Sequence Distribution Analysis of Isobutyiene—Styrene and Isobutylene—Isoprene Copolymers

Joseph P. Kennedy[a]; Tom Chou[a]

[a] Institute of Polymer Science The University of Akron, Akron, Ohio

PLEASE SCROLL DOWN FOR ARTICLE

Sequence Distribution Analysis of Isobutylene—Styrene and Isobutylene—Isoprene Copolymers

JOSEPH P. KENNEDY and TOM CHOU

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

ABSTRACT

The sequence distribution of isobutylene–styrene and isobutylene–isoprene copolymers prepared with $EtAlCl_2$ in CH_3Cl diluent at $-100°C$ have been investigated by the use of PMR spectroscopy. The basis for PMR analysis was the great environmental sensitivity of the chemical shifts of gem-dimethyl groups. A variety of calculation methods indicate that the isobutylene–styrene pair does not give random copolymers, and that the simple two parameter copolymerization model cannot be used to describe correctly the system. In contrast, poly(isobutylene-co-isoprene) is a perfectly random copolymer.

INTRODUCTION

In the course of our fundamental investigations on the cationic isomerization copolymerization of isobutylene and β-pinene [1] we have

1357

identified and assigned three PMR resonances characteristic for gem-dimethyl groups

$$
\begin{array}{c}
CH_3 \\
| \\
-C- \\
| \\
CH_3
\end{array}
$$
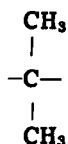
in various environments. Thus in polyisobutylene, when the gem-dimethyl group is flanked on both sides by two other gem-dimethyl groups, i.e.,

$$
\begin{array}{ccccccc}
& CH_3 & & CH_3 & & CH_3 \\
& | & & | & & | \\
-CH_2-C & -CH_2- & C & -CH_2- & C- \\
& | & & | & & | \\
& CH_3 & & CH_3 & & CH_3
\end{array}
$$

a "fully crowded" gem-dimethyl group

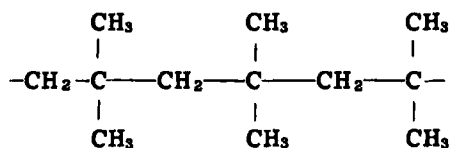a strong singlet appears at 1.1δ. Poly-β-pinene, a molecule that contains "uncrowded" gem-dimethyl groups, i.e., groups that are relatively freely rotating, shows a resonance band at 0.8δ.
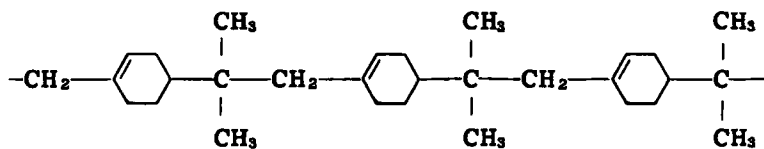
two "uncrowded" gem-dimethyl groups

Interestingly, random copolymers of isobutylene and β-pinene exhibited a new resonance at 1.0δ which we assigned to "half-crowded" gem-dimethyl groups, i.e., gem-dimethyls that are flanked by another gem-dimethyl group and are preceded (or followed) by another group which is sterically less crowded than a gem-dimethyl and allows relatively free methyl rotation. It can readily be seen that such a sequence can only occur in isobutylene copolymers, for example, with isobutylene–β-pinene sequences.

$$\begin{array}{c}
\text{CH}_3 \qquad\quad \text{CH}_3 \qquad\qquad\qquad \text{CH}_3 \qquad\quad \text{CH}_3 \\
| \qquad\qquad | \qquad\qquad\qquad | \qquad\qquad | \\
-\text{CH}_2-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\langle\bigcirc\rangle-\text{C}-\text{CH}_2-\text{C}- \\
| \qquad\qquad | \qquad\qquad\qquad | \qquad\qquad | \\
\text{CH}_3 \qquad\quad \underline{\text{CH}_3} \qquad\qquad\qquad \underline{\text{CH}_3} \qquad\quad \text{CH}_3
\end{array}$$
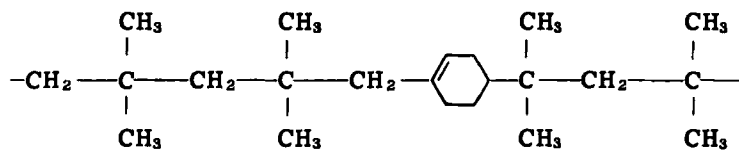
two half-crowded gem-dimethyl groups

Figure 1 shows typical PMR spectra of polyisobutylene, poly(isobutylene-co-β-pinene) and poly-β-pinene, together with all the proton assignments.

