The Microstructure of Poly(Isobutylene-*co-p*-Methylstyrene) by NMR Spectroscopy

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THE MICROSTRUCTURE OF POLY(ISOBUTYLENE-*co-p*-METHYLSTYRENE) BY NMR SPECTROSCOPY

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ABSTRACT

The microstructure of isobutylene-*para*-methylstyrene (IB–pMeSt) copolymers was studied by NMR spectroscopy. ^{1}H- and ^{13}C-NMR spectra were used to obtain overall copolymer compositions. ^{13}C-NMR signals were assigned in terms of triad monomer sequences, and triad distributions were obtained over a wide copolymer composition range. According to statistical tests, the IB–pMeSt copolymerization cannot be described by zero- (Bernoullian) or first-order Markov models because reactivity ratios r_{IB} and $r_{p\text{MeSt}}$ were found to change with the monomer feed composition. Additional insight into the microstructure of IB–

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*p*MeSt copolymers was gained by calculating sequence numbers, run numbers, and sequence lengths from triad distributions. Further, the Kelen–Tüdös plot showed a distinct curvature indicating that the Kelen–Tüdös method, applied over the entire monomer feed composition range, cannot give meaningful reactivity ratios for this monomer pair. Evidently the simple two-parameter Mayo–Lewis model is inadequate to describe the IB–*p*MeSt copolymerization system.

INTRODUCTION

The objective of this research was the elucidation of the microstructure of IB–*p*MeSt copolymers prepared by living carbocationic polymerization [1, 2]. Our earlier work in this field concerned a study of the effect of experimental variables on the composition and molecular weight of poly(IB-*co-p*MeSt), the determination of reactivity ratios r_{IB} and r_{pMeSt} by kinetic analysis supplemented by dual detector gel permeation chromatography, and, ultimately, the definition of conditions for the reproducible synthesis of desirable high molecular weight copolymers [3, 4]. Previous research, however, focused only on a rather narrow copolymer composition range (i.e., ≤ 10 mol% *p*MeSt), the range of interest for technologically useful second generation butyl rubbers [5–9]. These earlier investigations have now been extended by elucidating the microstructure of poly(IB-*co-p*MeSt) by NMR spectroscopy over the entire IB/*p*MeSt composition range.

EXPERIMENTAL

Copolymerization

The source and purification of chemicals have been described [3].

Copolymerizations were carried out in a glove box under a dry nitrogen atmosphere in 75 mL test tubes. Typically, 0.05 mmol 1,3-bis(1-methoxy-1-methylethyl)-5-*t*-butylbenzene, 0.15 mmol Et$_3$N, 0.25 mmol 2,6-di-*tert*-butylpyridine (D*t*BP), and a mixture of IB and *p*MeSt were added sequentially to 20 mL ethyl chloride (EtCl) at $-50°C$. The charge was stirred for about 1 minute, and 0.734 mmol TiCl$_4$ in 1 mL EtCl was rapidly introduced into the vigorously shaken test tube. Copolymerization was terminated with 3 mL prechilled methanol. Copolymers were washed with acidified methanol and dried in vacuo to constant weight.

Spectroscopy

^{1}H-NMR spectra were obtained at ambient temperature by a Varian Gemini-200 spectrometer operating at 200 MHz; 128 transients were accumulated with 60° pulses, 2.7 seconds acquisition time, and 3 seconds delay. Sample concentrations were 20 mg in 1 mL CDCl$_3$.

^{13}C-NMR spectra were obtained at ambient temperature by a Varian Gemini-200 and a Varian XL-400 spectrometer operating at 50.3 and 100.6 MHz, respectively. Typically 10,000–15,000 transients were accumulated with 60° pulses, 1 second acquisition time, and 3 seconds delay. The spectra were obtained with gate

decoupling to suppress the nuclear Overhauser effect. Sample concentrations varied from 200 to 350 mg in 1 mL CDCl₃. The internal standard was tetramethylsilane.

DEPT (*D*istortionless *E*nhancement by *P*olarization *T*ransfer) [10] spectra were obtained at 50.3 MHz using a standard Gemini microprogram with 10,000 transients, 1 second acquisition time, and 2 seconds delay.

2D *¹H-¹³C HETeronuclear chemical shift CORrelated* (*HETCOR*) *spectra* [11–13] were acquired and processed with a Gemini HETCOR microprogram. Spectra were obtained over the aliphatic region only with the 760 Hz spectral width along the F_1 (proton) axis and 2800 Hz along the F_2 (carbon) axis, 256 increments, 128 acquisitions, 512 data points, 1.1 seconds pulse repetition time.

Spin-lattice relaxation times (T_1's) were determined by the inversion-recovery experiment [14, 15]. Experimental details have been described [16]. The longest T_1 (~0.7 second) in the ¹H-NMR spectrum was observed for aromatic protons. Scheme 1 shows ¹³C T_1's. The spin-lattice relaxation data are necessary to determine conditions for obtaining quantitative spectra.

RESULTS AND DISCUSSION

Assignments of NMR Resonances

¹H-NMR Spectra

¹H-NMR spectra were used to determine copolymer compositions. A representative ¹H-NMR spectrum is shown in Fig. 1(a). The aromatic region, 6.2–7.1 ppm, is due to 4 aromatic protons of the *p*MeSt units, whereas the aliphatic region, 0.1–3.0 ppm, is due to 6 protons of the *p*MeSt plus 8 protons of the IB units. Thus, the IB content ($B_\%$) can be calculated by:

$$B_\% = \frac{(I_{\text{aliph}} - 1.5 I_{\text{arom}}) \cdot 100\%}{I_{\text{aliph}} + 0.5 I_{\text{arom}}}$$

where I_{aliph} and I_{arom} are integrated intensities of the aliphatic and aromatic signals, respectively.
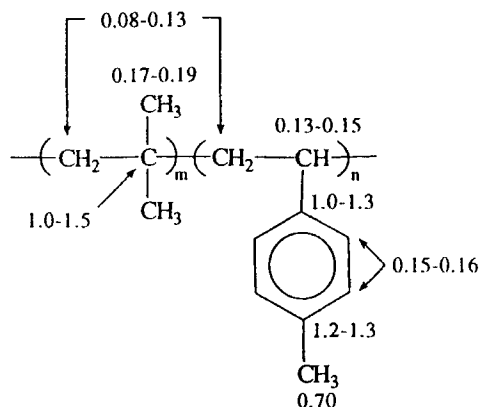
SCHEME 1.   ¹³C spin-lattice relaxation times (seconds) for poly(isobutylene-*co*-*p*-methylstyrene). 50.3 MHz, 70 mol% IB in copolymer, $\overline{M}_n$ = 9600 g/mol, 350 mg in 1 mL CDCl₃.

FIG. 1.   NMR spectra of poly(isobutylene-*co-p*-methylstyrene) containing 45 mol%
IB: (a) ¹H-NMR spectrum; (b) ¹³C-NMR spectrum.

