are assigned to stereoisomers of the head-to-head structure and the low-field line to stereoisomers of head-to-tail containing structures.

The main-chain methine ^{13}C nmr spectrum of poly(propylene oxide) is very similar to the corresponding triglycol spectrum and is interpreted in the same way. That is, the polymer spectrum is interpreted in terms of dyads and triads of units in the chain with the relative chemical shifts determined both by structural and steric differences within these sequences. The regularity in the chain is reflected for the most part by the line at lowest field and the defects by the higher field lines. The line assignments are given in Table I. Just as for the triglycol spectrum, the choice of the structural triad assigned to the higher field group of lines (648 Hz) is arbitrary.

The main features of the methylene region of the polymer ^{13}C nmr spectrum can be interpreted exclusively in terms of structural dyads in the chain with steric differences having a minor but observable effect on the spectrum. These line assignments are also presented in Table I. The relative concentrations of sequences in all the spectra for both methine and methylene regions are consistent with the restrictions on the relative numbers of head-to-head and tail-to-tail structural defects. These values are presented in Table II.

Frequently, analysis of the diastereosequence or structural sequence probabilities will yield information about the mechanism of the polymerization. An elaborate statistical analysis of the ^{13}C nmr observed sequence concentrations is not justified because this polymer actually may be a sum of several different polymers generated by several different types of catalytic sites associated with the heterogeneous diethylzinc catalyst. Thus, sequence distributions cannot be reliably analyzed by a reasonable Markoffian scheme and insufficient information is available for a non-Markoffian analysis.

However, one qualitatively interesting comparison can still be made. The direct determination of the degree of steric purity of the crystalline poly(propylene oxide) fraction by ^{13}C nmr is in agreement with the predictions made by Aggarwal[4] using a modified version of a crystallization theory of Flory.[7] Aggarwal calculated head-to-tail isotactic dyad concentrations of 99 and 96% for polymers having melting points of 75 and 66°, respectively, so that the observed structurally regular, isotactic dyad concentration of 89% for a polymer with a melting point of 60° seems fairly reasonable.

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Nuclear Magnetic Resonance–Analog Computer Method for "Block Styrene"

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ABSTRACT: A method is described for determining "block styrene" in copolymers by using an analog computer to resolve overlapped aromatic proton nmr peaks. The method was applied to emulsion butadiene–styrene copolymers. It was shown that styrene sequences as small as two or three units are included in the "block styrene" determination. This technique should prove useful in obtaining sequence distribution information in most copolymer systems or in tacticity studies in which the resolution of overlapped peaks is important.

It was previously shown[1] that nmr composition analysis of some *n*-butyllithium-catalyzed butadiene–styrene copolymers yielded "block styrene" values in agreement with the chemical method[2] which uses osmium tetroxide for chain degradation. The question of how long the styrene sequences must be before nmr can detect them as "block styrene" was unanswered, although it was suggested that sequences as small as two or three might be observed. This paper describes a "block styrene" method which employs an analog computer to resolve the overlapped aromatic peaks of the styrene portion of nmr spectra. By use of a monomer sequence distribution computer program written by Harwood,[3] it was established that this method includes styrene sequences as short as two to three units in its "block styrene" determination.

Experimental Section

The emulsion butadiene–styrene copolymers were prepared at 50° with a common recipe. The copolymer solution concentration was 10% (weight/volume) in carbon tetrachloride or in hexachlorobutadiene. A small amount of tetramethylsilane was added as internal reference for nmr.

The 60-MHz nmr spectra were run at 28° with a Varian Model DA-60-IL spectrometer. The curve analysis was accomplished with an E.A.I. TR-48 analog computer

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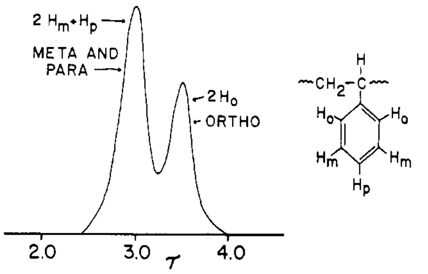

Figure 1. Aromatic proton resonance of atactic polystyrene in CCl_4 at 28°.

which was programmed by Claxton and Clarke.[4] Seven gaussian or lorentzian peaks, or any combination of seven peaks, can be used to resolve the overlapped peaks in question. The integrated relative areas of these peaks are then read out on a digital voltmeter with an accuracy of about 0.1% which is a small error compared to the precision of the curve analysis.

