The importance of clearly defining the experimental time scale has been demonstrated. By working with large molecular weight polystyrene, we have been given access to regimes both short and long compared with the gel renewal time. The analysis presented here shows that the spin echo attenuation in the short time scale experiment can yield not only the cooperative diffusion coefficient of the gel but also the distribution of wavelengths present in these cooperative gel disturbances. Pulsed field gradient NMR thus offers an experimental probe not envisaged in previous theoretical studies.

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Cationic Copolymers of Isobutylene. 2. Nuclear Magnetic Resonance Investigation of the Structure of Isobutylene–Isoprene Copolymers

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ABSTRACT: The structure of isobutylene (I_B)–isoprene (I_P) copolymers, obtained in a homogeneous medium with a cationic catalyst, has been investigated by ^1H and ^{13}C NMR spectroscopy. The spectra of these copolymers and their hydrogenated derivatives were interpreted. From the assignments made, which allow the calculation of monomer triad, tetrad, and pentad fractions, the I_B–I_P copolymer was found to have an almost completely head-to-tail structure. The incorporation of the monomers arises by 1,2 addition of I_B and trans-1,4 addition of I_P to the growing carbenium ion.

We have previously undertaken the study[1a] of isobutylene–butadiene copolymers by means of ^1H and ^{13}C NMR spectroscopy since little detailed information was available on their copolymerization mechanism and copolymer structure. The calculation of the triad fractions of the original and hydrogenated copolymers revealed that both *trans*-1,4- and -1,2-butadiene units are present and that they have an essentially block distribution. These conclusions are clear evidence of the complicated structure of isobutylene–butadiene copolymers which cannot be described by the two-component copolymerization equation, even in a revised form.[2]

In order to investigate the crucial role of the diene in the cationic copolymerization of isobutylene, we have extended our investigations to isobutylene (I_B)–isoprene (I_P) copolymers. Because of the great and long-standing industrial significance of these elastomers,[3] several papers have been published on their structural characterization by both chemical and physicochemical methods,[4-7] in particular ^1H NMR spectroscopy. ^{13}C NMR spectroscopy provides substantial information on the distribution of the monomers and on the nature of their linkages which is not available from ^1H NMR. This paper describes mainly the interpretation of the ^{13}C NMR spectra of the I_B–I_P copolymers and their hydrogenated derivatives. The quantitative aspects and the correlation of the structural features with the mechanism of the cationic copolymerization of I_B and I_P will be the subject of a subsequent paper.[8]

Experimental Section

Materials. Both isobutylene and isoprene were commercial pure-grade products and were treated before use as reported previously.[9] Solvents (n-pentane and CH_2Cl_2) and catalyst ($C_2H_5AlCl_2$) were purified and used as reported elsewhere.[9]

Procedure. Catalyst, monomer, and solvent handling was performed under a dry N_2 atmosphere. The copolymerization equipment and procedure were essentially the same as described previously.[9] In practice, I_B and I_P were added to a mixture of n-pentane and CH_2Cl_2 (1:1 by volume) in varying mole ratios, depending on the desired content of the diene in the copolymers. Their total concentration was kept constant at 3.3 mol/L. $EtAlCl_2$ (0.005–0.020 mol/L) was added to the polymerization system, maintained at −70 °C, and the reaction was allowed to continue for 15 min. The copolymers formed under these conditions were completely soluble and the resulting reaction mixture was homogeneous. The monomer conversion was controlled by using an appropriate concentration of catalyst. The conditions adopted for preparing a typical sample and the main characteristics of the copolymer obtained were as follows: $[I_B]/[I_P] = 1.20$, $[I_P] = 1.5$ mol/L, $[EtAlCl_2] = 0.015$ mol/L, yield = 42%; I_P content of the copolymer = 35 mol %; $[\eta] = 0.36$ dL/g (in cyclohexane at 30 °C). The copolymer was hydrogenated in cyclohexane at 180 °C, in the presence of Pd on charcoal, as described previously.[1a]

Analyses. ^1H NMR spectra were obtained in the CW mode at 100 MHz, using a Varian XL-100 spectrometer and $CDCl_3$ solutions at 25 °C. ^{13}C NMR spectra were recorded at 25.14 MHz at 25 °C on a Varian XL-100 NMR spectrometer equipped with

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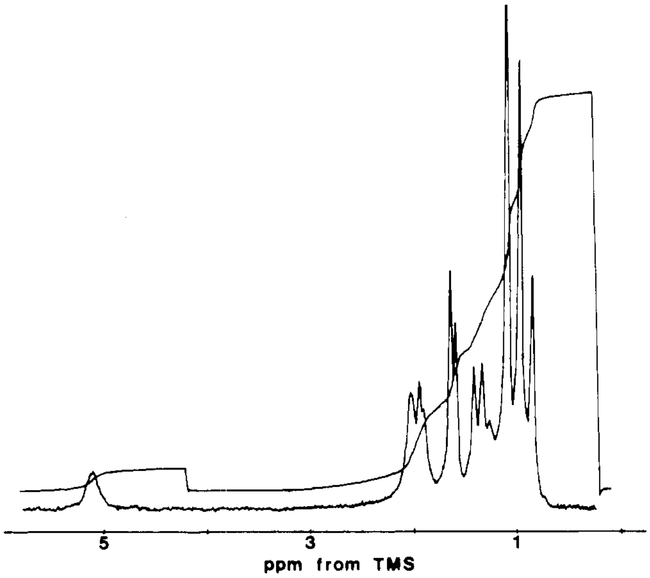


