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Quasiliving Carbocationic Polymerization. XII. Forced Ideal Copolymerization of Isobutylene with Styrene

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ABSTRACT

Forced ideal carbocationic copolymerization of isobutylene/styrene systems has been achieved by continuous addition of mixed monomer feeds to 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ in n-hexane/methylene chloride charge by keeping the input rate equal to the overall rate of copolymerization. The composition of the copolymers was identical to that of the feeds over the entire monomer concentration range. The number-average molecular weight of the copolymers increased almost linearly with the amount of consumed monomers at higher isobutylene concentrations in the feed. The

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molecular weight increase was less pronounced at higher styrene concentration because more methylene chloride had to be used in the solvent system to keep the copolymer in solution. The microstructure of the copolymers is uniform as determined by gel permeation chromatography (UV plus RI) and ^{13}C-NMR spectroscopy. According to these studies, true copolymers have formed. The probability of triads in the copolymer has been determined.

INTRODUCTION

Homo- and block polymerizations of a variety of olefins have been achieved by the use of quasiliving polymerization, i.e., by the slow continuous monomer addition technique [1-8]. In quasiliving polymerization systems initiation is instantaneous, termination is reversible or absent, and chain transfer to monomer is strongly depressed. It has also been demonstrated that the feeding of monomer mixtures instead of a single monomer with the quasiliving technique led to random copolymers having the same composition as the monomer feed, i.e., "forced ideal copolymerization" [9].

A basic requirement for forced ideal copolymerization is that the rate of replenishment of consumed monomers should not exceed the rate of overall copolymerization, i.e., conversions should be complete. Forced ideal quasiliving copolymerizations can be achieved provided conditions can be found under which initiation is instantaneous, termination is reversible, and chain transfer is depressed. Under these conditions the overall composition and the molecular weight of the copolymer can be controlled, the former by the feed composition and the latter by the amount of monomer added.

This paper concerns forced ideal quasiliving copolymerization of the isobutylene/styrene pair with the 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ initiating system. It has been demonstrated that the composition of the copolymers was identical to that of the mixed monomer feed and that their molecular weights increased with monomer input.

EXPERIMENTAL

Materials

The purification of styrene, isobutylene, n-hexane, and methylene chloride has been described [3, 9, 10]. $TiCl_4$ was distilled from P_2O_5 under slight nitrogen pressure. 2-Chloro-2,4,4-trimethylpentane was prepared from 2,4,4-trimethyl-1-pentene by hydrochlorination and was distilled at least twice under high vacuum at a temperature not exceeding 30°C.

Procedures

Polymerizations were carried out in a stainless steel enclosure under dry N_2 at -90°C in 300 cm^3 three-neck round-bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. The initial volume of solvent(s) was 100 cm^3; the concentration of 2-chloro-2,4,4-trimethylpentane initiator was 1×10^{-2} M and that of $TiCl_4$ coinitiator was 2.5×10^{-2} M. Monomers were condensed in a 500-cm^3 two-neck round-bottom flask and were diluted with methylene chloride (1/3 of the total volume) to prevent freezing of styrene. The mixed monomer feed was introduced continuously into the reactor containing the initiator/coinitiator solution by forcing it through a precision bore glass capillary by nitrogen pressure.

During polymerization, samples (0.1 cm^3) were withdrawn with a syringe from the mixture and were injected into capped vials containing excess methanol. Polymerizations were stopped by adding methanol. Conversions were determined gravimetrically.

Molecular weights were determined by a Waters Associates high pressure GPC equipped with five Microstyragel columns (10^5, 10^4, 10^3, 5×10^2, and 10^2A) and dual UV/RI detectors. Molecular weights were calculated by the use of a calibration curve obtained with polystyrene standards.

Copolymer compositions were determined by integration of ^{1}H-NMR resonances using a Varian T-60 NMR spectrometer and $CDCl_3$ solutions at room temperature. Copolymer structures were investigated by ^{13}C-NMR spectroscopy using a Varian FT-80A instrument and $CDCl_3$ solutions at room temperature. Integration was carried out manually using enlarged spectra.