A detailed investigation of the methyl proton region by high resolution (300 MHz) PMR spectroscopy revealed that the half-crowded sequence is, in fact, a doublet probably indicative of isobutylene-β-pinene (iβ) and β-pinene–isobutylene (βi) sequences. This is shown in Figure 2 with a random poly(isobutylene-co-β-pinene) containing 59% isobutylene and 41% β-pinene [1].

A quantitative evaluation of these three resonances at 1.1, 1.0, and 0.8δ resulted in a detailed sequence analysis of poly(isobutylene-co-β-pinene) [1].

This paper concerns an extension of this work to other isobutylene copolymers namely, poly(isobutylene-co-styrene) and poly(isobutylene-co-isoprene). According to our sequence analysis based on PMR information, the isobutylene–styrene system does not give a random copolymer and cannot be described by the simple two parameter copolymerization scheme. In contrast the isobutylene–isoprene pair appears to yield perfectly random copolymers.

EXPERIMENTAL

The materials used and equipment employed have been described [1]. A variety of poly(isobutylene-co-styrene) samples were synthesized by using EtAlCl$_2$ in methyl chloride diluent at -100° C. Conversions were kept in the 5-15% range.

The copolymer composition of poly(isobutylene-co-styrene) was determined from the ratio of PMR signals in the phenyl and aliphatic regions by the equation

$$S\% = 800Ap/[5(Ap + Aa)] \qquad (1)$$

where S% is the mole percent of styrene in the polymer, Ap the proton signal area in the phenyl region, and Aa that in the aliphatic region.
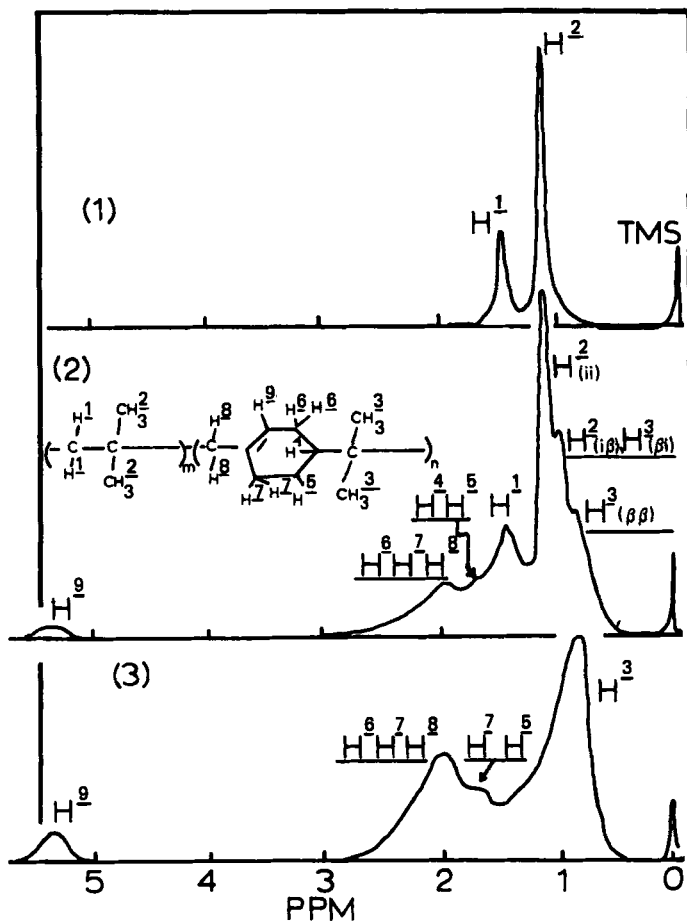
FIG. 1. PMR assignment of poly(isobutylene-co-β-pinene). Spectrum at 60 MHz in CCl₄: (1) polyisobutylene; (2) poly(isobutylene-co-β-pinene); (3) poly-β-pinene.

