

## Compositional Analysis of the Styrene-Isobutylene Copolymer

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### Synopsis

Analysis for composition of the styrene-isobutylene copolymer has been accomplished by independent techniques which include carbon-hydrogen analysis and infrared and NMR spectroscopy. The use of blends of homopolymers presents difficulties in establishing true absorptivities for the solution of two-component systems, and appropriate corrections were applied to enable use of IR as an analytical technique. Carbon-hydrogen elemental analysis and NMR spectroscopy were used to verify the IR results.

### INTRODUCTION

The compositional analysis of polymeric systems has been known and described in many publications over the past three decades using infrared spectroscopy. Though the general techniques have been narrowed to a few types, each article has some unique method of coping with the general problem of providing adequate standards. This is especially true for complex systems whether they be blends or heteropolymers.

When dealing with blended systems, the difficulties are reduced since the components are usually available for calibration purposes. Once the system has been characterized, an IR technique is then relatively easy to conduct. However, in a copolymer system, the spatial or geometric location of the atoms and groups in the molecule is not the same as that in the corresponding homopolymers. Since the homopolymers are the only true standards available, they must be used singly or in blends to determine absorbance-versus-concentration dependence. Usually, blends do not provide the same absorbance for a particular group frequency as the copolymer molecule. The end result is that it is difficult to obtain accurate absorptivities for the dynamic range. Determination of the monomeric groups in the copolymers is dependent on the accuracy of the group absorptivities, and hence the error in the measurement by infrared analysis is usually unknown.

In this paper, we will show how the application of multiple techniques was used in defining the compositional structure of the styrene-isobutylene copolymer. Analysis of the copolymer was carried out by elemental analysis, nuclear magnetic resonance, and infrared spectroscopy.

## EXPERIMENTAL

### Synthesis of Styrene-Isobutylene Copolymer

Copolymers were prepared in the range of 10–80% styrene content by addition polymerization using ethyl aluminum dichloride catalyst in hexane solvent. Homopolymers of styrene and isobutylene were similarly prepared. Purification was accomplished by precipitation in methanol and vacuum drying.

### Analysis of Styrene-Isobutylene Copolymer

**Elemental.** Determination of the carbon and hydrogen content was performed using an F+M Model 185 C, H, and N analyzer. In a copolymer of this type, it is possible to calculate the weight per cent of the styrene and isobutylene segments from elemental analysis. The method of calculation is shown under section 1 in the Appendix. Though small variances in the elemental analysis have a considerable effect on the results, the data as shown in Table I are in reasonable agreement with the expected synthesis level.

**NMR.** Spectra were obtained using a Varian A-60A spectrometer at ambient temperature. A 0.3-g sample was dissolved in 1 ml carbon tetrachloride, and its spectrum was obtained using standard tubes and TMS reference. The spectrum as shown in Figure 1 easily differentiates the aromatic from the aliphatic protons in the repeating unit. The areas under these resonance peaks are determined by the instrument's integrator.

Since the aliphatic and aromatic protons are always found in the same ratio in the repeating unit, the only change is the quantity of monomeric units present. The integrated areas are then directly related to the theoretical aliphatic-to-aromatic proton ratio calculated to molecular weight per cent. A theoretical working curve may be generated for calculating the per

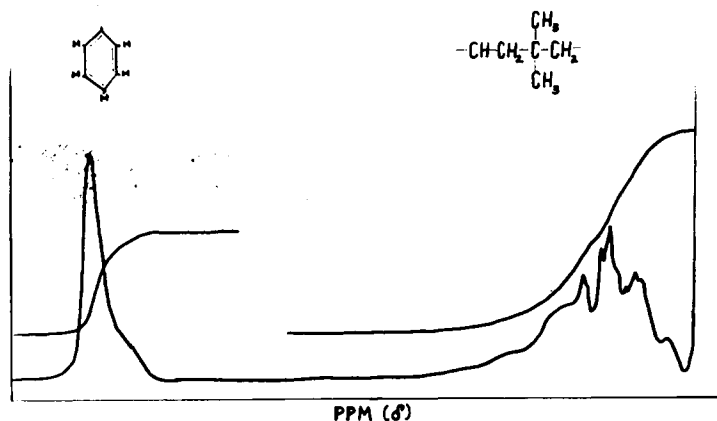


Fig. 1. NMR spectrum of styrene isobutylene copolymer.