RESULTS AND DISCUSSION

The composition of copolymers obtained by forced ideal copolymerization can be described by [9]

$$[M_1^p]/[M_2^p] = A_1/A_2 \qquad (1)$$

where $[M_1^p]$ and $[M_2^p]$ are the respective molar concentrations of Monomers 1 and 2 in the copolymers, and A_1 and A_2 are the monomer input rates. Thus the copolymer composition is determined only by the addition rate of the monomers and does not depend on the reactivity ratios r_1 and r_2. While in forced ideal copolymerization the average copolymer composition is independent of r_1 and r_2, the sequence distribution is still governed by these fundamental parameters.

The number-average degree of copolymerization ($\overline{DP}_n$) is given by

$$\overline{DP}_n = \cfrac{1}{\cfrac{[I]_0}{(A_1 + A_2)t} + C} \tag{2}$$

where $[I]_0$ = the number of active centers and C = the transfer constant of the copolymerization. With increasing time (t), $\overline{DP}_n$ approaches a maximum:

$$\lim_{t \to \infty} \overline{DP}_n = \overline{DP}_{n,max} = 1/C$$

Forced Ideal Copolymerization of Isobutylene/Styrene Feeds

Forced ideal copolymerization of isobutylene/styrene was carried out at three monomer compositions. Table 1 shows the composition of the monomer feeds and the solvent systems, the composition and molecular weight of the copolymers, and the final conversions together with other pertinent information.

Since n-hexane is a good solvent for polyisobutylene (PIB) but a poor solvent for polystyrene (PSt), and methylene chloride is a good solvent for PSt but a poor solvent for PIB, the composition of the solvent mixture had to be changed with changing monomer composition so as to keep the copolymer in solution during the polymerization. In the first and second examples the solvent system was 60 vol% n-hexane/40 vol% methylene chloride and the mole fractions of isobutylene in the feeds were 0.815 and 0.60, respectively. By increasing the styrene content in the feed, the copolymer precipitated during the polymerization. To avoid precipitation, the methylene chloride content was increased from 40 to 70 vol% in the third experiment. In all three experiments, conversions were close to 100 vol% and the compositions of the copolymers (by ^{1}H-NMR) were close to that of the monomer feed, i.e., forced ideal copolymerizations have been achieved.

Figure 1 is a plot of $\overline{DP}_n$ against the cumulative amount of monomers consumed. Evidently $\overline{DP}_n$ increases strongly in Experiments A8-A15 and A1-A7. $\overline{DP}_{n,max}$ was 350 in Experiments A1-A7, and 425 in Experiments A8-A15. In Experiments A16-A20 the increase in $\overline{DP}_n$ was less pronounced than in the former cases; in these experiments the styrene concentration was higher so that the amount of methylene chloride in