RESULTS AND DISCUSSION

The analysis employed for the elucidation of sequence distribution of poly(isobutylene-co-β-pinene) [1] was thought to be also useful for the investigation of the structure of other isobutylene copolymers e.g., poly(isobutylene-co-styrene) and poly(isobutylene-co-isoprene).
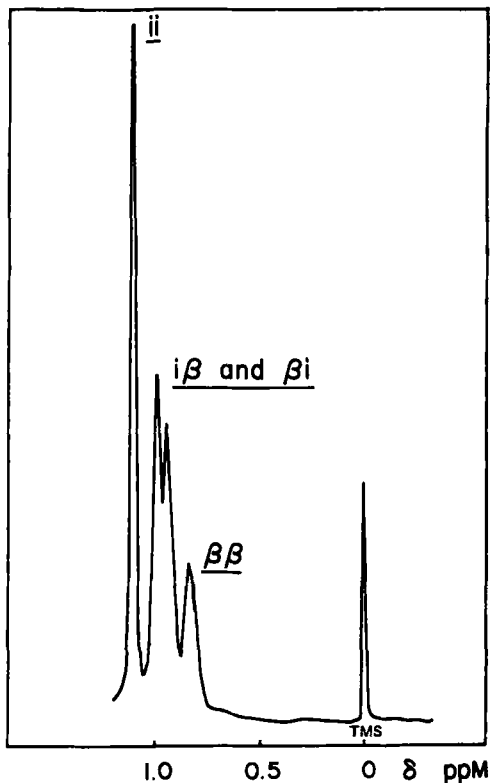
FIG. 2. PMR spectrum of poly(isobutylene-co-β-pinene); 300 MHz, isobutylene content 59 wt %, β-pinene content 41 wt %.

Poly(Isobutylene-co-Styrene)

The composition of isobutylene-styrene copolymers was plotted against monomer charge as shown in Fig. 3. The reactivity ratios calculated from the Fineman-Ross plot shown in Fig. 4 are r_i = 2.5 ± 0.2 for isobutylene and r_s = 1.4 ± 0.2 for styrene. Alternatively, the reactivity ratios calculated by Mortimer-Tidwell by using a nonlinear least-square method [2] are r_i = 2.8 ± 0.2 and r_s = 1.5 ± 0.2. These r values are somewhat different from those obtained by Imanishi et al. [3], who investigated the copolymerization
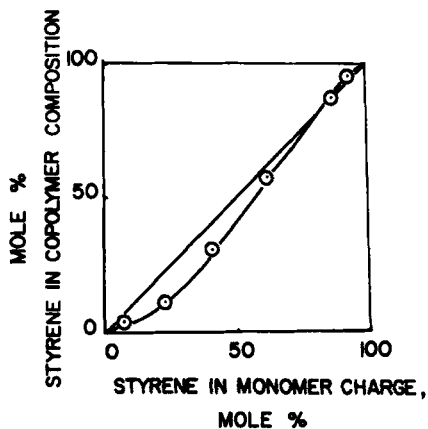
FIG. 3. Monomer charge vs. copolymer composition for isobutylene–styrene system (EtAlCl₂ in MeCl at -100° C).
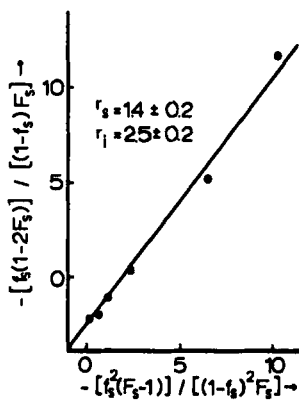
FIG. 4. Fineman-Ross plot for copolymerization of isobutylene and styrene (EtAlCl₂ in MeCl at -100° C).

of isobutylene and styrene by the use of $TiCl_4$ in CH_2Cl_2 at -78° C (r_i = 4.48 ● 0.28, r_s = 1.08 ± 0.07).