TABLE I  
Copolymer Composition from Carbon-Hydrogen Data

Synthesized	% Carbon	% Hydrogen	% Styrene	% Isobutylene
10	86.38	13.87	8.0	92.3
25	87.85	12.76	25.5	75.1
40	88.86	11.80	40.1	60.5
50	89.03	11.24	47.7	52.5
60	90.20	10.64	58.0	42.8
70	90.96	9.65	72.4	28.2
80	91.32	9.23	77.4	23.2

TABLE II  
Copolymer Composition from NMR Data

Synthesized	Aliphatic/aromatic ratio	% Styrene
10	25.07	10.1
25	13.67	25.7
40	6.034	36.1
50	3.552	50.2
60	2.695	58.5
70	1.918	69.8
80	1.380	79.5

cent styrene as shown in Figure 2 and described in section 4 in the Appendix. Data from NMR analysis are shown in Table II.

**Infrared.** Analysis was conducted using a Perkin-Elmer Model 337 infrared spectrophotometer with normal slit and slow scan speed settings. In the case of determinations made on solutions, 0.1-mm matched NaCl cells were used. Cast films were prepared directly on polished NaCl plates for direct measurement on solid copolymers.

Two infrared techniques were employed which will be discussed later. The analysis of the copolymer in solution was conducted on solutions made by weighing 1.0–1.2 g copolymer in a 25-ml volumetric flask and dissolving in carbon disulfide. The sample is dissolved in an initial quantity of CS<sub>2</sub> and then brought to volume. The infrared scan using 0.1 mm cells is made between 7.0 and 8.0  $\mu\text{m}$  for the isobutylene component and between 12.0 and 15.0  $\mu\text{m}$  for the styrene component, using the solvent as reference. Absorbances are determined by drawing a baseline across the minima near 7.05 and 7.82  $\mu\text{m}$  for the 7.3- $\mu\text{m}$  isobutylene band and across the minima near 13.8 and 15.0  $\mu\text{m}$  for the 14.3- $\mu\text{m}$  styrene band. Calibration was conducted in the same manner except that the homopolymers, polyisobutylene and polystyrene, were used. While polyisobutylene shows good linearity in an absorbance-versus-concentration plot, the polystyrene is not linear throughout its entire range, as shown in Figure 3. A smooth curve may be drawn through the points. A two-segmental linear portion is seen with a slope change near 50% styrene concentration. Ignoring the small deviation from linearity, the calibration data are treated as if both components

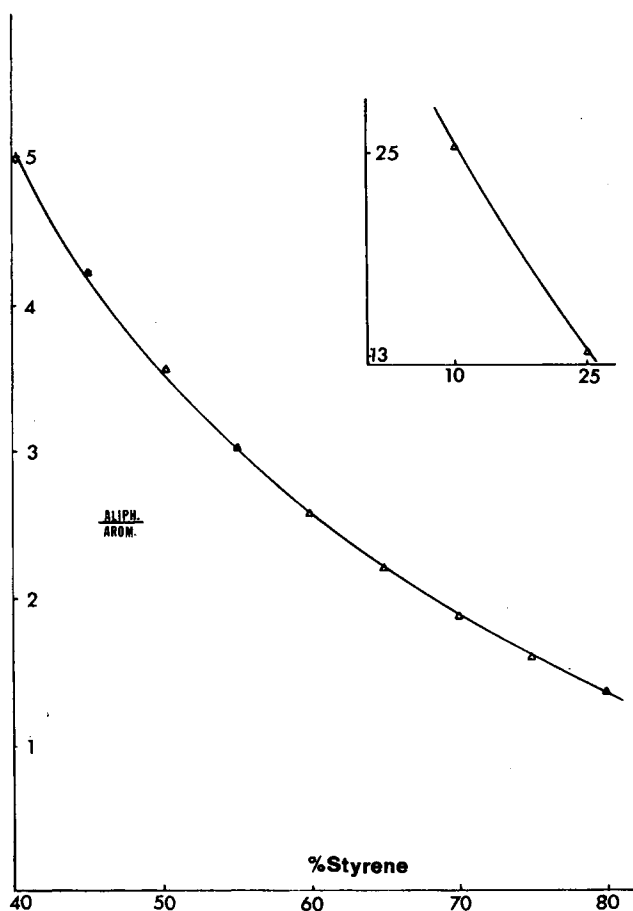


Fig. 2. Calibration curve for NMR analysis.

obeyed the Lambert-Beer law, and calculations were made in the manner shown in section 2 of the Appendix. The data obtained using the method are shown in Table III. The calculated data show the effect of polystyrene nonlinearity in the calculated totals for the two components. Normalization results in changes in the values at the ends of the range.

