関税中央分析所報　第33号　1994

Note

Determination of average degree of polymerization of polyethylene glycol by infrared spectrometry

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A simple and rapid method for determining the average degree of polymerization of polyethylene glycol (PEG) was developed utilizing IR spectrometry. Two absorption bands at near 940cm^{-1} and 880cm^{-1} were selected as the characteristic bands for the determination of the average degree of polymerization of PEG. The relation between the intensity ratio of their absorption bands and the degree of polymerization of oligoethylene glycols exhibits a good linearity. It was found that this spectrometry could be used for the determination of the average degree of polymerization of PEG at regional customs laboratories.

1　Introduction

PEG have been widely used as raw materials and intermidiates in chemical industries to produce surface active agents, polishes, waxes and other chemical products. In the present HS－based Customs Tariff Schedule, the classification of PEG depend on the average number of repeating monomer units of ethylene glycol in the molecule.Those mixtures with an average of repeating less than five monomer units are classified in Chapter 38. On the other hand, those mixtures with an average of five or more monomer units are classified in Chapter 39. Thus, the determination of the average number of repeating monomer units（average degree of polymerization）is required for HS classification.

At present, the determination of the average degree of polymerization of polyethers are usually achieved by gas chromatography (GC) [1], gel permeation chromatography (GPC) [2, 3], thin layer chromatography（TLC）, or infrared spectrometery (IR) [4, 5]. Gas chromatography－mass spectrometry（GC－MS）is also sometimes used. The GC and TLC require the identification of indivisual component after separation. The GPC method requires the use of a specialized column and instrument for separation. GC－MS instrument is more expensive than other instruments. In order to finding a simpler and more rapid method for the determining the average degree of polymerization of PEG, we examined by infrared spectrometry.

2　Experimental

2．1　Standard substance

Tri－, penta－, and hexa－ethylene glycol were purchased from Aldrich Co.. Tetraethylene glycol was purchased from Tokyo Kasei Industry Co..Polyethylene glycols (PEG Mw 200and300) were purchased from Wako Jyunyaku Co.. Heptaethylene glycol was obtained by separation from other components of PEG 300 by recycling separation mode in GPC.

2．2　Apparatus

2．2．1　Infrared spectrometer

Japan spectroscopic Co. Ltd., Model JASCO IR 700 version 200,

2．2．2　Gel permeation chromatograph

Japan Analytical Industry Co. Ltd., Model LC－200

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2．3 Procedures

2．3．1 Separation and purification of heptaethylene glycol

PEG 300 was dissolved in chloroform to obtain a 5% solution. The solution was injected to gel permeation chromatograph to separate its components. The heptaethylene glycol—rich component was obtained by recycling separation mode in GPC.

2．3．2 Measurement of absorption intensity ratio in lR spectrometry

The infrared spectra were measured by sandwich method with KBr plate. The thikness of sample was adjusted to obtain transmittance between 20% to 80% in the 1000cm^{-1} to 800cm^{-1} region.

3 Results and Discussion

3．1 Separation and purification of heptaethylene glycol by recycling GPC

Since heptaethlylene glycol could not be obtained as a pure substance, this compound was prepared from PEG 300 by recycling and repeating separation mode in GPC. The chromatograms of PEG by GPC separation are shown in Fig. 1. Fig. 1 shows incomplete resolution chromatograms of mixed components.

Finally, we obtained about 50 mg heptaethylene glycole by this method. The purity of heptaethylene glycol was confirmed by GC method to be more than 95%.

3．2 Selection of characteristic infrared absorption bands

First, we carried out the selection of characteristic infrared absorption bands for the determination of the average degree of polymerization of PEG. The infrared spectrum of heptaethylene glycol PEG is shown in Fig. 2. As shown in Fig. 2, the spectrum exhibits the strong absorption bands due to OH stretching vibration in the near 3400cm^{-1}, CH_2 stretching vibration in the near 2950cm^{-1}, CH_2 bending vibration in the near 1450cm^{-1}, C—O—C stretching vibration in the 1100cm^{-1}, CH_2 rocking vibration in the near 940cm^{-1} and CH_2 wagging vibration in the 880cm^{-1} [4]. Although the infrared spectra of tri—, tetra—, penta—, hexa—and heptaethylene glycols gave similar spectral patterns, its seemed that the absorption intensity ratio (absorbance ratio) at near 940cm^{-1} to 880cm^{-1} in the spectra relate to the degree of polymerization in these compounds.