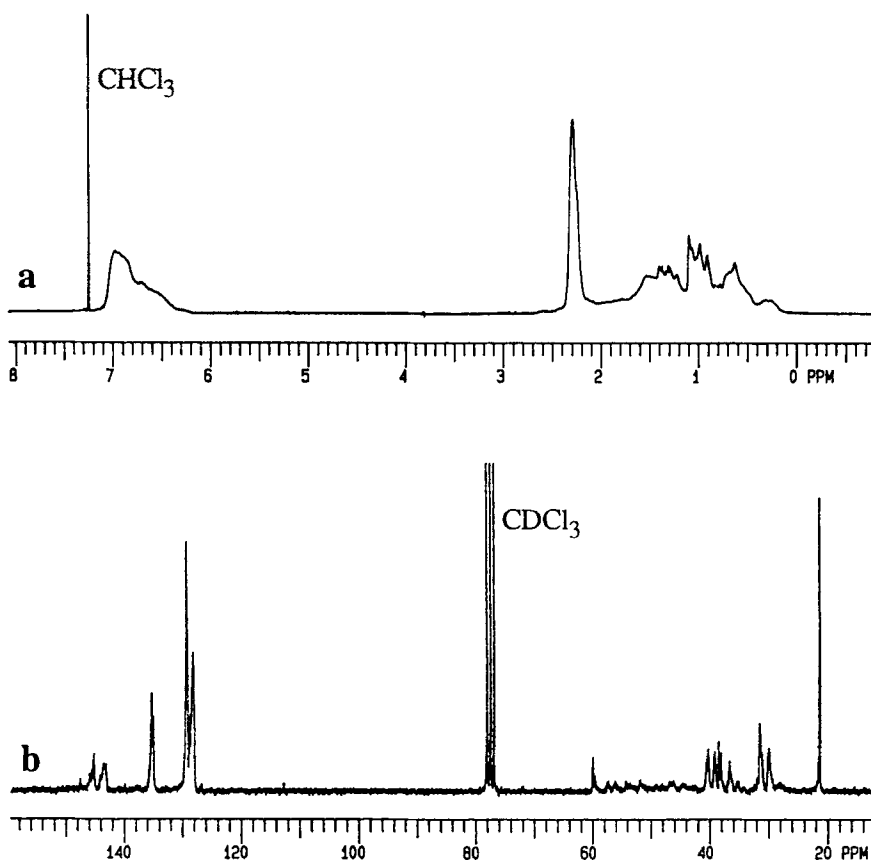The aliphatic region of the proton spectrum is poorly resolved at the applied
magnetic field (200 MHz resonance frequency). Moreover, the HETCOR spectrum
(Fig. 2) reveals overlapping of different types of signals. Therefore ¹H-NMR spec-
tra were not further analyzed.

¹³C-NMR Spectra

A representative ¹³C-NMR spectrum of an IB–*p*MeSt copolymer is shown in
Fig. 1(b). DEPT spectral editing (Fig. 3) allows the identification of the signals
with respect to the number of hydrogens attached to a carbon. The following
regions have been identified: CH_3: 21–33 ppm; aliphatic CH: 37–41 ppm; CH_2: 42–
60 ppm; aromatic CH: 128–130 ppm. Quaternary carbon signals are absent from
DEPT spectra since they do not bear hydrogens. Aliphatic quaternary carbon sig-
nals appear at 35–39 ppm in the conventional ¹³C-NMR spectrum (Fig. 1b) and they
overlap with the methine carbon signals. Aromatic quaternary carbons resonate at
135–148 ppm.

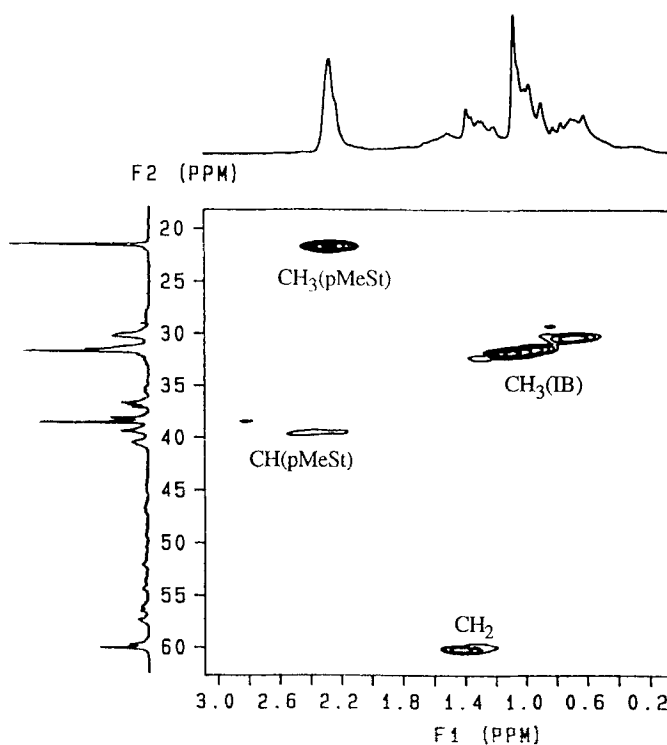Signal assignments starting at high field follow.

FIG. 2.   2D ^{1}H-^{13}C heteronuclear shift correlated (HETCOR) contour map of poly-(isobutylene-*co-p*-methylstyrene) (60 mol% IB content). F_1 = conventional proton spectrum and F_2 = conventional ^{13}C spectrum.

Methyl Region (21-33 ppm).   A comparison of the spectra of a copolymer and poly-*p*MeSt (Fig. 4) indicates that the signal at 21.3 ppm is due to the methyl group in *p*MeSt units. The signals at 27-33 ppm are due to methyl groups in IB units. These assignments are consistent with the results of isotopic labeling (see later).

Since the methyl signals are well resolved, this part of the spectrum was used to determine copolymer composition. The molar *p*MeSt content ($S_{\%}$) is given by:

$$S_{\%} = \frac{I_{21.3} \cdot 100\%}{I_{21.3} + 0.5I_{27\text{-}33}}$$

where I is the integrated signal intensity with the corresponding chemical shifts indicated in the subscript.

Signals due to the methyl carbons of IB units can be assigned in terms of IB-centered triads: BBB, SBB, BBS, and SBS, where BBB stands for three consecutive IB units, SBB for a *p*MeSt followed by two IB units, and so forth. Scheme 2 shows the structures of all possible triads in an IB-*p*MeSt copolymer. Only head-to-tail monomer placement is considered.