Figure 1. ^{1}H NMR spectrum of the I_B–I_P copolymer.

a 16K Varian FT-100 pulsed NMR Fourier transform accessory, using 5–10% solutions in $CDCl_3$. Chemical shifts are reported in ppm from Me_4Si.

The spectra, except when selective decoupling was employed, were ^{1}H noise decoupled and were obtained by accumulation of 15 000–20 000 transients, using low pulse powers (a flip angle of approximately 35°). Other experimental FT conditions were as follows: sweep width = 5000 Hz, acquisition time = 0.8 s, pulse interval = 1.2 s, Hz/point = 1.25. Selective decoupling experiments were run by irradiating at a single frequency with a power of 110–115 dB.

Results and Discussion

Cationic Copolymerization of I_B and I_P. Cationic I_B–I_P copolymers having high molecular weight, i.e., $\bar{M}_n > 10^5$, can be synthesized with different catalyst systems which are active under different experimental conditions.[3] The most extensively studied systems are (1) classical catalysts, based on $AlCl_3$ or $EtAlCl_2$[11] and very active in CH_3Cl at −100 °C, (2) systems based mainly on Et_2AlCl and alkyl halides working at "high" temperature,[12] i.e., in the range between −30 and −50 °C, (3) systems forming radical cations at "high" temperature from the photoinduced decomposition of some Lewis acids,[13] and (4) systems based mainly on Et_2AlCl and halogens or interhalogen compounds, active at "high" temperature.[3] For some of these systems the reactivity ratios of the monomers have been studied. The results for the systems $AlCl_3$–CH_3Cl[14] and $EtAlCl_2$–CH_3Cl at −100 °C,[15] and for the latter also at other temperatures,[16] were very similar. For the system Et_2AlCl–Cl_2 we obtained[3a] at −35 °C a reactivity ratio of I_B close to that for classical systems. The reactivity of the monomers and the structures of the copolymers appear scarcely influenced by the varied experimental conditions.

In the present work we have adopted the same catalyst and experimental conditions used in the study of the I_B–butadiene system[1] since they yielded soluble copolymers of rather high molecular weight over a broad range of composition, i.e., between 10 and 90 mol % of I_P. Furthermore, the linearity of the base line in the ^{13}C NMR spectra confirms the absence of cyclization and the regularity of the copolymers studied.

^{1}H NMR Analysis. Figure 1 shows the ^{1}H NMR spectrum of a typical I_B–I_P copolymer, the characteristics of which are reported in the Experimental Section. In the double-bond region, the signal at 5.12 ppm can be assigned to the unique proton of the unsaturation arising from the trans-1,4 enchainment of I_P, known from the literature[6] and confirmed by ^{13}C NMR spectra (see below). The peaks due to the 1,2 and 3,4 units are practically negligible. In fact, no signal of appreciable intensity is present in the region between 4.6 and 4.8 ppm in which vinyl and vinylidene resonances are expected. In the upfield region a signal at 2.03 ppm is assigned to the methylenes of the dyad I_PI_P indicated by an asterisk, $CH_2C(CH_3){=}CH{*}CH_2{*}CH_2C(CH_3){=}CHCH_2$, while a signal at 1.95 ppm is assigned to the following methylenes of the dyad I_BI_P and I_PI_B: $CH_2C(CH_3)_2{*}CH_2C(CH_3){=}CHCH_2$ and $CH_2C(CH_3){=}CH{*}CH_2CH_2C(CH_3)_2$, respectively. The signals observed at 1.65 and 1.61 ppm are attributed to the methyl of I_P, while the peaks at 1.43 and 1.35 ppm are due to the methylene of I_B present in I_BI_B dyads and I_PI_B dyads, respectively. Finally, three peaks occurring at 1.11, 0.96, and 0.86 ppm are assigned to the *gem*-dimethyl group of I_B in triads $I_BI_BI_B$, $I_PI_BI_B + I_BI_BI_P$, and $I_PI_BI_P$, respectively. As was observed previously,[1] the resonances of CH_2 and CH_3 of I_B are shifted upfield when they belong to sequences lacking *gem*-dimethyl groups. Therefore, the ^{1}H NMR spectra of the I_B–I_P copolymers allow the calculation of the triad fractions centered on I_B by using the signals of the *gem*-dimethyl group, as was possible in the case of other isobutylene-based copolymers.[1]

^{13}C NMR Analysis. Further information on the structure and the monomer distribution is provided by the analysis of ^{13}C NMR spectra of the I_B–I_P copolymers and their hydrogenated derivatives.