Accordingly, the two absorption bands (near 940cm^{-1} and 880cm^{-1}) selected as the characteristic bands for determining the average degree of polymerization of PEG (Fig. 3).

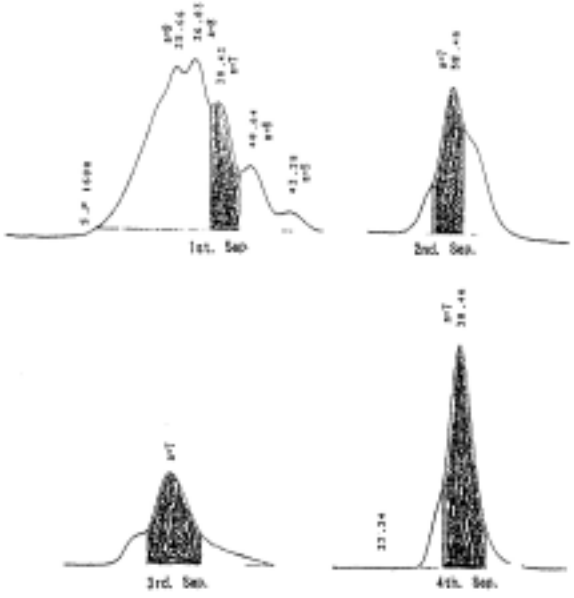

Fig. 1 Separation of polyethylene glycol (Mw 300) by recycling Gel Permeation Chromatography for obtain hepta ethylene glycol
Separation condition
Colnmn : JAIGEL 1 HF
Eluent : CHC 1 $_3$
RI detector : 100
UV detector : 1.0 (FS) 254 nm
Flow rate : 3.5 ml／min.
Pressure : 45 kg／cm^2
Chart speed : 5 ml／min.