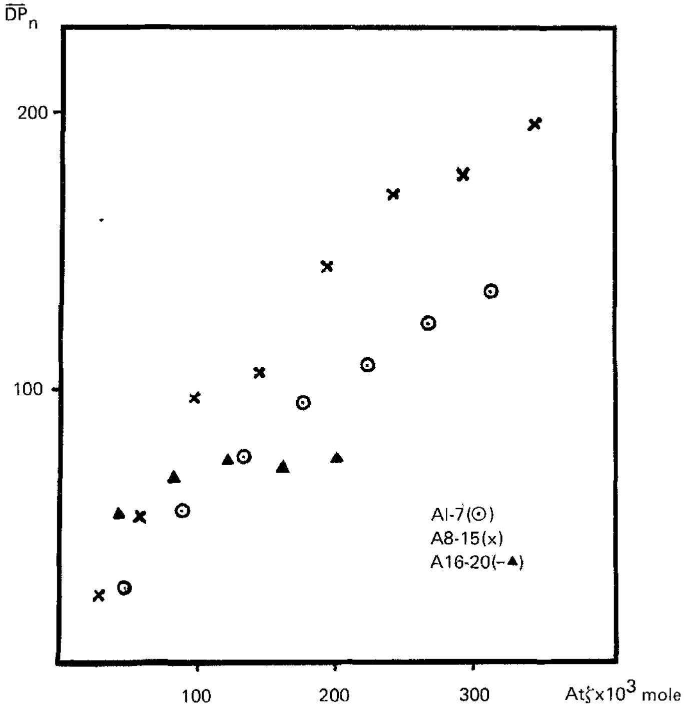


FIG. 1. $\overline{DP}_n$ vs cumulative amount of consumed monomer in the copolymerization of isobutylene and styrene. ζ = conversion.

the solvent had to be increased to prevent copolymer precipitation from the n-hexane-rich system. Due to the larger concentration of methylene chloride, the rate of chain transfer, most likely by indane-skeleton formation, increased, which depressed $\overline{DP}_{n,max}$ to 85.

The fact that higher methylene chloride concentrations lead to reduced $\overline{DP}_n$'s has been proven by independent experiments. Thus two styrene homopolymerizations have been carried out under conditions essentially identical to those used in the forced ideal copolymerizations except a styrene feed was used (addition rate 2.6×10^{-2} mol/min) instead of a mixed styrene/isobutylene feed; one experiment was conducted with the use of 100% methylene chloride, the other with 1/1 v/v methylene chloride/n-hexane. Conversions were close to 100% in both experiments; the initiator efficiency was 80% in pure methylene chloride and 90% in the methylene chloride/n-hexane run. Figure 2 shows a plot of the number of polystyrene molecules formed [P] against the cumulative amount of sytrene input. Evidently [P] increased strongly

TABLE 1. Copolymerization of Isobutylene and Styrene with 2-Chloro-2,4,4-trimethylpentane/$TiCl_4$ in Methylene Chloride/n-Hexane Mixtures[a]

Sample	Cumulative amount of consumed monomers $\times 10^3$ mol	Mole fraction of IB in the copolymer	$\overline{M}_n \times 10^{-3}$	$\overline{DP}_n$	P, number of polymer molecules $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
$A_1 = 3.81 \times 10^{-2}$ mol/min, $A_2 = 8.66 \times 10^{-3}$, ($A = A_1 + A_2 = 4.68 \times 10^{-2}$ mol/min); Mole fraction of IB in feed = 0.815; $\overline{M}_a = 64.9$; Conversion = 94 wt%						
A1	44	-	1.7	26	1.69	5.2
A2	88	-	3.6	55	1.55	4.5
A3	132	-	4.8	74	1.77	3.1
A4	176	-	6.1	94	1.85	2.9
A5	220	-	7.0	108	2.01	2.7
A6	264	-	7.9	122	2.14	2.6
A7	308	0.81	8.7	134	2.27	2.3
$A_1 = 5.91 \times 10^{-3}$ mol/min, $A_2 = 4.03 \times 10^{-3}$ mol/min, ($A = A_1 + A_2 = 9.94 \times 10^{-3}$ mol/min); Mole fraction of IB in feed = 0.60; $\overline{M}_a = 75.3$; Conversion = 98 wt%						
A8	28.8	-	1.8	23.9	1.21	3.6
A9	57.5	-	4.0	53.1	1.08	3.1

A10	95.9	-	7.2	95.6	1.00	2.7
A11	143.8	-	8.0	106.2	1.35	2.6
A12	191.8	-	10.8	143.4	1.34	2.4
A13	239.7	-	12.8	170.0	1.41	2.4
A14	287.6	-	13.3	176.6	1.63	2.3
A15	335.6	0.64	14.7	195.2	1.72	2.3
$A_1 = 1.31 \times 10^{-2}$ mol/min, $A_2 = 2.68 \times 10^{-2}$ mol/min, ($A = A_1 + A_2 = 3.99 \times 10^{-2}$ mol/min); Mole fraction of IB in feed = 0.33; $M_a = 88.3$; Conversion = 97 wt%						
A16	40	-	4.7	53	0.75	2.0
A17	80	-	6.0	68	1.18	2.0
A18	120	-	6.5	74	1.63	1.9
A19	160	-	6.2	70	2.28	2.3
A20	200	0.29	6.7	76	2.63	2.2

