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RAMAN SPECTRUM OF POLYSTYRENE[1]

ANN PALM

Department of Chemistry, The Polytechnic Institute of Brooklyn, Brooklyn, New York

In the course of an investigation of the Raman spectrum of polystyrene, the depolarization factors were measured and some of the observed vibrational Raman frequencies were assigned. In particular, this was made possible by comparing the Raman spectrum of polystyrene with those of benzene and styrene monomer.

EXPERIMENTAL PROCEDURE

The double-exposure method, as described previously by Crawford and Horowitz (3), was adapted to the study of the Raman spectrum of transparent polystyrene. The Schmidt & Haensch double-prism spectograph used presently has a dispersion of 13 Å./mm. at 4358 Å., which was chosen as the exciting line in these experiments. The Raman spectra of the polystyrene samples were obtained by replacing the conventional Raman tube by a polystyrene rod of approximately 1.5 cm. diameter and 10 cm. length to which was attached a 5-cm. long black brass tube at the upper end. The effective optical windows of these polystyrene rods were 1 cm. in diameter and were prepared by pressing the end of a polystyrene rod on a preheated glass plate and allowing it to cool slowly.

In order to measure depolarization factors, two exposures of $3\frac{1}{2}$ hr. each were required. No. 103 a-O antihalation backed Eastman Kodak plates were employed. The wave numbers and the intensities of the Raman lines were determined in the usual manner by making use of previously established calibration curves. The precision in the determination of the unknown wave numbers was 8 cm.$^{-1}$, because of the diffuse and broad character of the Raman lines.

[1] This paper is based on part of a dissertation presented by Ann Palm to the Faculty of the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

The styrene monomer was freed of inhibitor and distilled under reduced pressure. It boiled at 46°C. and 20 mm. mercury pressure and had a refractive index of 1.5463. The purified reagent was then poured into clean dry Pyrex tubes, which were sealed and put into an oven for 3 days at 80°C., for $\frac{1}{2}$ day at 100°C., for $\frac{1}{2}$ day at 120°C., and for another $\frac{1}{2}$ day at 135°C. to ensure complete polymerization. The tubes were placed in a horizontal position to permit the rise of bubbles of styrene vapor which formed as the polymerization proceeded, thus avoiding their being trapped. This procedure proved to be an easy way in which to form the clear solid polystyrene rods which were required for the spectroscopic studies.

EXPERIMENTAL RESULTS AND DISCUSSION

In the present studies involving polymer systems, an attempt was made to identify the characteristic frequencies of a number of specific groups rather than to present a detailed assignment of the vibrational spectra. The observed Raman frequencies, relative intensities, and depolarization factors of benzene, styrene, and polystyrene are summarized in table 1. Benzene and styrene, being similar and structurally related, were employed for comparison studies. It may be noted that the Raman lines of benzene recur slightly shifted in both the styrene and the polystyrene spectrum. This means, of course, that these frequencies are due to the benzene ring solely. The fact that the styrene monomer has a more complicated Raman spectrum than that of benzene may be ascribed to its lack of symmetry. Lack of symmetry, however, should give rise to polarized Raman lines, whereas the Raman lines actually observed do not substantiate this at all. According to the polarizability theory, complicated molecules with no symmetry elements possess mostly symmetric vibrations, whose corresponding spectral lines should be polarized. However, the polarizability theory holds strictly for free molecules (gaseous) only and does not consider the molecular interactions which occur in liquid systems.

Among the Raman lines not appearing in either the benzene or the polystyrene spectrum, there is a frequency of 1637 cm.$^{-1}$ which may definitely be ascribed to a C=C frequency of styrene. According to the literature, the C=C group has a frequency in the region of 1645 cm.$^{-1}$ (6). In analyzing the Raman spectrum of polystyrene, it is to be noted that all frequencies appearing here occur in the benzene as well as in the styrene spectrum, with the exception of the following lines: 657 cm.$^{-1}$, 1275 cm.$^{-1}$, 2886 cm.$^{-1}$, and 2935 cm.$^{-1}$ According to Elliott, Ambrose, and Temple (1, 5), the frequencies 2935 cm.$^{-1}$ and 2886 cm.$^{-1}$ may be assigned to the symmetric and antisymmetric CH_2 valency vibrations, respectively. Thus, two of the above frequencies which occur in the spectrum of polystyrene are explained. No frequency due to a C=O group, which might result from oxidation during the polymerization, was discernible. The frequencies depending upon structural features of either the ring or the ring double bonds show a slight shift toward the red. The two completely polarized Raman lines occurring in benzene recur in the Raman spectra of styrene and polystyrene partially polarized. The most notable feature of the spectrum of the polystyrene