The signal at 31.3 ppm appears in the spectrum of PIB [16]; therefore, signals in this area of the copolymer spectra are assigned to BBB triads.
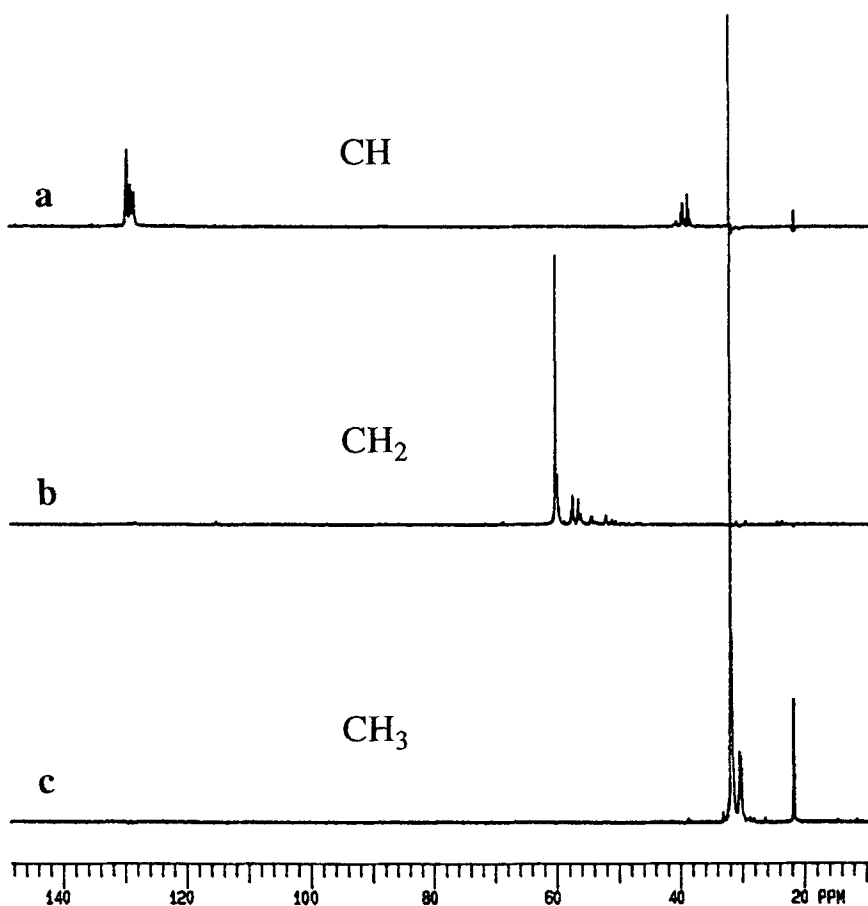
FIG. 3. DEPT spectra of poly(isobutylene-*co-p*-methylstyrene) (80 mol% IB content): (a) "CH" subspectrum; (b) "CH₂" subspectrum; (c) "CH₃" subspectrum. Compare with Fig. 1(b).

The resonances at 29.2–30.7 ppm are due to SBB and BBS triads. At low *p*MeSt contents they form a doublet (Fig. 4a). Scheme 2 (see SBB and BBS) helps to visualize the reason for this: The chiral methine group renders the two adjacent IB methyls diastereotopic and hence magnetically nonequivalent. Thus, each signal of the doublet represents one of the two nonequivalent methyl carbons rather than SBB and BBS sequences.

The broad resonances in the 27–29.2 ppm range are observed only when the *p*MeSt content is high; hence they are assigned to SBS triads.

Aliphatic Methine and Quaternary Carbon Region (35–41 ppm). A comparison of ¹³C-NMR and DEPT spectra (Figs. 3a and 4a) indicates that the quaternary carbon signals of IB and the methine signals of *p*MeSt overlap in the 35–41 ppm region. The DEPT technique can be used to resolve this overlap, and *p*MeSt-

FIG. 4. ^{13}C-NMR spectra of (a) poly(isobutylene-*co-p*-methylstyrene) (96 mol% IB content); (b) poly(*p*-methylstyrene).
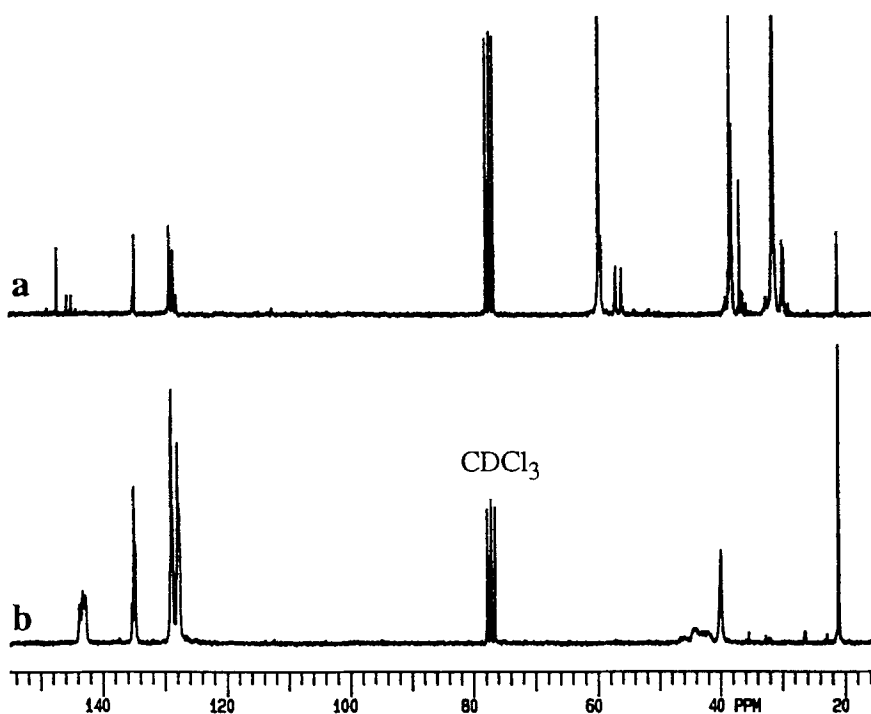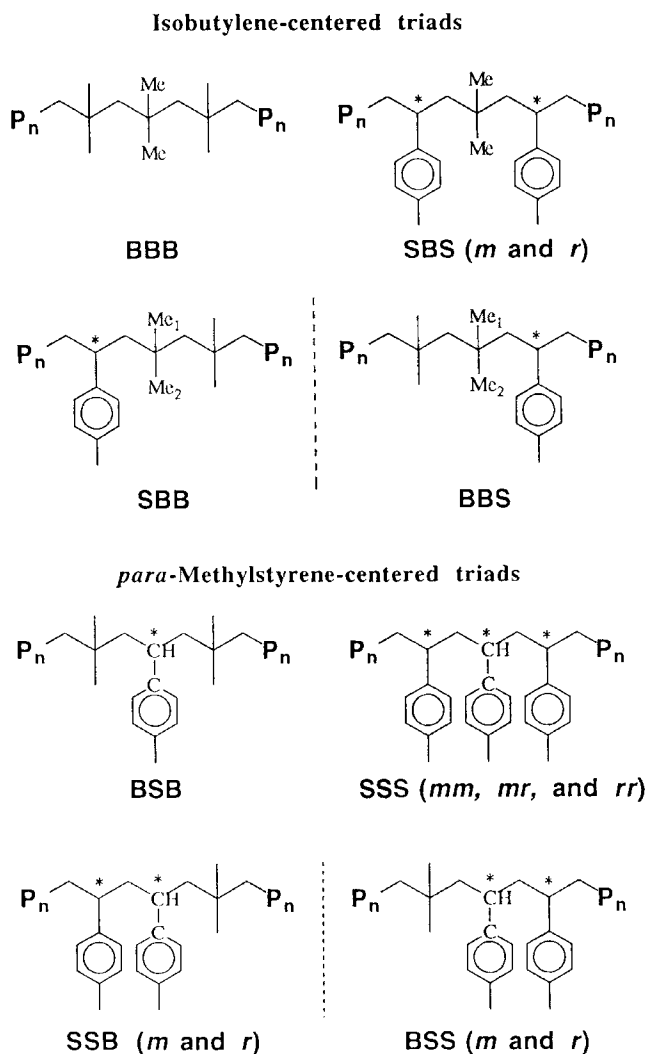
centered triad distribution can be obtained. Since the DEPT pulse sequence transfers the polarization from protons to carbons, DEPT spectra show only the signals of carbons directly bonded to hydrogens, and signals due to quaternary carbons are absent. In this manner the congested 35–41 ppm region (Fig. 1b) can be simplified by the DEPT technique so that the spectrum will show only three groups of *p*MeSt methine signals due to different neighbors of the central *p*MeSt unit (Fig. 5a–c).