The detailed PMR spectra of the methyl region are shown in Fig. 5 for copolymers containing various amounts of styrene. An inspection

FIG. 5. PMR spectra of poly(isobutylene-co-styrenes); 300 MHz.

of these spectra reveals characteristic resonances in the ranges δ
= 0.1-0.4, 0.4-0.8, and 0.8-1.1.

Similar to the assignment of poly(isobutylene-co-β-pinene) spectra
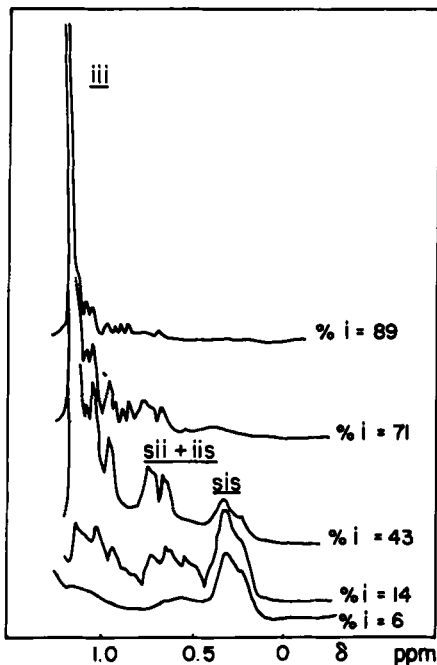[1], the peak at δ = 1.1, characteristic of gem-dimethyl resonance
of homopolyisobutylene, is assigned to the fully crowded isobutylene-
isobutylene-isobutylene or iii sequence. The broad methyl band at
δ = 0.1 to 0.4, most abundant in the spectrum of high styrene content
copolymer, is assigned to styrene-isobutylene-styrene or sis sequence
because the gem-dimethyl group of high styrene content copolymer
must be mostly in the sis sequence. The other broad range from
δ = 0.4 to 0.8 is assigned to the half-crowded or sii and iis sequences.
The latter two ranges represent composite unresolved resonances,
suggesting pentades or other molecular interactions. We have not
further examined these complicated resonances.

In accord with the above assignments, the PMR spectra of homo-
polyisobutylene, mixtures of polyisobutylene and polystyrene, and a

TABLE 1. Run Numbers for Isobutylene Copolymers

Sample	Isobutylene content in copolymer (%)	$A_1 : A_2 : A_3$	R
Poly(isobutylene-co-styrene)			
i-s-2	89	86:11: 3	11
i-s-3	71	68:26: 6	23
i-s-4	43	63:23:14	20
i-s-5	14	29:43:28	15
i-s-6	6	15:27:58	9
Poly(isobutylene-co-isoprene):			
i-p-81	19	75:22: 3	22
i-p-30	70	50:32:18	39
Poly(isobutylene-g-styrene):			
s-36	64	100: 0: 0	0
s-60	40	100: 0: 0	0

graft copolymer, poly(isobutylene-g-styrene), show only a single gem-dimethyl resonance at $\delta = 1.1$, indicating the absence of hetero linkages (run number 0, Table 1).

The PMR area ratio of these gem-dimethyl chemical shifts corresponds to the mole ratio of monomer units in the respective placements:

$$A_1 : A_2 : A_3 = P_{sis} : (P_{sii} + P_{iis}) : P_{iii} \qquad (2)$$

where P_{sis}, P_{sii}, P_{iis}, and P_{iii} are the probabilities or the percentages of an isobutylene unit in the polymer preceded by a styrene unit and followed by a styrene unit (sis), preceded by a styrene and followed by an isobutylene (sii), preceded by an isobutylene and followed by a styrene (iis), and preceded by an isobutylene and followed by an isobutylene (iii), respectively.