[a] Monomer 1 = IB; Monomer 2 = St; $\overline{M}_a$ = average molecular weight of the monomers in the mixture; $\overline{M}_n$ = number-average molecular weight of copolymer; $\overline{DP}_n$ = number-average degree of polymerization; $\overline{M}_w/\overline{M}_n$ = polydispersity; $[I] = 1 \times 10^{-2}$ mol/dm^3; $[TiCl_4] = 2.5 \times 10^{-2}$ mol/dm^3.

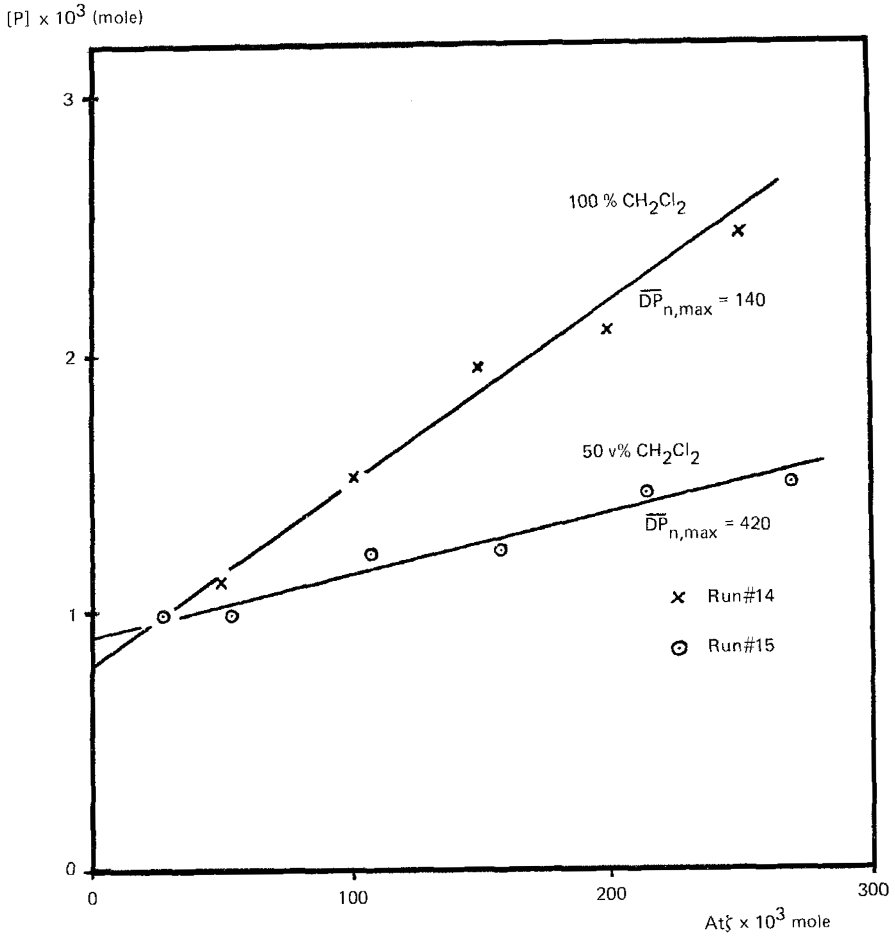


FIG. 2. Number of polymer molecules (P) vs cumulative amount of consumed monomer in the homopolymerization of styrene.

in pure methylene chloride, indicating extensive chain transfer; $\overline{DP}_{n,max}$ was 140. In contrast, [P] increased only moderately from ~1.0 to ~1.4 in the methylene chloride/n-hexane system, and $\overline{DP}_{n,max}$ was 420. It is possible that a completely chain transferless system could be obtained by further decreasing the methylene chloride concentration.