To obtain assignments, spectra of copolymers of different compositions were recorded. Representative spectra and assignments are shown in Fig. 5(a–c) and Table 1. The most intense signal at the high IB content (37.5–38.3 ppm) is assigned to the BSB triad while the signal which is most intense at the low IB content (39.5–40.9 ppm) is assigned to the SSS triad. The signal at 40 ppm in the spectrum of poly-*p*MeSt (Fig. 4b) serves as a reference for SSS triads.

Methylene Region (42–60 ppm).   The methylene region of the spectra was analyzed by the use of a method developed for end-group analysis of polymers [17, 18]. It combines selective deuteration of polymers and DEPT. Since the response of a carbon to the DEPT sequence is sensitive to the number of carbon-bonded hydrogens, the replacement of hydrogens with deuteriums leads to unique spectral changes and provides for unambiguous assignments. The efficacy of this method

Isobutylene-centered triads

BBB

SBS (*m* and *r*)

SBB

BBS

para-**Methylstyrene-centered triads**

BSB

SSS (*mm, mr,* and *rr*)

SSB (*m* and *r*)

BSS (*m* and *r*)

SCHEME 2. Structures of monomer triads of poly(isobutylene-*co-p*-methylstyrene); head-to-tail placement. An asterisk indicates a chiral center.

has been demonstrated by end-group analyses of various polymers [17, 18]. We applied this approach for the analysis of IB-*p*MeSt copolymers.

Thus, conventional (nondeuterated) *p*MeSt was copolymerized with perdeuterated isobutylene, C_4D_8, and the spectra of the copolymers were recorded by using the DEPT pulse sequence. Figure 6 demonstrates the power of this method.

Due to incomplete deuteration of IB (^2H isotope content ~80%), the copolymer contains in addition to CD_2 and CD_3 considerable amounts of CHD and CHD_2 groups (traces of CH_2 and CH_2D groups can also be detected). The DEPT-90° pulse sequence leaves in the spectrum (Fig. 6b) only the signals of carbons connected to
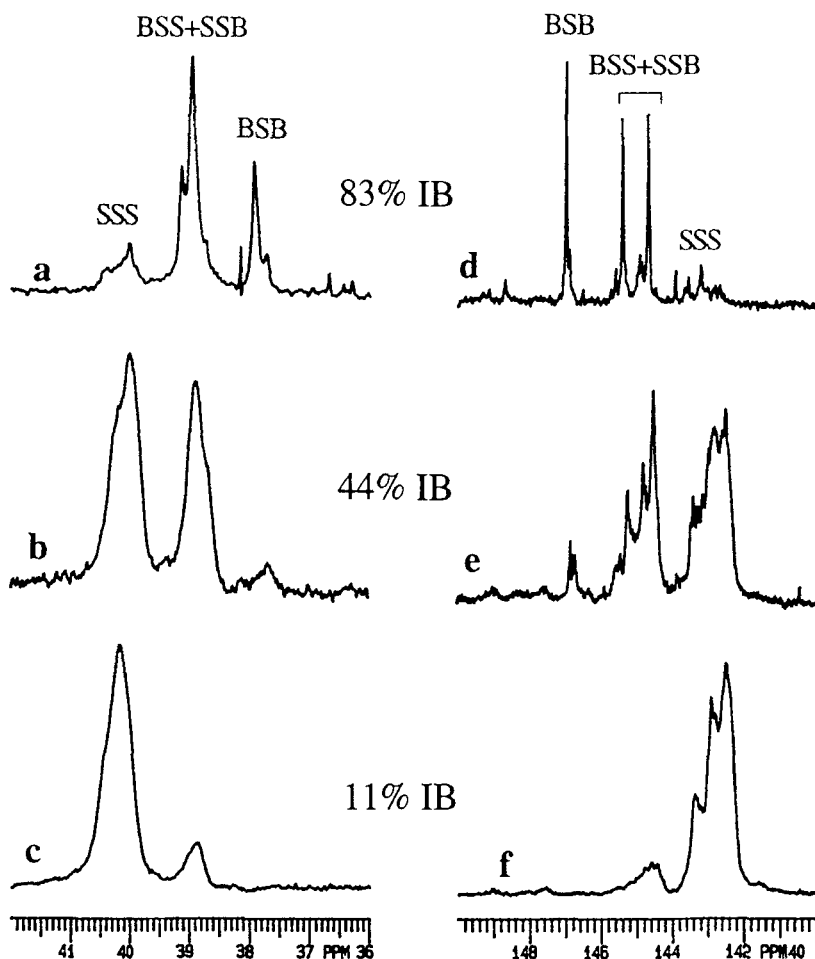
FIG. 5. DEPT and conventional ^{13}C-NMR spectra of copolymers: (a) "CH only" DEPT spectrum, 83 mol% IB; (b) "CH only" DEPT spectrum, 44 mol% IB; (c) "CH only" DEPT spectrum, 11 mol% IB; (d) ^{13}C-NMR spectrum, 83 mol% IB; (e) ^{13}C-NMR spectrum, 44 mol% IB; (f) ^{13}C-NMR spectrum, 11 mol% IB.

one hydrogen, i.e., the CH of the pMeSt units (37–41 ppm), and the residual CHD_2 (27–32 ppm) and CHD (55–60 ppm) of the IB units. A direct assignment of the signals can therefore be made: The three signals at ~ 55.3, 56.5, and 59.1 ppm in spectrum 6b are due to the IB methylene carbons connected to residual protons (CHD). The corresponding signals at 55.0–60.0 ppm in the ^{13}C-NMR spectrum of the protic copolymer (Fig. 6a) are due to CH_2 signals of nondeuterated IB units. All the signals of partially deuterated methylenes are shifted upfield by ~ 0.7 ppm relative to the signals of the protic polymer because of the isotropic shift caused by the replacement of hydrogens with deuteriums.

