Studies of Polybutene. I. Determination of the End-groups and the Molecular Weight by the Infrared Method*

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A practical method for the determination of the molecular weight of commercial liquid polybutenes of a low molecular weight has been developed by an infrared technique. Moreover, the types of unsaturated terminal groups of the polymer chain have been ascertained. However, the application of this method to polymers of a higher molecular weight would be difficult, because of the undetectably weak relative-intensity of the band assignable to the end-group.

Experimental

Materials.—The samples of the commercial polybutenes used in this investigation are Indopol from Amoco, Oronite from California Chemicals, and Polyvis from Cosden. Benzene was washed with sulfuric acid and water, and distilled after drying over calcium chloride. The treated benzene was purified by fractional distillation over sodium wire before use.

Technique.—The molecular weight of the samples was determined by a cryoscopic method, using benzene as the solvent, and also by an iodine-value method1) reported on in a preceding paper. The infrared absorption was measured by a Hitachi EPI-2 infrared spectrometer with an NaCl optical system. A group-type analysis was applied in the determination of the content of the end group and of the molecular weight. In this case, the absorption coefficient of the band characteristic of the type of structure must usually be determined. In the present work, however, this procedure was eliminated by applying the data of the absorption coefficients, reported by McMurry and Thornton,2) of the bands caused by the structural types in question; the proportionality of the absorption coefficient can be held between the data reported by McMurry and our measurements.

Results and Discussion

The Molecular Weight of the Polybutenes.—Table I gives the molecular weight obtained by the iodine-value method on the assumption that each polymer molecule contains only one unsaturated double bond at the end, and those obtained from the cryoscopic method. As may be seen in the table, there is a close agreement in molecular weight between the two methods. This fact justifies the assumption indicated above when the molecular weight is determined by the iodine-value method.

TABLE I. THE MOLECULAR WEIGHT OF POLYBUTENES

Sample	Cryoscopic method	Iodine-value method
Polyvis 3	650	660
Polyvis 5	710	690
Polyvis 10	900	870
Polyvis 30	1300	1150
Indopol L-10	310	310
Indopol H-35	630	640
Indopol H-50	700	660
Indopol H-100	780	840
Indopol H-300	1090	1100
Oronite 24	680	830
Oronite 32	1240	1030

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1) R. Endo, K. Iimura and M. Takada, to be pubeished in this Bulletin as Part II.

2) H. I. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

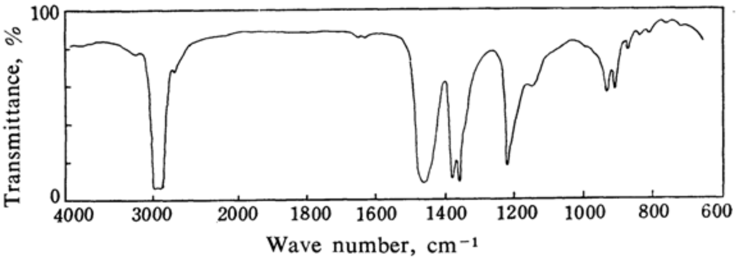

Fig. 1-a. Infrared spectrum of Polyvis 10.

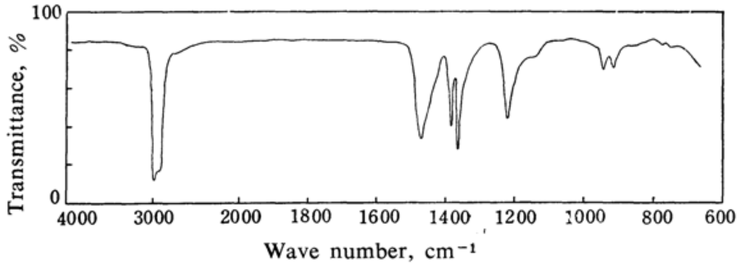

Fig. 1-b. Infrared spectrum of polyisobutylene (Vistanex LM-MH).