The relation between the run number R [4] and this ratio is given by Eq. (3):

$$P_{sis}:(P_{sii} + P_{iis}):P_{iii} = R^2/4:R(i\%-R/2):(i\%-R/2)^2 \qquad (3)$$

where i% is the concentration of isobutylene units in the copolymer. Thus, R can be obtained by determining the respective areas in the ranges δ = 0.1-0.4, 0.4-0.8, and 0.8-1.1 in the PMR spectra associated with P_{sis}, $(P_{sii} + P_{iis})$, P_{iii}, and the overall copolymer composition. We used a trial-and-error, least-squares method to select the best R values shown in Table 1.

A representative calculation is shown below, for a poly(isobutylene-co-styrene) sample containing 3% styrene (i-s-3 in Table 1).

Step 1. Measure the PMR signal ratio $A_1:A_2:A_3$ and copolymer composition, i%; e.g., $A_1:A_2:A_3$ = 68:26:6 (normalized) i% = 71%, from Eq. (1).

Step 2. Assume an R value, and use it to calculate the probability ratio, $P_{sis}:(P_{sii} + P_{iis}):P_{iii}$ from Eq. (3) and repeat this calculation in the possible R value range (Table 2).

Step 3. Determine errors between measured (step 1) and calculated (step 2) probability ratios, square and sum (Table 3).

Step 4. Plot R versus squared errors and determine the least-square error graphically. Thus, R = 23, from Fig. 6.

Figure 7 shows our results in a run number versus composition plot. The circles indicate experimental points determined from PMR measurements and the line is calculated from reactivity ratios determined in this work. All the experimental points are consistently lower than the theoretical line for random copolymers, indicating that the reactivity ratio product is larger than unity and that the

TABLE 2. Calculation of Probability Ratio

R	$P_{sis}:(P_{sii} + P_{iis}):P_{iii}$ (normalized)
18	77:22:2
20	74:24:2
22	71:26:3
24	69:28:3
26	67:30:3
28	65:32:4

TABLE 3. Sum of Squares of Errors in Probability Ratios[a]

R	Δ_1^2	+	Δ_2^2	+	Δ_3^2	=	Δ^2
18	9^2	+	4^2	+	4^2	=	113
20	6^2	+	2^2	+	4^2	=	56
22	3^2	+	0^2	+	3^2	=	18
24	1^2	+	2^2	+	3^2	=	14
26	1^2	+	4^2	+	3^2	=	26
28	3^2	+	6^2	+	2^2	=	49

[a] Here Δ_1 is $|A_1 - P_{sis}|$, $\Delta_2 = |A_2 - (P_{sii} + P_{iis})|$, and $\Delta_3 = |A_3 - P_{iii}|$.
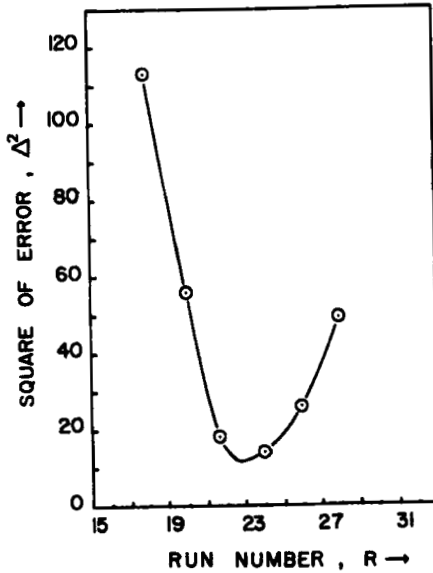

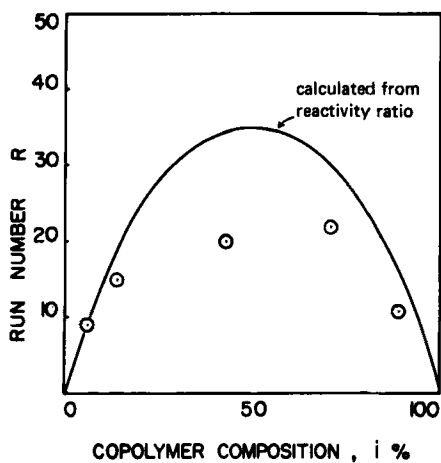FIG. 6. Run number vs. square of error.