In the DEPT-135° spectrum the CH and CH_3 signals are positive while the CH_2 signals are negative (Fig. 6c). The positive CHD signals at 55–57 ppm of IB
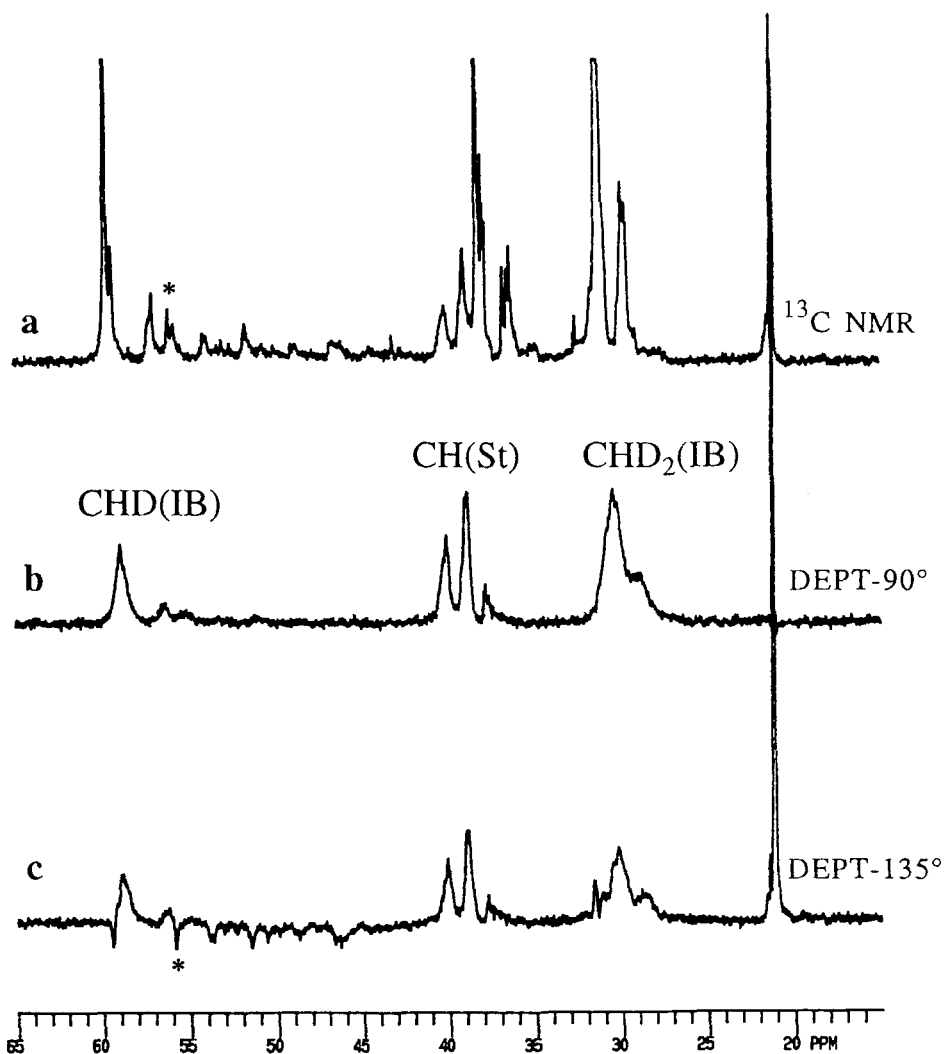
FIG. 6.   Spectra of isotopomeric copolymers (70 mol% IB content): (a) ^{13}C-NMR spectrum of conventional (nondeuterated) copolymer; (b) DEPT-90° ("CH" only) spectrum of copolymer of deuterated IB and conventional pMeSt; (c) DEPT-135° (CH and CH$_3$ "+", CH$_2$ "−") spectrum of copolymer of deuterated IB and conventional pMeSt.

overlap with the negative CH$_2$ signal (marked by an asterisk). The latter can be due only to the methylenes of nondeuterated pMeSt. Scheme 3 explains this overlap: One of the two methylenes which flank the pMeSt blocks is due to the pMeSt unit while the other to IB. Because of structural symmetry, they resonate at the same frequency. Because of this overlap, we did not pursue further assignment in this region.

As mentioned above, the DEPT spectra of deuterated copolymer confirm the assignments of methyl signals: The signal at 21.3 ppm due to pMeSt units remains unchanged in the spectrum of the copolymer synthesized with deuterated IB; in
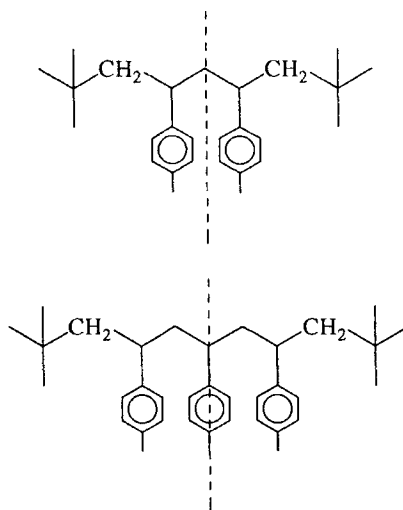
SCHEME 3. Structure of poly(*p*MeSt) blocks.

contrast, the signals at 27–33 ppm shift upfield and become less intense and broader because of coupling with deuterium, which indicates that these signals are due to IB (Fig. 6c).

Aromatic Region (128–148 ppm). In this region only the quaternary carbon next to the backbone methine group is sufficiently sensitive with respect to the chemical environment to provide quantitative microstructure information. The assignments were made in terms of *p*MeSt-centered triads by comparison with the aliphatic CH subspectra (Fig. 5). The spectrum of poly-*p*MeSt (Fig. 4b) was the reference for SSS triads.

The appearance of the BSS + SSB resonance as a doublet in Fig. 5(d) is due to the two disastereomers of these triads and not to BSS and SSB triads (Scheme 2).

Table 1 summarizes the assignments obtained by a combination of various NMR techniques, isotopic labeling, and from studies of copolymers with different compositions. Three sets of signals are available for triad distribution analysis: One set of methyl resonances at 27–33 ppm for IB-centered triads, and two sets for *p*MeSt-centered triads at 37–41 ppm (DEPT spectra) and 142–148 ppm.

Indanyl End-groups. The low-intensity signals consistently observed in all spectra at 120–122 and 148–150 ppm are characteristic of the aromatic initiator fragment incorporated in the copolymer [19]. In most of the spectra the integrated intensities of these signals are close to what is expected from the molecular weights (determined by GPC). However, for copolymers obtained at high conversions, integrated intensities are somewhat higher (up to 60%) than anticipated. This difference is most likely due to indanyl end-groups formed by intramolecular alkylation [20]:
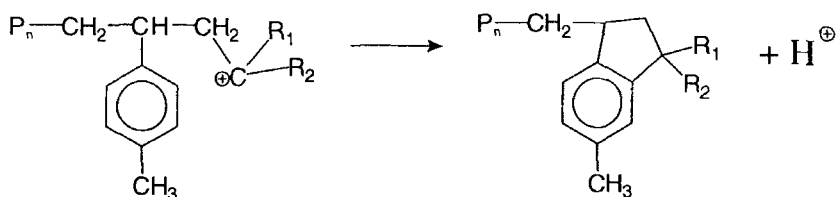
where R_1 = H and R_2 = p-MeAr, or R_1 = R_2 = Me.

This proposition is supported by comparing the spectrum of the copolymer (Fig. 7a) with that of a low molecular weight PIB prepared to contain indanyl