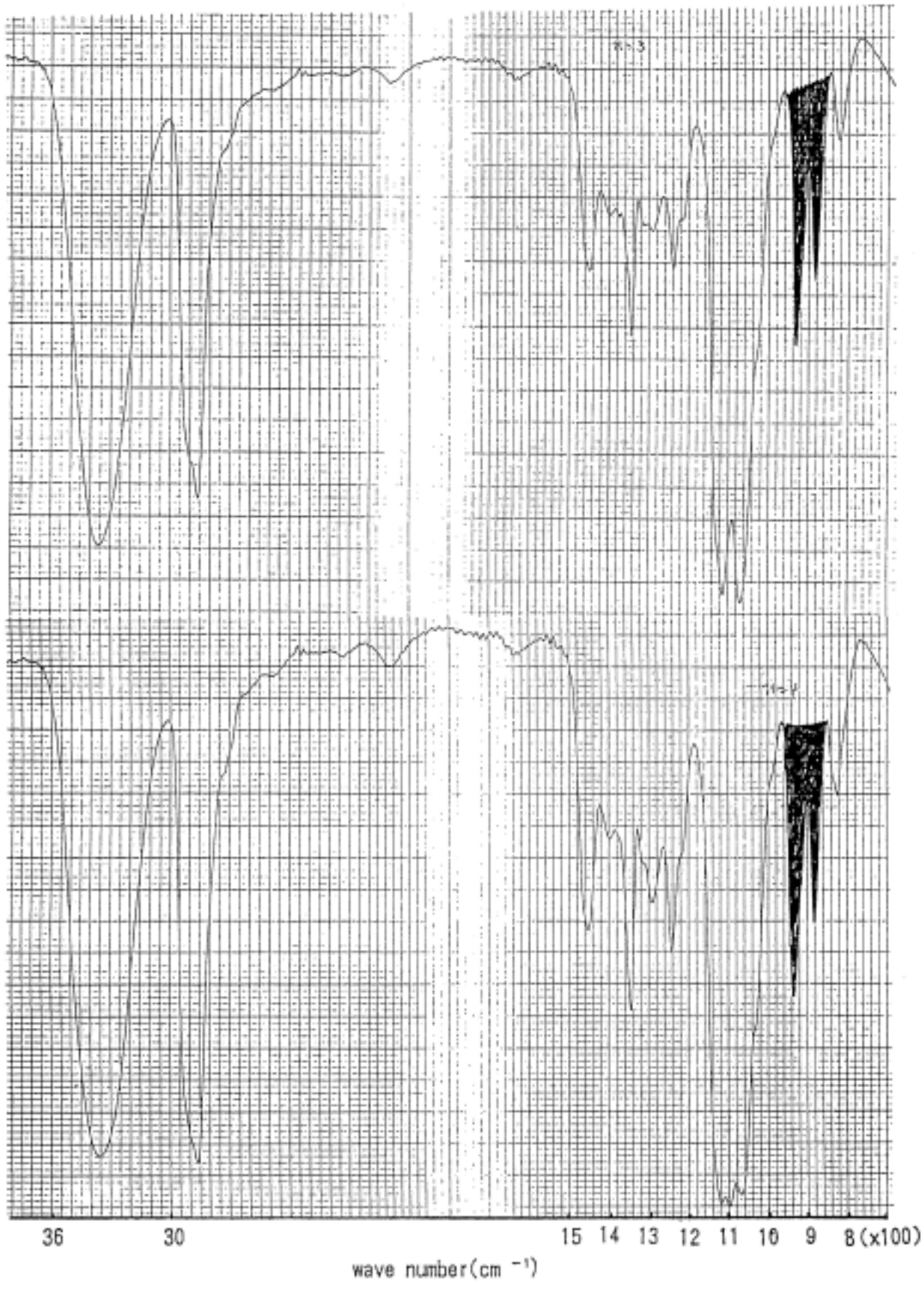

Fig. 2　Infrared spectra of tri and tetraethylene glycol
(A)：Triethylene glycol,　(B)：Tetraethylene glycol

