willis, *Discuss. Faraday Soc.*, **9**, 235 (1950).
6. J. A. Anderson, Jr., and W. D. Seyfried, *Anal. Chem.*, **20**, 998 (1948).
7. K. Shirayama, T. Okada, and S. Kita, *J. Polym. Sci.*, **3**, 907 (1965).
8. M. Tokuda and M. Kawase, Measurements of Low Dielectric Loss Materials at VHF~UHF Band, The Material for the Study Group of the Institute of Electronics and Communication Engineers of Japan, Material No. CPM 72-32. 1972.
9. H. A. Stuart, *Molekülstruktur*, 1934, p. 130.
10. J. B. Miles, *Phys. Rev.*, **34**, 964 (1924).
11. R. C. Weast, S. M. Selby, and C. D. Hodgman (Eds.), *Handbook of Chemical and Physics*, 1964, p. E-38.
12. D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

Received March 29, 1976

Revised February 17, 1977