TABLE 1. Chemical Shifts and Assignments of Signals in ^{13}C-NMR Spectra of Poly(Isobutylene-co-p-Methylstyrene)s (B = IB, S = pMeSt)
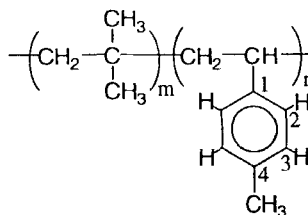
Group	Sequence	Chemical shift, ppm
	Aliphatic Region	
$CH_3(S)$		21.3
$CH_3(B)$	SBS	27.0–29.2
	SBB + BBS	29.2–30.7
	BBB	30.7–32.2
C(B)		35–39
CH(S)	BSB	37.5–38.3
	BSS + SSB	38.4–39.5
	SSS	39.5–40.9
$CH_2(S)$		42.0–56.5
$CH_2(B)$		55.0–60.0
	Aromatic Region	
CH(S)		128.0–129.5
$C^4(S)$		135–136
$C^1(S)$	SSS	142–144
	BSS + SSB	144–146
	BSB	147.3
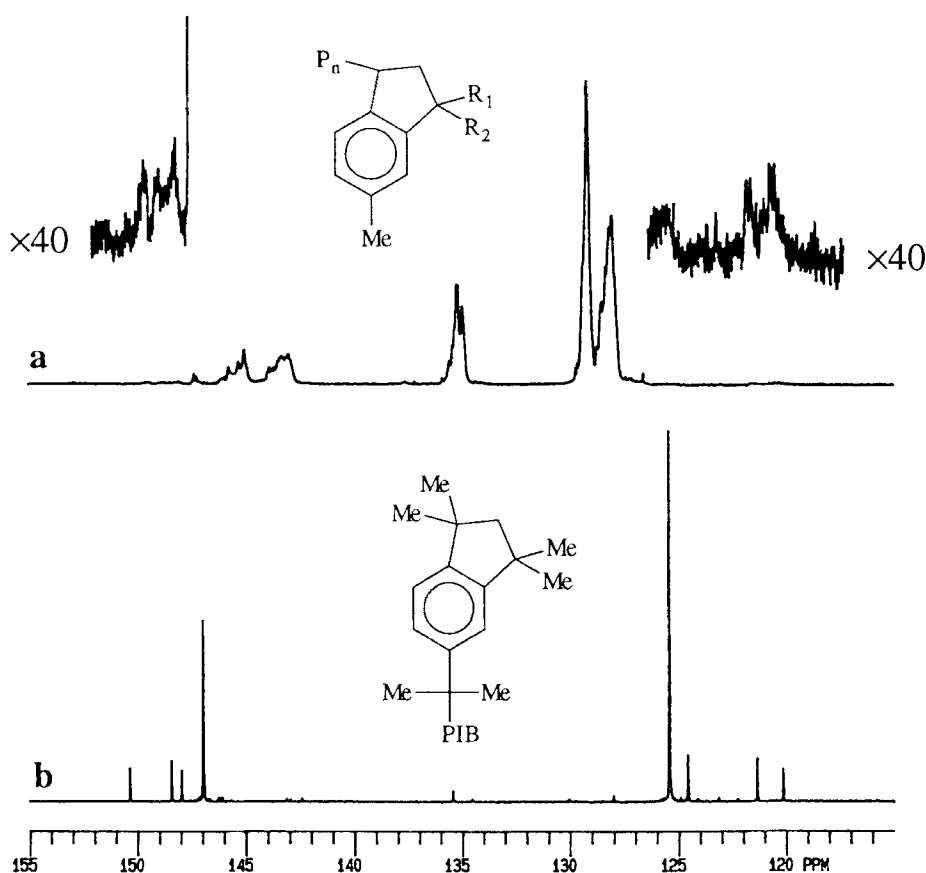
FIG. 7.   Aromatic region of ^{13}C-NMR spectra: (a) poly(isobutylene-co-p-methylsty-rene) (44 mol% IB content, $\overline{M}_n$ = 20,300 g/mol); (b) polyisobutylene synthesized at −40°C with the 1,4-bis-(1-chloro-1-methylethyl)benzene initiator: $\overline{M}_n$ = 1000 g/mol, ~15% of all end-groups are indanyl end-groups. R_1 = H and R_2 = pMeAr, or R_1 = R_2 = Me.

groups (Fig. 7b). The two major peaks at 125.4 and 147.0 ppm in spectrum 7b are due to the symmetric p-phenylene fragment of the initiator incorporated in the middle of the PIB. The six small resonances (120.1, 121.4, 124.6, 148.0, 148.4, and 150.4 ppm) are due to the aromatic carbons of the indanyl group formed after the addition of a single IB unit followed by intermolecular alkylation. These signals appear in the same region as the low intensity signals in the spectra of IB–pMeSt copolymers (Fig. 7).

Evidently pMeSt induces chain transfer in IB–pMeSt copolymerization simi-larly to isoprene in IB–isoprene copolymerization [21].

Microstructure of Isobutylene–p-Methylstyrene Copolymers

Triad Distribution Analysis

A series of copolymers were synthesized by the use of a wide range of mono-mer feed compositions. Experimental details together with characterization data are

shown in Table 2. Monomer conversions were kept as low as possible; however, due to very fast polymerizations, conversions could not be precisely controlled. For statistical analysis only copolymers obtained at or below 20% conversions were used.

Table 3 shows triad distribution data calculated from ^{13}C-NMR spectra.
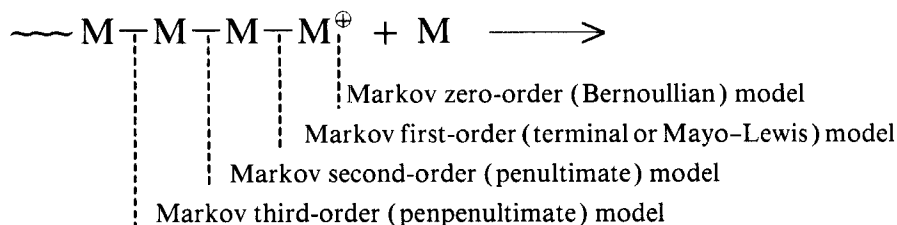
Chain growth in copolymerizations is usually described by Markov statistics of various orders [22]:

$$\sim\!\!M\!-\!\!M\!-\!\!M\!-\!\!M_i^{\oplus} + M \longrightarrow$$

Markov zero-order (Bernoullian) model

Markov first-order (terminal or Mayo–Lewis) model

Markov second-order (penultimate) model

Markov third-order (penpenultimate) model

The validity of a particular model can be tested by examination of monomer sequence distributions obtained from NMR spectra [22]. Table 4 shows a comparison of observed and calculated triad distributions and indicates that the IB–pMeSt copolymerization cannot be described by Bernoullian statistics.

Since Bernoullian statistics was found not to hold, we tested for the first-order Markov model. The reactivity ratios, i.e., the ratios of rate constants of homopropagation and cross-propagation, $r_{IB} = k_{BB}/k_{BS}$ and $r_{pMeSt} = k_{SS}/k_{SB}$ [23], can be calculated for every sample by

TABLE 2. Copolymerization of Isobutylene and p-Methylstyrene[a]

IB in charge, mol%	Time, min	Yield, %	IB units in copolymer ($B_{\%}$)			$\overline{M}_n$, g/mol	$\overline{M}_w/\overline{M}_n$
			^{1}H NMR, mol%	^{13}C NMR, mol%	Average mol%		
20	1	27.3	—[b]	7.8	7.8	19,000	1.69
24	1.3	27.0	—[b]	10.1	10.1	18,200	1.60
34	1.7	19.4	14.3	14.1	14.2 ± 0.1	15,000	1.61
50	2	14.3	27.3	25.3	26.3 ± 1.0	10,200	1.74
70	3	10.5	46.1	44.9	45.5 ± 0.6	9,100	1.60
80	5	9.2	58.9	62.4	60.7 ± 0.7	9,100	1.50
85	7	13.2	70.4	71.4	70.9 ± 0.5	12,100	1.50
87	8	7.3	74.7	75.2	75.0 ± 0.3	12,700	1.49
90	13	20.9	82.3	82.3	82.3 ± 0.0	20,300	1.48
95	20	30.8	92.4	92.1	92.3 ± 0.2	31,400	1.42
97	10	16.0	94.8	95.1	95.0 ± 0.2	19,300	1.35

[a]TiCl$_4$ (36.7 mmol/L) was added at −50°C to a 20-mL EtCl solution containing 2.5 mmol/L initiator, 7.5 mmol/L Et$_3$N, 12.5 mmol/L DtBP, and a mixture of comonomers (6–8 mL combined volume).

