Determination of Composition of Vinyl Copolymers by Infrared

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IN CONNECTION with work at this laboratory on the preparation of copolymers from fatty vinyl ethers and lower alkyl vinyl ethers, a simple, rapid, analytical method to determine copolymer composition was needed. The characteristic group in each monomeric unit of a vinyl ether polymer is the –C–O–C– ether linkage. A band at 1250 to 1110 cm.$^{-1}$ in ether spectra was assigned by H. M. Randall *et al.* (2) to ether –C–O–C–. Bellamy (1) states that aliphatic ethers absorb at 1150 to 1060 cm.$^{-1}$. An infrared method to determine copolymer composition from the intensity of this absorption has been developed.

Experimental

All spectra were obtained on a Perkin-Elmer Model 21[1] Double Beam Recording Infrared Spectrophotometer with a sodium chloride prism. The spectra of carbon disulfide solutions of the polymer *versus* the solvent were obtained by using 5.00-mm. fixed cells with sodium chloride windows.

The materials investigated were copolymers of soybean vinyl ether, in various ratios, with the following: *n*-butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, 2-methoxyethyl vinyl ether, ethyl vinyl ether, and 2-ethylhexyl vinyl ether. Soybean vinyl ether is a mixture of vinyl ethers prepared from the fatty acids of soybean oil.

Measurements were made on each solution in two ways, and absorption coefficients, K (l. gm.$^{-1}$ cm.$^{-1}$), were calculated. If Beer's law is obeyed, the reciprocal of the absorption coefficient should be proportional to the weight per ether linkage. Absorption coefficients were determined first at a frequency of 1100 cm.$^{-1}$, which is the frequency of maximum absorption in soybean vinyl ether polymer. They were also determined at the frequency of maximum absorption in the particular copolymer spectrum.

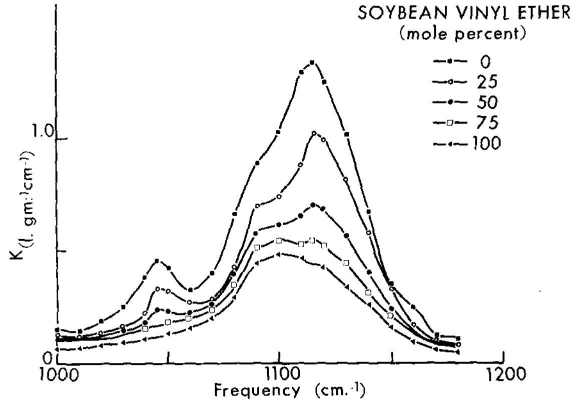

FIG. 1. Absorption coefficient *versus* frequency for the copolymers of 2-chloroethyl vinyl ether and soybean vinyl ether.

Infrared measurements were made of sets of compounds, each consisting of the following. a) a pure polyvinyl ether prepared from a given low molecular weight vinyl ether, b) pure stearyl vinyl ether polymer, which is taken as representative of the several vinyl ethers in soybean vinyl ether, and c) copolymers of the low molecular weight vinyl ether with 25%, 50%, and 75% of soybean vinyl ether on a mole-percentage basis. For each set the data were assumed to satisfy an equation of the type:

$$P = mK + b$$

where "P" is the weight percentage soybean vinyl ether in the copolymer, K is the absorption coefficient at the frequency the measurements were made, and m and b are proportionality and intercept constants, respectively, to fit the data to a straight line. The best set of constants was determined for each set by least squares method, *i.e.,*

$$m = \frac{n \Sigma PK - \Sigma P \Sigma K}{n \Sigma K^2 - (\Sigma K)^2}$$

$$b = \frac{\Sigma K^2 \Sigma P - \Sigma K \Sigma PK}{n \Sigma K^2 - (\Sigma K)^2}$$

where n is the number of members in the set. The equations derived are given in Table I.

TABLE I

Constants in Equations of the Type: $P = mK + b$. Relating Percentage by Weight Soybean Vinyl Ether (P) and Absorption Coefficient (K)

Copolymer compound	Fixed frequency 1100 cm.$^{-1}$		Frequency of absorption maximum	
	m	b	m	b
n-Butyl vinyl ether	−105.6	147.6	− 99.3	147.8
Isobutyl vinyl ether	−121.1	158.8	− 92.7	142.8
2-Chloroethyl vinyl ether	−198.8	196.5	−110.7	153.3
2-Methoxyethyl vinyl ether	− 66.7	132.6	− 66.7	132.6
Ethyl vinyl ether	− 91.1	144.3	− 79.1	139.9
2-Ethylhexyl vinyl ether	−408.0	300.3	−293.4	238.1

Results and Discussion

The polymers studied have peak absorption in this region as follows: soybean vinyl ether polymer at 1100 cm.$^{-1}$; *n*-butyl vinyl ether polymer at 1090 cm.$^{-1}$; isobutyl vinyl ether polymer at 1109 cm.$^{-1}$; 2-chloroethyl vinyl ether polymer at 1115 cm.$^{-1}$; 2-methoxyethyl vinyl ether polymer at 1098 cm.$^{-1}$; ethyl vinyl ether polymer at 1105 cm.$^{-1}$; and 2-ethylhexyl vinyl ether polymer at 1090 cm.$^{-1}$. Figure 1 is an illustration of the effect of the composition of copolymers of 2-chloroethyl vinyl ether and soybean vinyl ether on the band in this region. It shows that in copolymers there will be an overlapping of the bands of different monomeric units. This variation in absorption makes it necessary to measure on steep slopes part of the time if measurements are made at a fixed frequency, or at changing frequency if the band maximum is measured. Although it is not correct to assume that a Beer's law plot will be linear, the errors introduced may be less than those in making measurements from

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[1] Mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over firms or similar products not mentioned.