Results and Discussion

The basis for this nmr curve analysis method lies in the fact that the aromatic proton resonance of polystyrene consists of two well-resolved peaks with an integrated intensity ratio of 3:2 as shown in Figure 1. Bovey, Tiers, and Filipovich[5] attributed the resonance at τ 3.0 to the *para* and the two *meta* protons and that at τ 3.5 to the two *ortho* protons. Both peaks are shifted upfield (to higher τ values) from the aromatic resonance of a single styrene unit or a model compound such as toluene (τ 2.86), but the *ortho*-proton resonance experiences the greater shift. These chemical shifts result from a "ring current" effect and an overlapping of the phenyl rings of neighboring styrene units.

From the relative intensity of the shifted *ortho*-proton resonance compared to the total styrene aromatic resonance, the nmr "block styrene" value can be determined in copolymers. If the sequence lengths (blocks) are large, the matter is simple because the peaks are well separated. However, if the styrene sequences are short, the *ortho*-proton resonance appears merely as a broadening or a shoulder on the main aromatic resonance. Resolving these curves by eye or with an electronic integrator with any reasonable accuracy is practically impossible. Curve analysis with the analog computer accomplishes the task quite satisfactorily.

The results to be presented will also show how long the styrene sequences must be to be included in the nmr "block styrene" value. That is, what is the minimum styrene sequence length which will cause the aromatic proton shift? Bovey and coworkers[5] studied emulsion butadiene–styrene copolymers and estimated that the styrene sequence length must be eight to ten units before the shoulder starts to appear in the main aromatic peak.

For this study a series of emulsion butadiene–styrene copolymers were prepared with styrene monomer initial compositions ranging from 16.8 to 94.7 mol % as shown in Table I. This table also lists the weight per cent conversion, the average styrene sequence lengths ($\bar{m}_s$), and the weight per cent of styrene in the copolymer as determined by nmr. $\bar{m}_s$ values were calculated[6] by eq 1

TABLE I

Sample	Styrene loaded, mole %	Wt % conversion	$\bar{m}_s$	Copolymer styrene, wt %
1	16.8	29.7	1.11	23.8
2	35.1	10.2	1.28	38.8
3	51.9	17.8	1.57	55.2
4	61.8	48.7	1.99	67.0
5	68.3	4.5	2.10	67.3
6	68.3	41.8	2.29	72.4
7	81.9	20.5	3.47	83.7
8	88.9	22.4	5.45	90.5
9	94.7	12.5	10.55	94.7

$$\bar{m}_s = \frac{2\%S}{R} \qquad (1)$$

where R is the run number and $\%S$ is the copolymer mole per cent styrene.

In the 60-MHz nmr spectra of these copolymers we observed the progressive formation of a shoulder, a gradual shifting to higher field, and finally the formation of a resolved peak in the aromatic resonance as $\bar{m}_s$ increased. This trend is shown in Figure 2 in which the $\bar{m}_s$ values are listed for each polymer. It is not until an $\bar{m}_s$ of 5.45 (or a copolymer composition of 90% styrene) is reached that the *ortho*-proton peak becomes resolved. An nmr spectrometer with a higher field strength would effect a separation at a lower $\bar{m}_s$, of course.

There should be three peaks under the aromatic resonance envelope—two for the "block styrene" and one for the "nonblock styrene." We used the analog computer which had been programmed for curve analysis to resolve these peaks. Since the two peaks in polystyrene are fitted very nicely by gaussian curves, these functions were chosen for "block styrene" peaks. Similarly, a lorentzian function was chosen for the "nonblock styrene" portion because the low styrene copolymer resonance best approximates it. The most physically meaningful solutions were obtained with this combination. The usual procedure of analysis is to make a Polaroid transparency of the spectrum and tape

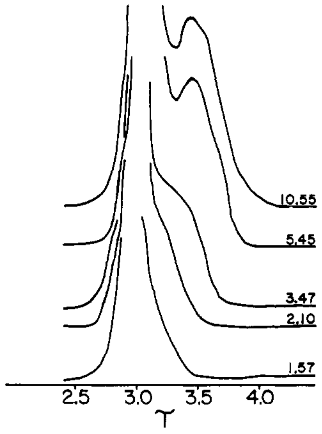

Figure 2. Aromatic resonance of samples of Table I. Shows formation of shoulder as $\bar{m}_s$ increases.