Copolymer Structure Analysis

In conventional batch copolymerizations, copolymer compositions are uniform and equal to the charge composition only if $r_1 = r_2 = 1$, or with azeotropic charges, i.e., when $[M_1]/[M_2] = (r_2 - 1)/(r_1 - 1)$. Further, the composition of copolymers shifts with conversions and a mixture of copolymers having different compositions and molecular weights is obtained. In contrast, forced ideal copolymerizations should yield uniform copolymers and copolymer compositions independent of the molecular weight. To demonstrate the uniformity of copolymers and to prove the independence of copolymer compositions from molecular weights, ^{13}C-NMR analysis and dynamic UV measurements have been carried out.

Dynamic UV measurements are readily accessible by a GPC instrument equipped with UV and RI detectors. The height of the UV trace at any elution volume is directly proportional to the number of chromophores (phenyl groups):

$$UV = k'n \frac{MW}{M_m} \chi_1 \tag{3}$$

where n is the number of polymer chains at a certain elution volume, MW is the molecular weight, χ_1 is the mole fraction of Monomer 1 in the copolymer, and

$$M_m = \chi_1 M_1 + (1 - \chi_1)M_2 \tag{4}$$

where M_1 and M_2 are the molecular weights of Monomers 1 and 2.

The height of the RI trace at any elution volume is directly proportional to the concentration of the sample:

$$RI = k \cdot n \cdot MW \tag{5}$$

Thus

$$\frac{UV}{RI} = \frac{k'}{k} \frac{\chi_1}{M_m} \tag{6}$$

In other words, if the composition of the copolymer is independent of the molecular weight, the UV/RI ratio must also be independent of the molecular weight.

TABLE 2. UV/RI Values of the Final Product of Experiments A1-A7 at Different Molecular Weights

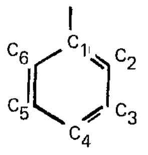
Elution volume	MW	UV/RI
32.8	154,000	0.58
33.6	112,000	0.65
34.4	81,500	0.67
35.2	59,200	0.60
36.0	43,000	0.57
36.8	31,200	0.59
37.6	22,700	0.61
38.4	16,500	0.63
39.2	12,000	0.64
40.0	8,700	0.63
40.8	6,300	0.61
41.6	4,600	0.64
42.4	3,300	0.57
43.2	2,400	0.62
44.0	1,800	0.61
44.8	1,300	0.67
	Average:	0.62

According to a representative data set shown in Table 2, UV/RI remained constant over the entire elution volume range, proving that the composition of the copolymer examined was in fact independent of molecular weights. (The average UV/RI values in Experiments A1-A7, A8-A15, and A16-A20 were 0.62, 0.94, and 1.33, respectively.)

^{13}C-NMR analysis of the microstructure of the products obtained provides direct proof for the formation of true copolymers. Table 3 shows the ^{13}C-NMR peak assignments of IB/St copolymers.

Figures 3 and 4 show the aliphatic and aromatic regions of a PSt together with a series of IB/St copolymers with different overall compositions. A closer inspection of the resonances in the 28-32, 35-38, and 145-149 ppm ranges (i.e., the resonances associated with the primary and quaternary carbons in the IB unit and that of the substituted aromatic ring carbon of the styrene unit, respectively) led to triad assignment. The spectrum of PIB (not shown) exhibits only one resonance at 31.3 ppm [11] while that of PSt does not show resonances

TABLE 3. Chemical Shifts in the ^{13}C-NMR Spectrum of an IB/St Copolymer

Chemical shift (ppm)	Identification of the carbon atom	
	IB unit (I)	St unit (S)
28.1	$-CH_3$ in SIS triad	
29.7	$-CH_3$ in IIS triad	
31.3	$-CH_3$ in III triad	
35.2	C in SIS triad	
36.7	C in IIS triad	
38.2	C in III triad	
39.1		$\mathrm{H}\overset{\vert}{\underset{\vert}{\mathrm{C}}}-$
43.7		
43.9		
44.2		$-CH_2-$ homopolymer
44.2	$-CH_2-$ in copolymer	$-CH_2-$ in copolymer
59.6		
59.6	$-CH_2-$ in homopolymer	
125.9		C_4
127.8		$C_{3,5}$
128.1		$C_{2,6}$
145.3		C_1
145.7		C_1 in homopolymer
146.0		C_1 in SSS triad
~146.9		C_1 in ISS triad
~148.1		C_1 in ISI triad