[b]At low IB contents, a small difference between two large numbers leads to significant errors. Thus, only ^{13}C-NMR data are given.

TABLE 3.   Distribution of p-Methylstyrene- and Isobutylene-Centered Triads

IB in charge, mol%	Fractions of pMeSt-centered triads						Fractions of IB-centered triads		
	SSS		BSS + SSB		BSB				
	^{13}C-NMR [a]	DEPT [b]	^{13}C-NMR [a]	DEPT [b]	^{13}C-NMR [a]	DEPT [b]	BBB	SBB + BBS	SBS
34	0.842	0.842	0.158	0.158	n.d. [c]	n.d. [c]	0.262	0.353	0.385
50	0.719	0.722	0.262	0.259	0.018	0.019	0.344	0.406	0.250
70	0.535	0.550	0.417	0.395	0.048	0.055	0.510	0.367	0.123
80	0.430	0.417	0.485	0.485	0.085	0.098	0.637	0.305	0.058
85	0.362	0.371	0.523	0.516	0.114	0.112	0.688	0.262	0.050
87	0.319	0.306	0.539	0.554	0.142	0.141	0.736	0.233	0.031
90	0.252	0.242	0.553	0.540	0.196	0.217	0.785	0.191	0.024
97	0.119 [d]	—[e]	0.441 [d]	—[e]	0.440 [d]	—[e]	0.920	0.080	n.d. [c]

[a] C^1-aromatic carbon signals (142–147 ppm) were used for calculations.
[b] Main chain methine carbon signals in DEPT-90° spectra (38–41 ppm) were used for calculations.
[c] Not detected.
[d] At this low pMeSt content, signals due to initiator fragment and indanyl end-groups are comparable with the C^1 signals of internal pMeSt units. They were not taken into account.
[e] At this low pMeSt content, the residual signal from IB quaternary carbons is relatively intense and does not allow accurate integration.

TABLE 4.   Test of Bernoullian Model[a]

	Fraction	
Triad	Experimental	Theoretical for Bernoullian model
BBB	0.232	0.094
SBB + BBS	0.170	0.226
SBS	0.056	0.135
SSS[b]	0.296	0.162
BSS + SSB[b]	0.221	0.270
BSB[b]	0.028	0.113
(SBB + BBS)/BSB	6.1	2
(BSS + SSB)/SBS	3.9	2

[a][IB]:[pMeSt] = 7:3 in feed; B = 0.455, S = 0.545 in copolymer.
[b]Average of ^{13}C-NMR and DEPT data.

$$r_{IB} = \frac{P_{BB}/P_{BS}}{[B]/[S]} \tag{1}$$

and

$$r_{p\text{MeSt}} = \frac{P_{SS}/P_{SB}}{[S]/[B]} \tag{2}$$

where P_{ij} is the transition probability of forming a M_iM_j diad, and [B] and [S] are the concentrations of IB and pMeSt in the feed, respectively. Equations (1) and (2) arise from the expressions connecting transition probabilities and reactivity ratios [24].

The transition probability ratios in Eqs. (1) and (2) are obtained from the corresponding diad ratios which in turn are calculated from triad distributions [25]:

$$\frac{P_{BB}}{P_{BS}} = \frac{BB}{BS} = \frac{BBB + \frac{1}{2}(SBB + BBS)}{SBS + \frac{1}{2}(SBB + BBS)}$$

and

$$\frac{P_{SS}}{P_{SB}} = \frac{SS}{SB} = \frac{SSS + \frac{1}{2}(BSS + SSB)}{BSB + \frac{1}{2}(BSS + SSB)}$$

Equations (1) and (2) can be used for testing the first-order Markov model: If this model is valid, the reactivity ratios should not change with feed composition. Table 5 shows the results of the test.

The reactivity ratios were calculated for both initial and terminal monomer feed compositions so that the error of the reactivity ratios covers the entire drift of monomer feed compositions (feed compositions at the moment of termination, second column in Table 5, were calculated from the initial feed composition, yield,

TABLE 5. Reactivity Ratios

[*p*MeSt]/[IB][a]		SS/SB[b]	$r_{p\text{MeSt}}$[c]	BB/BS	r_{IB}[d]
Initial	Terminal				
1.94	1.62	11.7 ± 0.00	6.6 ± 0.6	0.78	1.38 ± 0.14
1.00	0.87	5.73 ± 0.03	6.2 ± 0.5	1.21	1.13 ± 0.10
0.43	0.38	2.93 ± 0.03	7.3 ± 0.5	2.26	0.92 ± 0.07
0.25	0.22	2.00 ± 0.06	8.5 ± 0.8	3.75	0.88 ± 0.06
0.18	0.15	1.68 ± 0.02	10.3 ± 1.1	4.52	0.74 ± 0.07
0.143	0.132	1.41 ± 0.02	10.3 ± 0.6	5.78	0.80 ± 0.05
0.111	0.089	1.12 ± 0.01	11.4 ± 1.9	7.37	0.73 ± 0.09
0.031	0.027	0.514	12.5 ± 2.3	24.0	0.70 ± 0.08

[a]Molar monomer ratios in the initial charge and at the moment of termination.
[b]Averages of ^{13}C-NMR and DEPT data.
[c]The drift in monomer concentrations in the charge and the error of SS/SB have been taken into account.
[d]The drift in monomer concentrations in the charge has been taken into account and the error for BB/BS was assumed to be ±5%.

and copolymer composition). The triad distribution drift was estimated by determining the fractions of IB- and *p*MeSt-centered triads in copolymers obtained at a relatively high (35.5%) and low (16%) conversion (97 mol% IB in the feed):

BBB = 0.924 and 0.920, SBB + BBS = 0.076 and 0.080, SBS — not observed

SSS = 0.111 and 0.119, BSS + SSB = 0.425 and 0.441, BSB = 0.464 and 0.440

Evidently the error due to the drift of triad distributions is negligible. Thus we can confidently conclude that in line with the data in Table 5, the reactivity ratios are not constant over the wide feed composition range examined. Thus the first-order Markov model does not hold and the simple two-parameter model is inadequate to describe this copolymerization.

In the absence of more detailed microstructure information, we did not analyze for second- and higher-order Markov models.

Sequence Number, Run Number, and Average Sequence Length

Sequence numbers, run numbers, and average sequence lengths can be readily obtained from triad distributions and have often been used to augment the statistical description of copolymers. Table 6 shows these quantities for IB–*p*MeSt copolymers prepared over a wide copolymer composition range (From 14 to 95 mol% IB content).

Sequence numbers (i.e., the average numbers of uninterrupted sequences of like units of one kind per 100 monomer units in a copolymer chain) can be calcu-

TABLE 6. Sequence Number, Run Number, and Number-Average Sequence Length of IB–pMeSt Copolymers

IB in charge, mol%	Sequence number		Run number		Sequence length	
	pMeSt	IB			S(B)$_n$S	B(S)$_n$B
34	6.8	8.0	15	± 1	1.8	13
50	11.0	11.9	23	± 1	2.2	6.7
70	13.9	13.9	28	± 0	3.3	3.9
80	13.1	12.8	26	± 1	4.8	3.0
85	10.8	12.8	24	± 2	5.5	2.7
87	10.4	11.0	21	± 1	6.8	2.4
90	8.5	9.8	18	± 1	8.4	2.1
97	3.3	3.8	7.1	± 0.5	25	1.5

lated independently from normalized (BBB + SBB + BBS + SBS + SSS + BSS + SSB + BSB = 1) IB- and pMeSt-centered triad distributions [25]:

$$\text{Sequence number} = 100 \cdot [\text{SBS} + (\text{SBB} + \text{BBS})/2]$$
$$= 100 \cdot [\text{BSB} + (\text{BSS} + \text{SSB})/2]$$

For the infinite copolymer chain, sequence numbers obtained from both IB- and pMeSt-centered triad distributions should be identical and can be used to verify the accuracy of experimental data. The calculated sequence numbers shown in Table 6 are within ±10% from their averages and thus corroborate the accuracy of the experimental values. The small discrepancies may be due to the imperfect NMR spectra integration, signal overlap, and end-group effects.