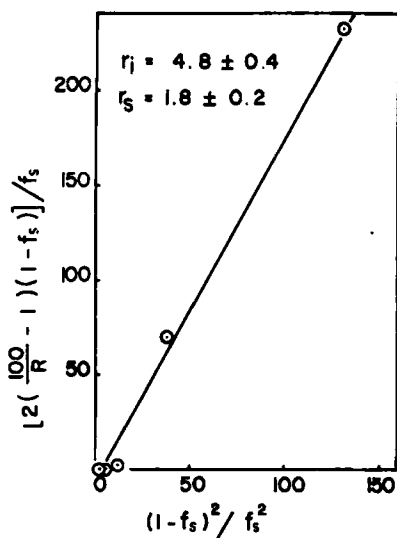FIG. 7. Run numbers of poly(isobutylene-co-styrene) vs. co-polymer composition.

FIG. 8. Harwood-Ritchey plot for isobutylene-styrene copolymer-ization (EtAlCl$_2$ in MeCl at -100°C).

TABLE 4. Reactivity Ratios of Isobutylene (r_i) and Styrene (r_s)
Obtained by Various Methods

Method	r_i	r_s
Fineman-Ross	2.5 ± 0.2	1.4 ± 0.2
Mortimer-Tidwell	2.8 ± 0.2	1.5 ± 0.2
Harwood-Ritchey	4.8 ± 0.4	1.8 ± 0.2

copolymer is "blocky" [4]. The discrepancy between experimental
and theoretical values calculated from reactivity ratios indicates that
the two parameter scheme is not valid for the cationic copolymeriza-
tion of isobutylene and styrene. The origin that causes this discrepancy
is not clear. Conceivably, it may be due to the presence of propagat-
ing chain ends of different reactivities [5-7].

To gain further insight into the composition of isobutylene–styrene
copolymers we have calculated the reactivity ratios for these mono-
mers from copolymer compositions and run numbers by the use of
the Harwood-Ritchey plot. Figure 8 shows such a plot. A compilation
of reactivity ratios obtained in this work by various methods is shown
in Table 4. Evidently, the reactivity ratio product is significantly
larger than unity and the two-parameter model does not describe this
copolymer system.

Poly(Isobutylene-co-Isoprene)

Stehling and Bartz [8] have also detected three kinds of gem-
dimethyl groups in the PMR spectrum of isobutylene–isoprene copoly-
mers. According to these authors, copolymers containing isobutylene
are ideal for monomer sequence distribution studies, because of the
sensitivity of the chemical shifts of gem-dimethyl groups to the nature
of neighboring groups. Using Stehling and Bartz's data [8], we have
calculated the run number for poly(isobutylene-co-isoprene). Addi-
tionally, we have prepared such a copolymer, using EtAlCl₂ in MeCl
at -100°C, obtained its PMR spectrum, and determined its run number.
These results are also included in Table 1. The run numbers of these
copolymers were found to be close to the theoretical values of random
copolymers. These PMR investigations are in accord with Flory's
work [9], which also indicated that poly(isobutylene-co-isoprene) is
random in nature.

REFERENCES

[1] J. P. Kennedy and T. Chou, Adv. Polym. Sci., 21, 1 (1976).

[2] G. A. Mortimer and P. W. Tidwell, J. Polym. Sci. A, 3, 369 (1965).

[3] Y. Imanishi, T. Higashimura, and S. Okamura, J. Polym. Sci. A, 3, 2455 (1965).

[4] H. J. Harwood and W. M. Ritchey, J. Polym. Sci. B, 6, 277 (1968).

[5] K. F. O'Driscoll, T. Higashimura, and S. Okamura, Makromol. Chem., 85, 178 (1965).

[6] K. F. O'Driscoll, P. W. Tidwell, and G. A. Mortimer, J. Polym. Sci. B, 5, 575 (1967).

[7] P. W. Tidwell and G. A. Mortimer, Macromol. Sci.-Revs., Macromol. Chem., C4, 281 (1970).

[8] F. C. Stehling and K. W. Bartz, Anal. Chem., 38, 1467 (1966).

[9] P. J. Flory, Ind. Eng. Chem., 38, 4417 (1946).