The Structures of the Polybutenes. — The infrared spectra of eleven samples are all identical to that of polyisobutylene except in the double-bond stretching and the out-of-plane =CH deformation regions. For example, the infrared spectra of Polyvis 10 and polyisobutylene (Vistanex LM-MH from the Esso Standard, $\overline{M}_w$: 10000$\sim$11700) are shown in Fig. 1. The absorption caused by the unsaturated double bonds is observed in all samples. The two weak absorption bands at 1660 and at 1640 cm^{-1} can be assigned to the C=C stretching vibrations. The disappearance of the bands at 892 and at 830 cm^{-1} on the iodation of the samples (cf. Fig. 2) suggests that these bands arise from the CH out-of-plane bending vibration at the C=C bond. The bands at 1660 and 830 cm^{-1} are assigned to the vibration of the tri-substituted ethylenic double bond, while those at 1640 and 892 cm^{-1} have been assigned to the vibration of the vinylidene-type double bond by Dainton and Sutherland[3] and by other investigators.[4-6]

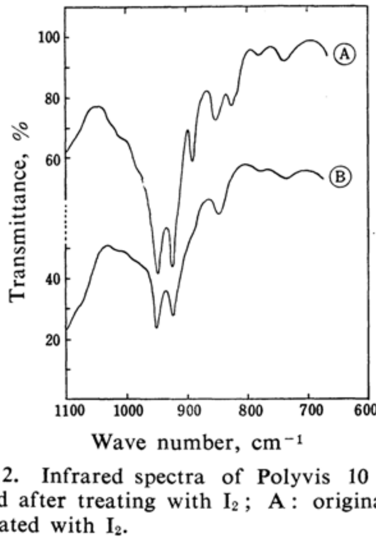

Fig. 2. Infrared spectra of Polyvis 10 before and after treating with I_2; A: original, B: treated with I_2.

From this finding, together with that obtained in the first section, it would seem that the commercial polybutenes are low molecular weight polyisobutylene, and that they are mixtures of two types of polymer chains consisting of one vinylidene-type end-group per one polymer molecule and one tri-substituted ethylenic end-group per another polymer molecule.

The Quantitative Determination of the End-groups.—In the infrared study of low molecular weight polyisobutylene, Dainton and Sutherland[3] and Flett and Plesch[6] have suggested that the termination of the polymer occurs mainly in the vinylidene-type unsaturation. In the sample used in this investigation, however, a considerable amount of the tri-substituted ethylenic end-group exists in the polymer chain, together with the vinylidene-type end-group.

The measurement of the absorption intensities of the bands at 892 and 830 cm^{-1}, which

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[3] F. S. Dainton and G. B. B. M. Sutherland, *J. Polymer Sci.*, **4**, 37 (1949).

[4] W. S. Richardson, ibid., **10**, 353 (1954).

[5] W. S. Gallaway and M. J. Murray, *J. Am. Chem. Soc.*, **70**, 2584 (1948).

[6] M. St. C. Flett and P. H. Plesch, *J. Chem. Soc.*, **1952**, 3355.

are assigned to the CH out-of-plane vibration of the vinylidene-type end-group and that of the tri-substituted ethylenic end-group respectively, gives the concentration of the end-groups. The absorption coefficients of the bands at 892 and 830 cm^{-1} have been determined as 14×10^4 mol./ml./cm. and 4.0×10^4 mol./ml./cm. respectively by McMurry and Thornton.2) Using these values, it is possible to obtain the content of the end-groups from the measured intensity ratio of the bands.

If the intensities of the bands at 830 and 892 cm^{-1} are proportional to the concentrations of the respective end-groups, the following relation can be proved:

$$\begin{aligned} C_{830}/C_{892} &= (k_{892}/k_{830}) \times (D_{830}/D_{892}) \\ &= (14/4.0) \times (D_{830}/D_{892}) \qquad (1) \end{aligned}$$

where C is the molar concentration of the end-group, k is the absorption coefficient, and D is the optical density of the band at the wave numbers shown by the subscript. The ratio of the contents of the tri-substituted ethylenic end-group to that of the vinylidene-type end-group is given by C_{830}/C_{892}. The contents calculated from C_{830}/C_{892} are listed in Table II.