The second technique using a cast film was utilized to provide a more rapid analysis for production control purposes. The standards used in calibration of the technique were actual copolymers which had been analyzed using the solution technique. Since this is a two-component system, mutual interferences within the two bands are automatically corrected. To circumvent the correction for film thickness, the absorbance ratio method was used. The bands selected were  $6.7 \mu\text{m}$  for styrene and  $7.4 \mu\text{m}$  for isobutylene. The baseline technique was used to determine the individual absorbances. A film is prepared by placing one to two drops of polymerization solution on a NaCl plate. Cover the plate with an inverted 15-ml

TABLE III  
Copolymer Composition from Infrared Data

Synthesized	% Styrene		% Isobutylene		Calcd. Total
	Calculated	Normalized	Calculated	Normalized	
10	10.6	10.2	94.2	89.8	104.9
25	28.2	27.0	76.4	73.4	104.6
40	41.2	40.7	60.0	59.3	101.2
50	51.8	51.2	49.5	48.9	101.4
60	61.0	60.5	40.0	39.6	101.0
70	69.8	72.0	27.2	28.1	97.0
80	81.2	81.4	18.5	18.6	99.7

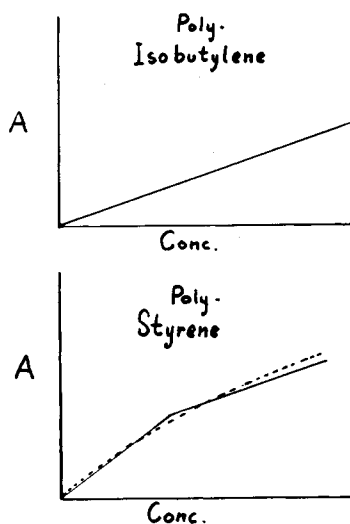


Fig. 3. Calibration curves for polyisobutylene and polystyrene.

beaker to prevent rapid evaporation of solvent which causes an uneven surface. Place an infrared heat lamp over the beaker and evaporate solvent. Add approximately ten drops of  $\text{CCl}_4$  and evaporate in the same manner. Repeat this operation twice to liberate all traces of solvent. With the cast film in the beam, check the region from  $6\ \mu\text{m}$  to  $8\ \mu\text{m}$  for any bands having less than 20% transmission; if present, a thinner film must be prepared. Scan the region from  $6.0\ \mu\text{m}$  to  $8.3\ \mu\text{m}$ .

The absorbance ratio  $R$  was calculated from  $A_{6.7}/A_{7.4}$  and plotted against concentration. As shown in Figure 4, the ratios were plotted using the per cent styrene as determined by solution IR, NMR, and elemental analysis. In all cases, the resulting curves (NMR and IR overlapped) closely approximated each other. The plot of these data was found to approximate a logarithmic function. Since it was not entirely linear (Fig. 5) throughout its entire range, two methods of calculation may be employed: (a) Using semilogarithmic graph paper, construct a working curve. (b) Since the