TABLE 1

Raman spectrum of polystyrene and comparison spectra of benzene and styrene

BENZENE			POLYSTYRENE			STYRENE		
$\Delta\bar{\nu}$ *	I	ρ	$\Delta\bar{\nu}$	I	ρ	$\Delta\bar{\nu}$	I	ρ
			152	vw	—	151	vw	0.95
						240	w	0.38
						562	w	0.44
						595	w	0.78
612	m	0.75	628	vw	1.00	624	w	1.07
			657	vw	—			
862	w	0.47				782	m	0.55
900	w	p	908	vw	—	912	w	1.18
945	m	p	952	vw	—	948	w	0.38
1000	s	p	1011	w	0.61	1005	s	0.38
			1034	w	0.88	1034	m	0.31
						1084	vw	—
						1107	vw	—
						1132	vw	—
			1165	vw	—	1163	m	1.28
1185	m	0.88	1190	vw	—	1185	m	0.53
			12.6	vw	—	1206	s	0.63
						1244	m	0.35
			1275	vw	—			
1300	s	0.50	1298	w	0.81	1298	m	0.81
						1322	vw	—
						1332	vw	0.64
						1365	vw	—
1393	vw	p				1412	s	0.65
1425	vw	p				1452	w	1.00
1488	m	0.32				1497	w	0.69
						1529	w	0.80
						1545	w	0.55
1595	m	0.83	1592	vw	0.86	1583	s	0.60
1615	w	0.82	1613	w	1.11	1609	s	0.50
						1637	w	—
2463	vw	0.38	2464	w	0.93	2464	vw	—
2498	vw	0.31	2507	w	1.10	2505	w	0.88
			2886	w	0.61			
			2935	vw	—			
2972	vw	p						
3022	vw	p				3017	w	0.75
			3057	s	0.89	3053	m	0.24
3075	s	0.39				3070	m	0.66
3136	vw	—	3138	m	0.79	3135	w	0.55

* $\Delta\bar{\nu}$ = Raman shifts in cm.$^{-1}$; I = estimated intensity; ρ = depolarization factor; p = small depolarization factor; — refers to lines which were too faint to be measured by the microphotometer.

sample is the decreased number of Raman lines when compared with the corresponding spectrum of the styrene monomer, as may be seen in figure 1.

Another characteristic of all polystyrene spectra is the occurrence of extensive

background which appears to be partially polarized. Several hypotheses have been advanced in trying to explain such a background. It was suggested that it may be caused by classical scattering of the weak continuous spectrum from the exciting light source. Signer and Weiler (7) believed that tiny amounts of catalyst in the polymer may be responsible for it. They further state that when styrene is polymerized below 150°C. and all the ultraviolet of the mercury excitation unit is filtered out, the background disappears.

In the case at hand none of these theories hold, since the styrene was heat polymerized without the presence of any catalyst. Also, the polaroid cylinders surrounding the polystyrene rod prevented any ultraviolet radiation from reaching the sample. Furthermore, it appears unlikely that the background originates from the light source, since the carbon tetrachloride as well as the benzene and styrene yielded satisfactory Raman spectra, free of any such background.
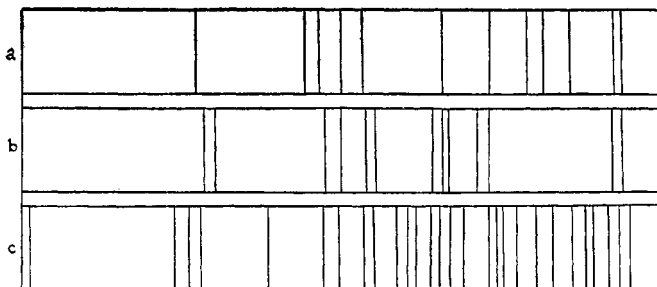

FIG. 1. Schematic representation of Raman spectra of (a) benzene, (b) polystyrene, and (c) styrene.

Placzek (8) attributed a strong continuum to the viscosity of the scattering substance on the basis of a study of the Raman spectrum of glycerol. He suggested that fluorescence or molecular complexes might be responsible for the background. An experiment designed to show the effect of viscosity on the Raman spectrum consisted in the 10 per cent conversion of styrene to polystyrene and the subsequent inspection of its Raman spectrum. The spectrum resulting from this solution had all the characteristics of that of pure styrene monomer, even though the viscosity was greatly increased. In other words, a small extent of polymerization does not modify appreciably the total spectrum, while at the same time it increases the viscosity enormously.

SUMMARY

An experimental procedure is described for measuring the Raman frequencies and depolarization factors of polystyrene. Crawford's double-exposure method was adapted successfully. The accuracy of the results was tested by measurements with purified carbon tetrachloride. The depolarization factors found were in good agreement with those obtained by other investigators (2, 3, 4).

An assignment of vibrational frequencies is carried out for the Raman lines

of polystyrene. The structure of the polystyrene spectrum is rather complex. A spectral analysis was possible, however, by comparing the spectrum of poly-styrene with those of benzene and styrene. In particular, all frequencies that appear in the Raman spectrum of polystyrene occur in the benzene as well as in the styrene spectrum with the exception of 657 cm.$^{-1}$, 1275 cm.$^{-1}$, 2886 cm.$^{-1}$, and 2935 cm.$^{-1}$

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ADSORPTION ISOTHERMS OF MIXED VAPORS OF BENZENE AND METHANOL ON ACTIVATED CHARCOAL AT 25°C.

W. B. INNES,[1] R. B. OLNEY,[2] AND H. H. ROWLEY

Department of Chemistry and Chemical Engineering, State University of Iowa, Iowa City, Iowa

A method has previously been described by this laboratory (3) for the meas-urement of adsorption isotherms of mixed vapors. This method entails keeping the adsorbate composition very nearly constant by introducing vapor of fixed composition to the adsorbent and then measuring the composition and total pressure of the vapor phase in equilibrium with the adsorbate. Determination of the vapor composition is accomplished by measuring the condensation pressure of the vapor with a modified McLeod gauge.

The previous study dealt with the system carbon tetrachloride–methanol on activated charcoal. The present investigation concerns the results obtained with benzene–methanol on activated charcoal.

[1] Present address: American Cyanamid Company, Stamford, Connecticut.

[2] From a dissertation submitted by R. B. Olney to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, August, 1942.