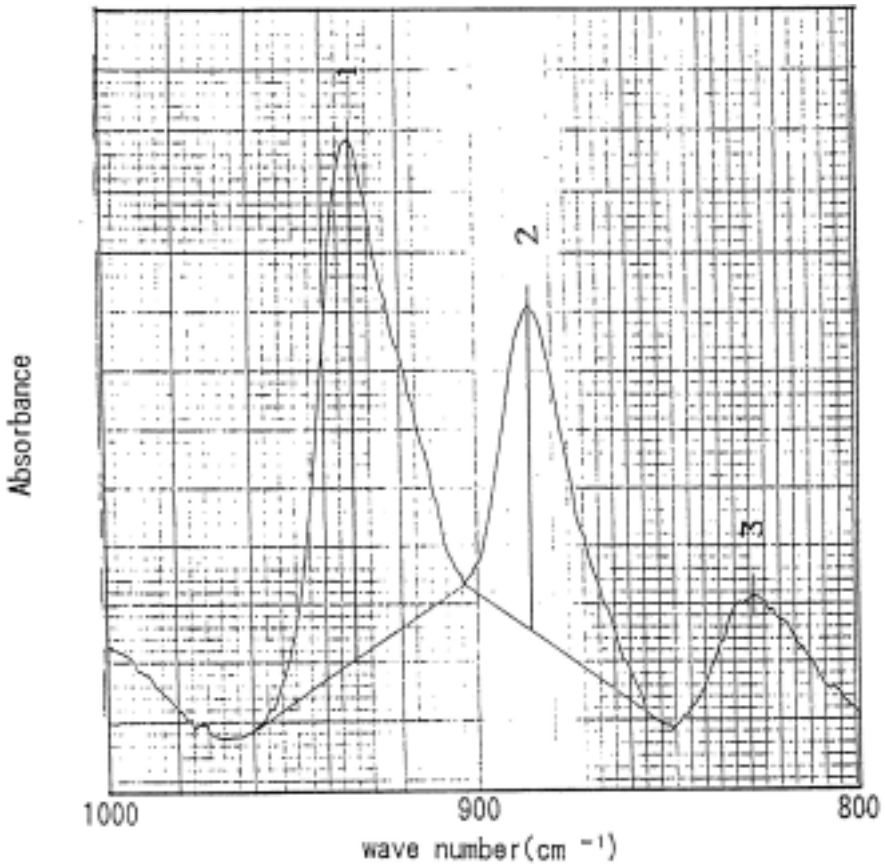

Fig. 3 Infrared spectrum of triethylene glycol in the 1000—800cm^{-1} region

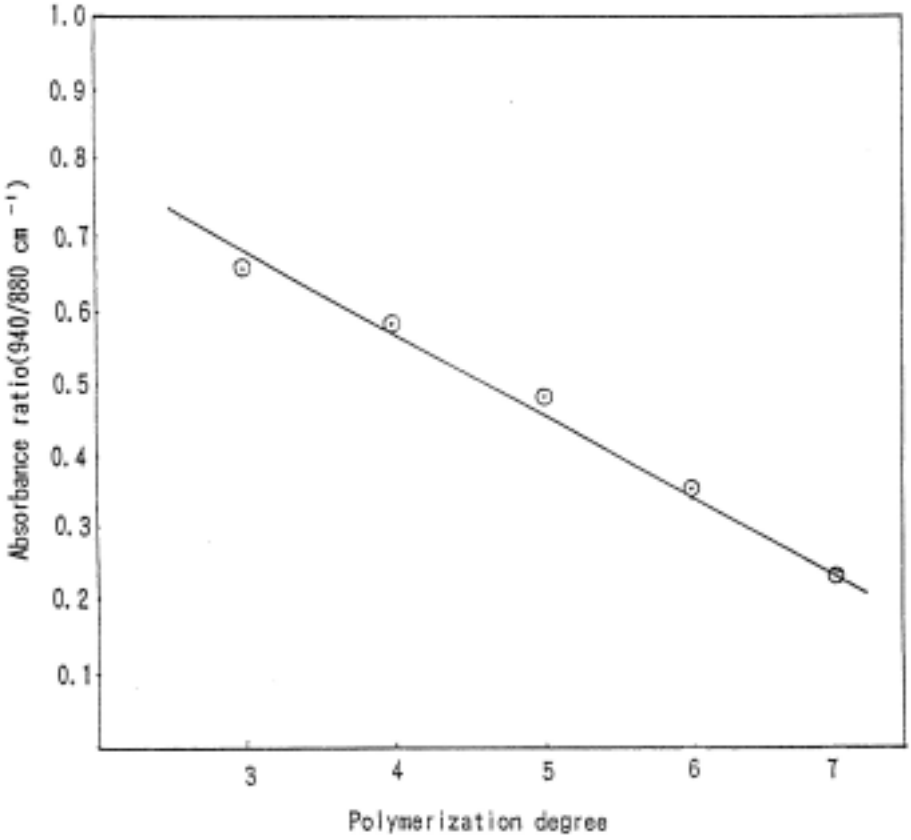

Fig. 4 Relationship between the ratio of absorbance intensity and the polymerization degree of oligoethylene glycols.

3.3 Correlation between the absorbance ratio and the average degree of polmerization.

The measurement results of the absorbance ratio of the degree of polmerization of each oligoethylene glycol which consist of different units of ethylene glycol are shown in table 1. Table 1 shows that the reproducibility in 5 measurements was within the range of 5% as coefficient of variation. The correlation between the absorbance ratios and the degree of polymerization of each oligoethylene glycol is shown in Fig. 4.

Table 1　The relative intensities ratio of IR absorption bands 940cm^{-1} to 880cm^{-1} in oligoethylene glycols

No	n=3	n=4	n=5	n=6	n=7
1.	0.65	0.56	0.49	0.35	0.24
2.	0.65	0.59	0.48	0.35	0.23
3.	0.65	0.59	o.48	0.37	0.24
4.	0.65	0.60	0.50	0.39	0.25
5.	0.66	0.60	0.50	0.38	0.25
Av	0.65	0.58	0.49	0.37	0.24
CV	0.77	2.81	2.04	4.87	3.61

The relation between the absorbance ratio and the degree of polymerization of oligoethylene glycol exhibited a good linearity, as shown in Fig.4. The correlation equation is as follows：

Y＝0.981－0.103 N, R＝0.9924

Where Y＝Absorbance ratio,

N＝the degree of polymerization,

R：Correlation coefficient

3．4 Application to actual samples

The above－mentioned methods were applied to the determination of the average degree of polymerization of PEG－200 and PEG－300. Analytical results of these samples are shown in table 2. The average repeating monomer units of PEG－200 and PEG－300 obtained by this IR spectrometry were 4.1 and 6.4, respectively, and their values were consistent with those of theoretical values.

Table 2　Analytical results on the average degree of polymerization of actual samples by IR spectrometry

No	Samples	Mw	Theo. A.D.P *	IRS Method
1	PEG 200	200	4.1	3.9
2	PEG 300	300	6.4	6.5

A.D.P * : Average degree of polymerization

Accordingly, this spectrometry could be used for the determination of the average degree of polymerization of PEG at regional customs laboratories.

Furthermore, this spectrometry is a simpler, more rapid and more reliable method for the determination of average degree of polymerization of PEG.

ACKNOWLEDGMENT

We thank previous Director General of CCL, Mr Fumio NISHIURA, previous chief chemist, Mr Kazuo WADA and another staffs of CCL in JAPAN.

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