TABLE II

Composition of Copolymers Determined at a Fixed Frequency (1100 cm.$^{-1}$)

Mole % Soybean VE	0			25			50			75			100			SD[d]
Copolymer system	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	
n-Butyl vinyl ether	1.38	0.0	1.9	0.973	51.1	44.9	0.689	75.8	74.9	0.570	90.5	87.4	0.482	100.0	96.7	4.0
Isobutyl vinyl ether	1.305	0.0	0.7	0.897	51.1	50.1	0.696	75.8	74.5	0.554	90.5	91.7	0.482	100.0	100.4	1.1
2-Chloroethyl vinyl ether	0.988	0.0	0.1	0.748	48.0	47.8	0.614	73.5	74.4	0.546	89.3	87.9	0.482	100.0	100.6	0.9
2-Methoxyethyl vinyl ether	1.99	0.0	0.1	1.247	49.0	49.4	0.878	74.3	74.0	0.649	89.8	89.3	0.482	100.0	100.4	0.4
Ethyl vinyl ether	1.588	0.0	0.4	0.942	57.6	58.5	0.691	80.2	81.3	0.590	92.5	90.5	0.482	100.0	100.4	1.2
2-Ethylhexyl vinyl ether	0.733	0.0	1.2	0.637	38.6	40.4	0.587	65.3	60.8	0.533	84.9	82.8	0.482	100.0	103.6	3.3

[a] Absorption coefficients.
[b] Theoretical soybean vinyl ether content (weight-percentage).
[c] Calculated soybean vinyl ether content of the copolymers (weight percentage).
[d] Standard deviation of each system.

TABLE III

Composition of Copolymers Determined at Frequency of Maximum Absorption

Mole % Soybean VE	0			25			50			75			100			SD[d]
Copolymer system	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	K[a]	% known[b]	% found[c]	
n-Butyl vinyl ether	1.48	0.0	1.1	1.000	51.1	48.6	0.708	75.8	77.6	0.579	90.5	90.4	0.482	100.0	100.0	1.6
Isobutyl vinyl ether	1.548	0.0	—0.8	0.975	51.1	52.4	0.717	75.8	76.3	0.554	90.5	91.4	0.482	100.0	98.1	1.3
2-Chloroethyl vinyl ether	1.34	0.0	5.0	1.029	48.0	39.4	0.713	73.5	74.4	0.554	89.3	92.0	0.482	100.0	100.0	5.2
2-Methoxyethyl vinyl ether	1.99	0.0	0.1	1.247	49.0	49.4	0.878	74.3	74.0	0.649	89.8	89.3	0.482	100.0	100.4	0.4
Ethyl vinyl ether	1.76	0.0	0.6	1.050	57.6	56.8	0.761	80.2	79.6	0.610	92.5	91.6	0.482	100.0	101.7	1.1
2-Ethylhexyl vinyl ether	0.821	0.0	—2.7	0.664	38.6	43.3	0.588	65.3	65.6	0.519	84.9	85.9	0.482	100.0	96.7	3.2

[a] Absorption coefficients.
[b] Theoretical soybean vinyl ether content (weight-percentage).
[c] Calculated soybean vinyl ether content of the copolymers (weight percentage).
[d] Standard deviation of each system.

recordings on steep slopes. The results are tabulated in Tables II and III.

Table II lists the absorption coefficients determined at a fixed frequency of 1100 cm.$^{-1}$ and the soybean vinyl ether weight percentage content found compared to the known content. The average standard deviation of the system is 1.82% with a range from 0.4% to 4.0%.

Table III gives the same information with the absorption coefficients determined at the frequency of maximum absorption. The standard deviations range from 0.4% to 5.2% with an average of 2.13%, but, by removing the 2-chloroethyl vinyl ether set, the average standard deviation of the other five is 1.52%. The set removed is the one having a frequency of maximum absorption of 1115 and the farthest removed from 1100 cm.$^{-1}$, the frequency of maximum absorption of soybean vinyl ether polymer.

From these investigations it appears that the analysis of copolymers of vinyl ethers may be accomplished equally well by considering the absorption maximum in this region, which is easy to do when using a recording spectrophotometer, providing the material being incorporated has a maximum absorption at a frequency not greatly different from soybean vinyl ether polymer. A further justification for peak measurements is that production samples would have a high soybean vinyl ether weight percentage content. If the absorption frequency becomes greatly different from 1100 cm.$^{-1}$, it would be best to measure at a fixed frequency.

Summary

Copolymers of soybean vinyl ether with each of six low alkyl vinyl ethers have been investigated in the infrared. The ether band in the 1100 cm.$^{-1}$ region has been found useful in determining the composition of copolymers. The composition of copolymers has been determined at a fixed frequency of 1100 cm.$^{-1}$ and at the absorption maximum in the region of 1100 cm.$^{-1}$. Determination may be accomplished with equal success at the absorption maximum in this region if the material being incorporated absorbs at a frequency not too far removed from 1100 cm.$^{-1}$. This would be the preferred method if using a recording instrument.

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