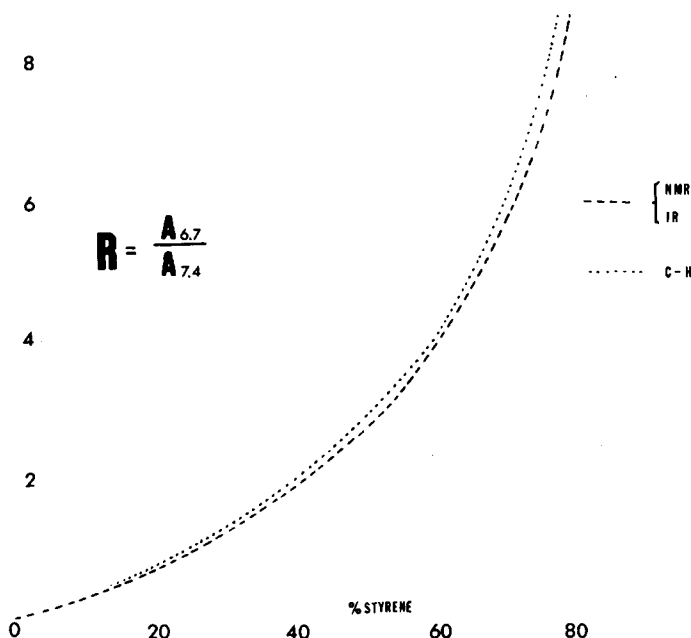


Fig. 4. Absorbance ratio vs. % styrene.

curve in Figure 5 appears to have two linear regions, two mathematical expressions can be derived for each segment. The calculation is shown in section 3 of the Appendix. The two sections selected were determined for amounts less than 60% and greater than 60% styrene.

### DISCUSSION

In the infrared analysis by the solution technique, the total components (especially at the high and low end) usually differed from 100%. Normalization of the results was employed; however, there was no evidence to conclude that the compositional analysis was improved by this method. To better justify application of normalization, it was decided to employ unrelated analytical methods. The collective results of the three techniques are shown in Table IV.

TABLE IV  
Comparison of Results (% Styrene) from Elemental, NMR, and IR Analysis

Synthesized	Carbon/hydrogen	NMR	IR
10	8.0	10.1	10.2
25	25.5	25.7	27.0
40	40.1	36.1	40.7
50	47.7	50.2	51.2
60	58.0	58.5	60.5
70	72.4	69.8	72.0
80	77.4	79.5	81.4

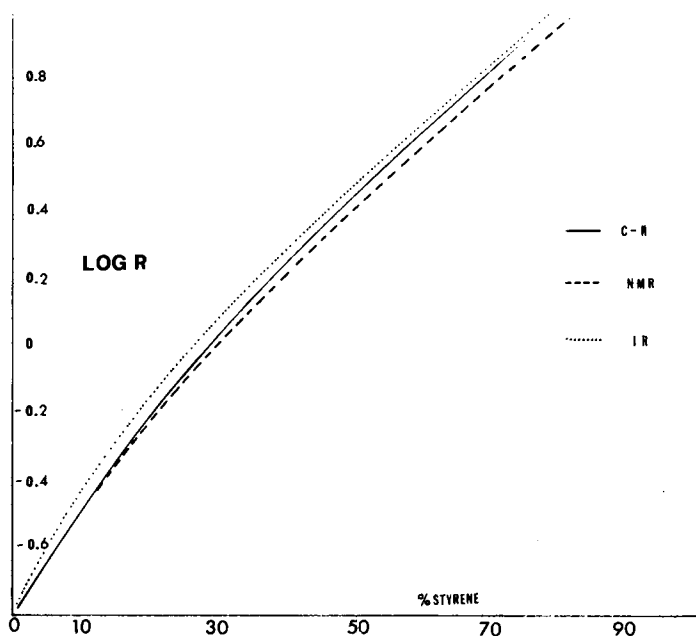


Fig. 5. Log of absorbance ratio vs. % styrene.

Carbon and hydrogen analysis was used, and the data obtained showed a general agreement with those obtained by IR. The only difficulty with this method is that it is very dependent on obtaining high accuracy for the hydrogen content. Measurement of hydrogen at the extreme ends of the range is more difficult and reflects the variance shown between the methods. Small traces of residual hydrocarbon solvent will also cause considerable error.

The NMR data showed for the most part even closer agreement with the infrared than did the elemental. This is especially significant since no standards were involved in conducting the analysis. Dependence for accuracy by this NMR technique is strictly a function of the accuracy of the NMR spectrometer to perform an accurate resonance peak intensity presentation and integration. The instrument was checked periodically for accuracy using reagent-grade ethylbenzene for integration reliability in the same regions of the spectrum as the copolymer. When discrepancy occurred, usually simple probe adjustment or tuning would correct the condition.