The run number (i.e., the average number of uninterrupted sequences of like units of both kinds per 100 monomer units of a copolymer chain [26]) is the sum of comonomer sequence numbers, and it can be viewed as the number of cross-propagations per 100 monomer units. According to these numbers our products are indeed true copolymers: e.g., a copolymer prepared with 70 mol% IB in charge (~46 mol% IB in the product) yielded 28 cross-propagations per 100 monomer units in the chain.

The number-average sequence length (i.e., the average number of units in the uninterrupted sequence of like monomer units) can be calculated from triad distributions [25]:

"B" average sequence length = (BBB + SBB + BBS + SBS)/[SBS + 0.5(SBB + BBS)]

"S" average sequence length = (SSS + BSS + SSB + BSB)/[BSB + 0.5(BSS + SSB)]

According to the results shown in Table 6, the pMeSt units tend to cluster. For example, the number-average sequence length of pMeSt units in a copolymer containing 5 mol% pMeSt is 1.5 (last line in Table 6), which indicates the presence of considerable amounts of two and more consecutive pMeSt units in the copoly-
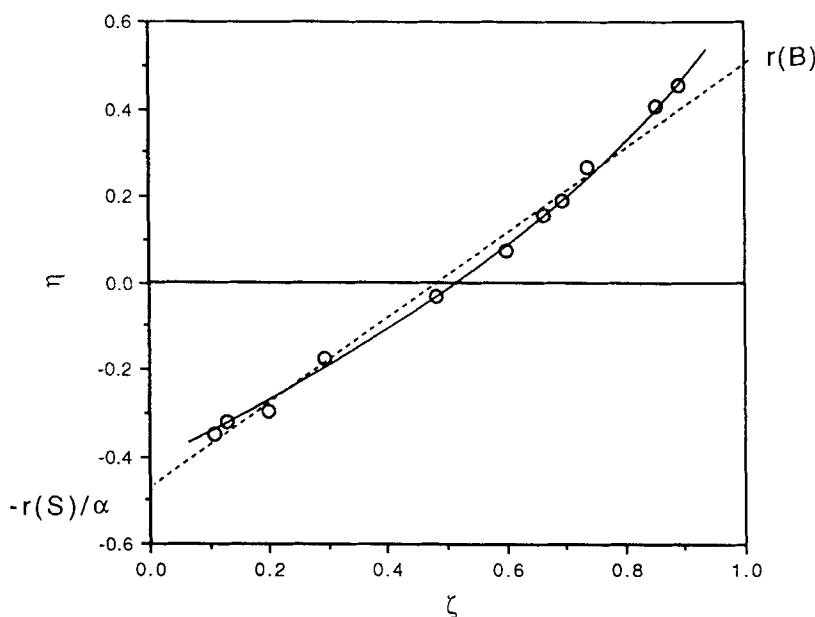
FIG. 8. Kelen–Tüdös plot ($\alpha = 7.68$): (- - -) linear approximation (leads to incorrect reactivity ratios); (——) interpolated line. Experimental data in Table 2.

mer. For a Bernoullian copolymer the pMeSt average sequence length would be ~1.05.

Reactivity Ratios by the Kelen–Tüdös Method

We were interested in comparing reactivity ratios obtained by statistical methods with those obtainable by the Kelen–Tüdös method [27] extended for high conversions [28]. The Kelen–Tüdös method was previously applied to copolymers only with low pMeSt contents (≤ 10 mol%), and the following reactivity ratios were obtained: $r_{IB} = 0.74 \pm 0.11$ and $r_{pMeSt} = 8.0 \pm 3.3$ [4]. These values are in very good agreement with the present data (see last two lines in Table 5), indicating that the terminal model provides reliable reactivity ratios only over a narrow range of copolymer compositions.

Figure 8 shows the Kelen–Tüdös plot constructed from data obtained over the entire monomer composition range shown in Table 2. Closer inspection of the Kelen–Tüdös plot reveals that the data in Fig. 8 fall on a slightly convex line (indicated by the solid line). A deviation of the Kelen–Tüdös plot from the straight line indicates that the two-parameter model is invalid for the system under investigation and that the Kelen–Tüdös method cannot provide reliable reactivity ratios (Class II system, see Ref. 29). It is of more than passing interest that none of the carbocationic copolymerization systems involving IB–styrene derivatives investigated to date can be described by the two-parameter copolymerization model and that all such systems fall into Class II or I (!) [29, 30].

ACKNOWLEDGMENTS

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Note Added in Proof. After the completion of this manuscript we became aware of a very recent paper by Fodor and Faust [*J. Macromol. Sci. — Pure Appl. Chem.*, A31(12), 1985 (1994)] in which the following reactivity ratios have appeared: $r_{IB} = 0.35 \pm 0.01$ and $r_{pMeSt} = 2.6 \pm 1.17$. These values were calculated by the Kelen–Tüdös method over quite a wide comonomer feed composition range (see Fig. 5). As we have indicated above, if the Kelen–Tüdös method is used to calculate reactivity ratios for this monomer pair, correct values can be generated only with copolymer compositions obtained over a rather narrow comonomer feed composition range. We have asked the Editor to share this conclusion with Professor Faust prior to the publication of our manuscript. [See page 1830.]

The manuscript entitled "The Microstructure of Poly(isobutylene-*co-p*-Methylstyrene) by NMR Spectroscopy" by A. V. Lubnin, I. Országh, and J. P. Kennedy was kindly shared with us along with the Note Added in Proof before publication, thus providing us the opportunity to add the following comment.

$r_{\mathrm{IB}} = 0.35 \pm 0.01$ and $r_{p\mathrm{MeSt}} = 2.6 \pm 1.17$ values reported in *J. Macromol. Sci. — Pure Appl. Chem.*, *A31*(12), 1985 (1994) were indeed calculated by the Kelen–Tüdös method. However, the η-ζ plot was linear in the studied composition range and curvature was not observed. This may be due to the different reaction conditions, i.e., CH_3Cl/hexanes 40/60 v/v and $-80°C$ versus C_2H_5Cl, a poor solvent for high molecular weight PIB (selective solvation?) and $-50°C$ in the present paper. It is interesting to note that even under the present conditions, r_{IB} can be considered constant within experimental error when pMeSt $<$ 50 mol% in the feed. $r_{p\mathrm{MeSt}}$ does appear to change somewhat even in this limited range under the present conditions. However, even if we assume a similar change in CH_3Cl/hexanes 40/60 v/v at $-80°C$, this change may be hidden in the large standard deviation reported for $r_{p\mathrm{MeSt}}$. We are not convinced, though, that the copolymerization behavior (Type I, II, or III) is entirely independent of the copolymerization condition.

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