in this region. Next, in the spectra of the copolymers obtained with $x_{St} = 0.40$ and 0.71 in the feed, a new resonance appears at 28.1 ppm and the resonance at 31.3 ppm is weaker. On the basis of these findings and additional information [12], it is suggested that the resonances at 31.3, 29.7, and 28.1 ppm indicate the presence of IB-IB-IB, IB-IB-St, and St-IB-St triads, respectively.

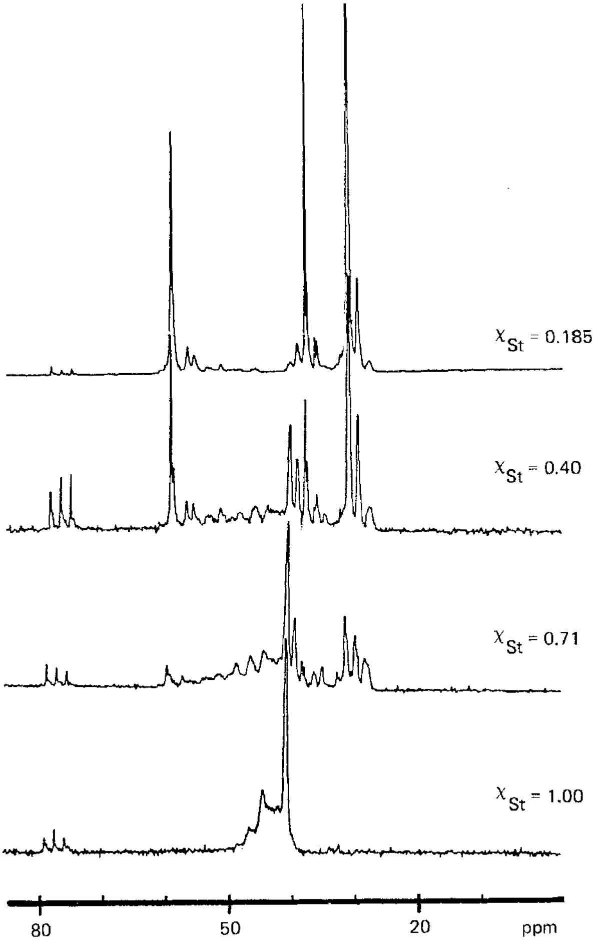


FIG. 3. ^{13}C-NMR spectra of various IB/St copolymers (χ_{St} = mole fraction of styrene in the feed) in the aliphatic region. Solvent: deuterochloroform.

A detailed investigation of the 35-38 ppm range, i.e., the resonance associated with the quaternary carbon in the IB unit, led to very similar results. The resonances at 35.2, 36.7, and 38.2 ppm are characteristic of the IB-IB-IB, IB-IB-St, and St-IB-St triads, respectively.

Analysis of the 145-149 ppm range led to similar conclusions. As shown in Fig. 4, the spectrum of PSt exhibits a strong resonance at 145.3-146 ppm. This resonance diminishes in the spectra of polymers obtained with feeds of decreasing St (increasing IB) content and, at the