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TABLE II
COMPARISON OF EXPERIMENTAL AND "BLOCK STYRENE" RESULTS

	Copolymer styrene, wt %		"Block styrene", wt %			
			Nmr	Calcd[b]		
Sample	Nmr	Calcd[a]	(curve anal.)	$\Sigma n > 3$	$\Sigma n > 2$	$\Sigma n > 1$
1	23.8	20.3	11.7	0.07	0.55	3.79
2	38.8	38.8	16.8	1.3	4.71	15.1
3	55.2	55.8	31.8	7.8	16.8	33.2
4	67.0	66.9	34.9	21.1	33.8	50.7
5	67.3	70.0	40.7	24.2	37.4	54.0
6	72.4	73.0	46.1	30.2	43.3	59.0
7	83.7	83.5	65.2	56.2	66.7	76.6
8	90.5	89.9	79.6	75.9	81.9	86.9
9	95.9	94.9	90.8	90.5	92.6	94.1

[a] Calculated with sequence distribution program assuming reactivity ratios of 0.5 and 1.6 for styrene and butadiene, respectively.
[b] Sum of contributions of all sequence lengths greater than n, where is the number of monomer units in a sequence.

it to the computer oscilloscope. The three curves are then fitted to the envelope. For further refinement the curves are adjusted and traced directly on the original nmr chart with an X–Y recorder hooked to the computer.

A typical solution is shown in Figure 3. The resolved peaks from left to right are due to "nonblock styrene," "block styrene" *meta* and *para* protons, and "block styrene" *ortho* protons. The numbers corresponding to each of the curves are relative areas compared to the total area of the aromatic envelope. The smooth, solid line is the computed envelope, and the jagged envelope is the experimental curve.

Since the ratio of the areas of the two "block styrene" peaks should be 3:2, an attempt was made to impose this restriction on all solutions. The question of the uniqueness of the solution is pertinent. We believe that with the above restriction, which is sometimes difficult to achieve, the solutions are quite unique. More complete details and results will follow in a later publication.

Table II shows a comparison of experimental and calculated results for the copolymers listed in Table I. The calculated values were obtained with a monomer sequence distribution computer program written by Harwood.[8] The essential input for the calculation consists of monomer feed compositions, monomer molecular weights, weight per cent conversion, and monomer reactivity ratios. The calculations in Table II resulted from reactivity ratios of 0.5 and 1.6 for styrene and butadiene, respectively.

Columns 2 and 3 indicate the good agreement between nmr and calculated copolymer compositions. This is important because it shows that the terminal model used in the calculation and the reactivity ratios are valid for this system. Furthermore, this gives confidence in the calculated sequence distribution and the calculated values for "block styrene" given in the last three columns. One of the outputs of the computer program is the weight fraction (or weight per cent) of the total polymer of A or B sequences containing one to ten monomer units. Sequence lengths over ten units are lumped into one figure. It is from the styrene sequence fractions that the calculated "block styrene" figures are obtained.

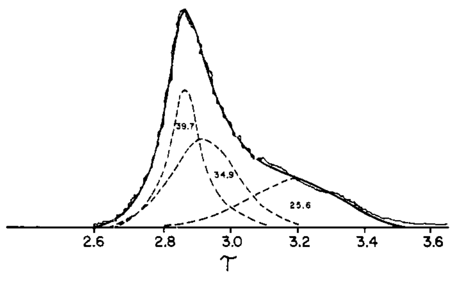

Figure 3. Curve analysis of sample 5. Expanded aromatic resonance has been offset from normal position by 360 Hz. Numbers under the peaks are integrated relative areas.

Since the nmr–curve analysis method does not disguish between the individual styrene sequences but includes the total of all sequences over a certain minimum length in the "block styrene" figure, we can sum the calculated styrene sequences from the longest to shorter ones until the accumulated total corresponds to the nmr value. This will demonstrate the lower limit of the nmr method.

The fifth column ($\Sigma n > 3$) is the sum of the weight per cents of all styrene sequences over three units in length, *i.e.*, four units and longer. Similarly, the sixth column includes all styrene sequences longer than two units. Finally, the seventh column includes all but isolated styrene units. Thus for sample 1 only 0.07 wt % of the copolymer is styrene in sequence lengths four and greater. Also, only 3.79% of the polymer is styrene in sequence lengths greater than one unit. For a particular sample there is a large jump in going from one column to the next except for sample 9 for which the difference between columns is only about 2%.

The nmr curve analysis figures for "block styrene" are high for sample 1, but lie close to the values in the seventh column and cross over to lie between columns 6 and 7 as we proceed down the table. Generally they tend to be closest to column 6. In sample 9 the nmr value is closest to column 5; but in considering the inherent inaccuracies in obtaining an absolutely unique solution in resolving the peaks and the experimental error of about ±1% in the nmr total styrene analysis, it can also be considered close to column 6.