TABLE II. END-GROUP CONTENT

Sample	D_{830}/D_{892}	C_{830}/C_{892}	V	T
Polyvis 3	0.431	1.51	0.40	0.60
Polyvis 5	0.427	1.49	0.40	0.60
Polyvis 10	0.461	1.61	0.38	0.62
Polyvis 30	0.437	1.53	0.40	0.60
Indopol L-10	0.306	1.07	0.48	0.52
Indopol H-35	0.436	1.53	0.40	0.60
Indopol H-50	0.490	1.72	0.37	0.63
Iodopol H-100	0.623	2.18	0.31	0.69
Indopol H-300	0.402	1.41	0.41	0.59
Oronite 24	0.573	2.01	0.33	0.67
Oronite 32	0.520	1.82	0.35	0.65

Note: V provides a vinylidene-type end-group. T provides a tri-substituted ethylenic end-group.

Unlike the results obtained by Dainton and Sutherland3) and by Flett and Plesch6) on their samples, the tri-substituted ethylenic end-group is predominant in our samples.

The Determination of the Degree of Polymerization by the Infrared Method.—The band at 855 cm^{-1} is caused by the $\mathrm{R{-}CH_2{-}C(CH_3)_2{-}CH_2{-}R}$ group in the polyisobutylene chain, and its absorption coefficient is estimated as 0.2×10^4 mol./ml./cm.2) As has been described in the second section, if we assume that these samples are mixtures of two kinds of polyisobutylene chains, one with the tri-substituted ethylenic end-group and the other with the vinylidene end-group, the contribution from the dimethyl branching of these two chains to the intensity of the band at 855 cm^{-1} must be considered. That is, the number-average degree of polymerization, $\bar{P}_n$, of the samples can be calculated from the following formulas:

$$\bar{P}_n = \{(V \times D_{855} \times k_{892})/(D_{892} \times k_{855})\} + 1 \qquad (2)$$

or

$$\bar{P}_n = \{(T \times D_{855} \times k_{830})/(D_{830} \times k_{855})\} + 1 \qquad (3)$$

where V is the content of the vinylidene-type end-group and T is that of the tri-substituted ethylenic end-group. The degree of polymerization, therefore, can be obtained from the content of the end-group by applying Eq. 2 or 3.

Table III gives the degree of polymerization obtained by the above method and those obtained from the cryoscopic and iodine-value methods. There is considerable agreement between the results obtained by the three methods. These experimental results demonstrate that the infrared technique can be used as a practical and rapid method for the determination of the types and numbers of the end-group in the commercial polybutenes and the molecular weight of polymers.

TABLE III. DEGREE OF POLYMERIZATION OBTAINED BY INFRARED AND OTHER METHODS

Sample	Infrared		Cryoscopic	Iodine-value
Polyvis 3	10.9a)	10.8b)	11.6c)	11.8c)
Polyvis 5	12.9	13.0	12.7	12.3
Polyvis10	15.0	15.1	16.0	15.5
Polyvis30	20.0	19.5	23.2	20.5
Indopol L-10	9.0	9.0	5.5	5.5
Indopol H-35	13.5	13.3	11.1	11.4
Indopol H-50	15.3	15.2	12.5	11.8
Indopol H-100	14.9	15.7	13.9	15.0
Indopol H-300	20.0	20.4	19.4	19.6
Oronite 24	16.3	16.4	12.1	14.8
Oronite 32	20.3	20.7	22.1	18.4

Note: a) From the content of the vinylidene-type end-group.
b) From the content of the tri-substituted ethylenic end-group.
c) Obtained by dividing the respective molecular weight by 56.1, the monomeric molecular whight.

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