From the elemental and NMR data, it is evident that normalization of the infrared data increases the accuracy. It is reasonable to conclude that the infrared analysis should be accurate to  $\pm 1\%$  absolute. The method of analysis is relatively simple to perform, and application of the cast film technique provides a more rapid method which may be used for production control.

TABLE V  
Comparison of Infrared Analysis by Solution and Cast Film Techniques

Cast film	Solution	Difference
Less than 60% Styrene:		
26.1%	25.6%	+0.5
44.9%	45.6%	-0.7
57.8%	56.6%	+1.1
More than 60% Styrene:		
62.8%	62.8%	0.0
71.7%	71.7%	0.0
80.7%	80.9%	-0.2

Precision data were also determined for each of the methods and are expressed as standard deviation based on the per cent styrene.

Method	Standard deviation, %
NMR	±0.5
IR, solution	±0.7
IR, film	±0.3 (over 60%) ±0.8 (below 60%)

In Table V, data are shown which compare the two infrared methods with respect to the differences which may be anticipated.

## CONCLUSIONS

Three techniques have been employed to measure the monomeric content of the styrene-isobutylene copolymer. By comparison of results obtained from these sources, it was demonstrated that the normalized data provided by infrared analysis are sufficiently accurate for all practical applications.

We wish to express our appreciation to Dr. T. Hokama who prepared the special copolymers for this study; also to Mr. Z. Srnak who provided the elemental analysis, Dr. F. Scardiglia who assisted with the NMR analysis, and the Velsicol Chemical Corporation for granting permission to publish this manuscript.

## Appendix

### Methods of Calculation for Various Techniques Described

1. From Carbon and Hydrogen Analysis:

$$\% \text{ total carbon} = 0.9225 (\% \text{ styrene}) + 0.8563 (\% \text{ isobutylene})$$

$$\% \text{ total hydrogen} = 0.0774 (\% \text{ styrene}) + 0.1436 (\% \text{ isobutylene})$$

Solving the equations using the method of determinants yields

$$\% \text{ styrene} = \frac{0.1436 (\% \text{C}) - 0.8563 (\% \text{H})}{0.0662}$$

$$\% \text{ isobutylene} = \frac{0.9225 (\% \text{H}) - 0.0774 (\% \text{C})}{0.0662}$$



2. Two-Component Infrared Analysis of Solutions:

$$A\lambda = A_1 + A_2$$

Then

$$A_1 = a_{11}bc_1 + a_{12}bc_2$$

$$A_2 = a_{21}bc_1 + a_{22}bc_2$$

Solving the equations using the method of determinants yields

$$A_1 = \text{styrene} \quad (14.3 \mu\text{m}) \tag{a}$$

$$A_2 = \text{isobutylene} \quad (7.3 \mu\text{m})$$

$$\Delta = a_{11} \times a_{22} - a_{21} \times a_{12} \tag{b}$$

$$C_1 = \frac{a_{22} \times A_1 - a_{12} \times A_2}{\Delta \times b} \tag{c}$$

$$C_2 = \frac{a_{11} \times A_2 - a_{21} \times A_1}{\Delta \times b}$$

3. Absorbance Ratio Method from a Cast Film:

A plot of absorbance ratios of the bands at 6.7  $\mu\text{m}$  and 7.4  $\mu\text{m}$  yields a curve which approximates a logarithm function. Then

$$\log R = mx + b$$

where  $R = A_{6.7}/A_{7.4}$ ,  $m = \text{slope}$ ,  $x = \%$  styrene, and  $b = \text{intercept}$ , and

$$x = \frac{\log R - b}{m}$$

4. Composition from NMR Integrated Areas:

A theoretical working curve is generated as a function of the ratio of aliphatic to aromatic protons for the styrene content. The ratio of the aliphatic protons to the aromatic protons is based on the number present in the repeating unit of the polymer as well as the percentage concentration:

Component	Mol wt	Protons	
		Aromatic	Aliphatic
Styrene	104.14	5	3
Isobutylene	56.10	—	8

An 80% styrene content would give the following theoretical ratio:

$$\frac{0.80 \frac{3}{104.14} + 0.20 \frac{8}{56.10}}{0.80 \frac{5}{104.14}} = 1.3411.$$