These preliminary data indicate that the lower limit for the nmr–curve analysis method for "block styrene" lies between styrene sequence lengths of two and three units. In other words, this quite quantitative method for "block styrene" includes all styrene sequences from two to three units and longer. This is much more sensitive than the chemical osmium tetroxide method. For example the chemical method detected only 1.3% block styrene for samples 4 and 5 and 4.3% for sample 7. Except for sample 1 the nmr method gave quite reasonable results.

This method has the potential of yielding information about the styrene sequences from the shape of the aromatic resonance and its resolution into its separate peaks in butadiene–styrene copolymers and in other styrene-containing copolymers. The technique should also prove extremely useful in obtaining sequence distribution information in other copolymer systems or in tacticity studies in which the resolution of overlapped peaks is important.

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The Raman Spectra of Polybutadiene Rubbers

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ABSTRACT: The Raman spectra of *cis*-1,4-, *trans*-1,4-, and 1,2-polybutadiene are presented. Analysis of the spectra of these model compounds, and the normal coordinate results, enable the Raman frequencies to be classified by configurational structure type. The Raman carbon–carbon double bond stretching vibrations can be used to describe uniquely the structure content in polybutadienes.

Polymerization of 1,3-butadiene produces either 1,4 addition or 1,2 addition products, as shown in Figure 1. The 1,4 addition forms either the *cis* or the *trans* isomer, while the 1,2 addition proceeds either isotactically or syndiotactically.

From the symmetry of the repeat unit and vibrational theory one can predict both the number and spectral activity of fundamental vibrations. In general, there will be more Raman active fundamentals than are infrared active modes. If the molecule possesses a center of symmetry, the fundamentals are only Raman active or only infrared active, but are not active in both.

The normal coordinate analysis for *trans*-1,4-polybutadiene[1] and syndiotactic 1,2-polybutadiene[2] have been reported, but no analysis has been reported for either *cis*-1,4-polybutadiene or isotactic 1,2-polybutadiene. Since *trans*-1,4-polybutadiene contains a center of symmetry, all of the Raman frequencies will be mutually exclusive from the infrared frequencies. Syndiotactic 1,2-polybutadiene has C_{2v} symmetry for two chemical units in the repeating cell, which generates four symmetry species; three of these are infrared active, but all four are Raman active. *cis*-1,4-Polybutadiene has only C_s symmetry in the rubbery state and all modes are active in both Raman and infrared. Isotactic 1,2-polybutadiene has a vertical plane between chemical repeat units, perpendicular to the chain axis, to produce C_s symmetry, which has both infrared and Raman activity for all the fundamental vibrations. Raman scattering supplies new vibrational information for the models with C_i and C_{2v} which cannot be obtained by infrared measurements.

Since the properties of butadiene rubbers are linked to the amount of each structural component, it is essential to characterize multicomponent, commercial butadiene rubbers in terms of each structural component. Infrared methods for determining the unsaturation distribution have been developed.[3] However, the symmetrical carbon–carbon double bond stretching vibration, ν(C=C), in *trans*-1,4-polybutadiene is infrared inactive, so the out-of-plane hydrogen deformation vibrations are employed. This analysis[3] requires one to account for the absorption of all three structures at each of the three analytical frequencies. Extinction coefficient ratios can be determined using a matrix expression, and an unsaturation distribution can be calculated. Since the ν(C=C) vibration is Raman active for all three structural species, a determination based on the Raman ν(C=C) vibration should be possible.

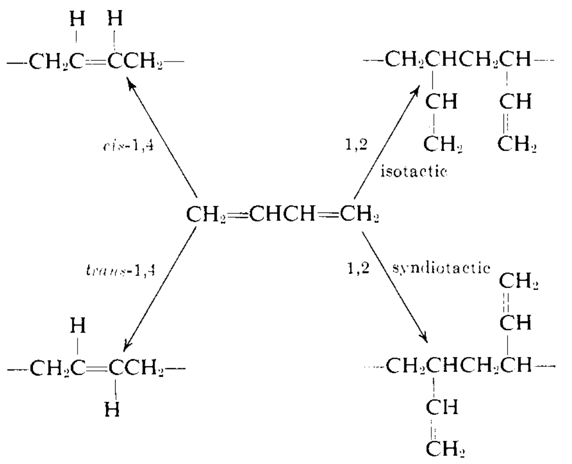

Figure 1. Polybutadiene polymerization routes.

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