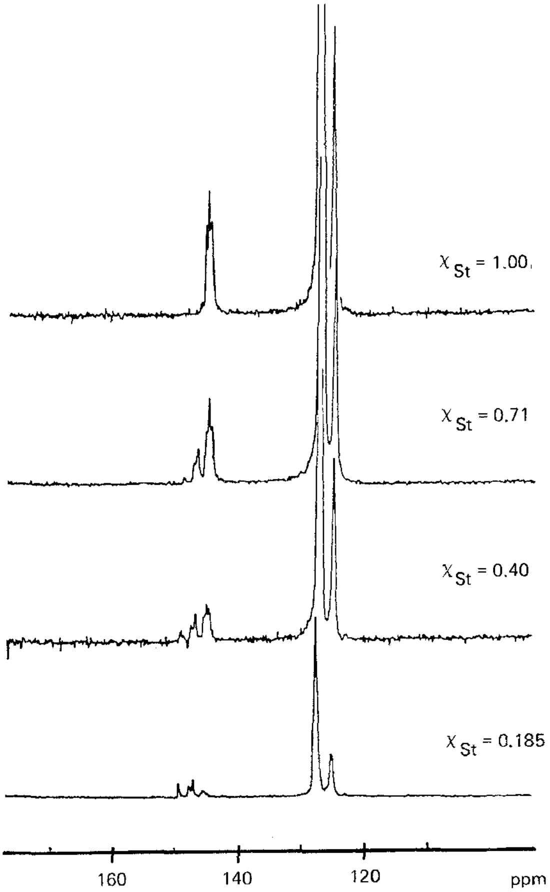


FIG. 4. ^{13}C-NMR spectra of various IB/St copolymers (χ_{St} = mole fraction of styrene in the feed) in the aromatic region. Solvent: deuterochloroform.

same time, two new resonances appear at 146.9 and 148.1 ppm. By the use of CAT spectra and the method mentioned above, we concluded that the resonances at 145.3-146, 146.9, and 148.1 ppm indicate the presence of St-St-St, St-St-IB, and IB-St-IB triads, respectively.

These assignments were substantiated by computing triad probabilities from integrated ^{13}C spectra, which in turn permitted the calculation of copolymer compositions [13].

According to these calculations, the calculated St content in the copolymer is essentially identical to that used in the feed, i.e., $\chi_{St,feed} \approx P(S)$.

TABLE 4. Triad Probabilities of IB/St Copolymers of Different Composition

	$P_3(SSS)$	$P_3(SSI)$	$P_3(ISI)$	$P_3(III)$	$P_3(IIS)$	$P_3(SIS)$
Experiments A1-A7: $x_{St,feed} = 0.185$ $P(S) = 0.20,^a$ $P(I) = 0.80$ $n_S = 1.25$, $n_I = 5.86$	0.054	0.054	0.038	0.637	0.071	0.020
Experiments A8-A15: $x_{St,feed} = 0.40$ $P(S) = 0.45,^a$ $P(I) = 0.55$ $n_S = 1.82$, $n_I = 2.22$	0.247	0.081	0.041	0.361	0.066	0.057
Experiments A16-A20: $x_{St,feed} = 0.70$ $P(S) = 0.73,^a$ $P(I) = 0.27$ $n_S = 3.70$, $n_I = 1.36$	0.512	0.100	0.019	0.104	0.047	0.071

[a] Calculated from triad probabilities.

In addition to ^{13}C-NMR spectroscopy, copolymer compositions have also been determined by the ^{1}H-NMR technique. Gratifyingly, the compositions calculated from ^{1}H-NMR spectra (not shown) corroborated those obtained by ^{13}C-NMR spectroscopy and calculated from triad probabilities. Number-average sequence lengths of styrene and isobutylene units n_S and n_I in the copolymer can be calculated by the use of triad probabilities P(S) and P(I), assuming that the copolymerization is random (Bernoullian) [14]:

$$n_S = \frac{1}{1 - P(S)} \tag{7}$$

Table 4 shows the results. Calculations by the use of Markov statistics led to highly unlikely sequence lengths.

Table 4 summarizes triad probabilities calculated by integrating the resonances characteristic of the primary carbon in IB and the substituted ring carbon in the St unit [13] and normalizing by the following equation [13]:

$$P_3(ISI) + P_3(SSI) = P_3(SSI) + P_3(SIS) \tag{8}$$

Integration of ^{1}H-NMR resonances gave very similar copolymer composition values.

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