^{13}C NMR Spectra of the Original I_B–I_P Copolymer. Figure 2 shows the ^{13}C NMR spectrum of the same copolymer reported in Figure 1. The assignments in the aliphatic region of the spectrum (Figure 2A) are listed in Table I. The assignments of signals to the carbons of the two monomers in different sequences have been carried out by studying samples of different composition with the selective decoupling technique and by comparing experimental and calculated chemical shift values. The latter cannot be calculated by using only the well-known additivity rules for the evaluation of the chemical shifts of alkanes[17] and alkenes[18] because of anomalous contributions of the *gem*-dimethyl group observed in our previous work.[1] Therefore, we have obtained a set of substituent parameters by means of a least-squares linear regression analysis. The index G refers to the *gem*-dimethyl group and M to the methyl group. The indexes 4 and 2 of the γ substitution denote that the substitution concerns a quaternary and a secondary carbon, respectively; i.e., the two substitutions are considered distinct, in agreement with the literature.[17] A β_t effect was introduced for the substitution on the quaternary carbon, due to a trans double bond in the β position relative to the carbon. This effect, as will be evident in the next section from the comparison with the spectrum of the hydrogenated copolymer, is not negligible. Besides a δ effect, a δ_β effect also appears for methylene substitutions, taking into account (as previously stated[1]) a δ substitution beyond an identical β substitution. The values used for assigning the peaks of the original I_B–I_P copolymer and its hydrogenated derivative (see below) are as follows. Quaternary carbons: $\beta_t = 0.50$, $\gamma_{4M} = 0.59$, $\gamma_{4G} = 2.23$, $\epsilon_G = 0.27$. All these values are positive, in particular the two γ_4 substitutions, in agreement with the literature.[17] Methylene carbons: $\beta_G = 10.98$, $\delta_{\beta_G} = 4.02$, $\delta_{\beta_M} = 0.79$, $\beta_M = 9.14$, $\alpha_t = 0.54$, $\gamma_{2M} = -2.54$, $\epsilon_G = 0.50$, $\epsilon_M \cong 0$, $\delta_M = 0.10$, $\delta_G = 0.79$, $\delta_{\beta_G}{}^* = 1.37$, $\gamma_{2G} = -6.95$. The values of the methyl contributions are in agreement with the substitutions reported in the literature,[17] while the

Table I
^{13}C NMR Chemical Shifts (ppm) of the I_B-I_P Copolymer: Aliphatic Region

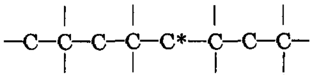
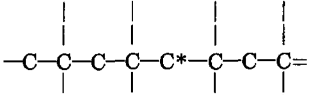
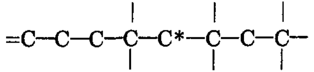
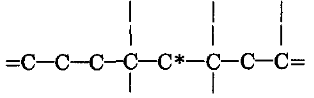
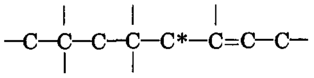
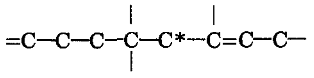
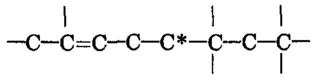
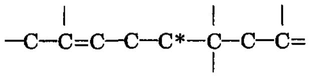
carbon	structure	sequence	peak	chem shift		substitution
				exptl	calcd	
CH_3 (I_B)		$I_BI_BI_B$	17	31.23		
		$I_BI_BI_P$ + $I_PI_BI_B$	18	29.38		
		$I_PI_BI_P$	19	27.46		
CH_3 (I_P)		/ I_B I_BI_P \\ I_P	23	19.20		
		/ I_B I_PI_P \\ I_P	24	15.96		
C		$I_BI_BI_BI_BI_B$	9	38.16	38.01	$\alpha_G + 2\gamma_{4G} + 2\epsilon_G$
		$I_PI_BI_BI_BI_B$ + $I_BI_BI_BI_BI_P$	10	37.88	37.74	$\alpha_G + 2\gamma_{4G} + \epsilon_G$
		$I_PI_BI_BI_BI_P$	11	37.60	37.47	$\alpha_G + 2\gamma_{4G}$
		/ I_B $I_BI_BI_BI_P$ \\ I_P	12	36.56	36.59	$\alpha_G + \gamma_{4G} + \gamma_{4M} + \epsilon_G - \beta_t$
		/ I_B $I_PI_BI_BI_P$ \\ I_P	13	36.26	36.32	$\alpha_G + \gamma_{4G} + \gamma_{4M} + \beta_t$
		I_B \\ $I_PI_BI_BI_B$ / I_P	14	35.07	35.51	$\alpha_G + \gamma_{4G} + \epsilon_G$
		I_B \\ $I_PI_BI_BI_P$ / I_P	15	34.87	35.23	$\alpha_G + \gamma_{4G}$
		I_B \\ / I_B $I_PI_BI_P$ / I_P \\ I_P	16	34.18	34.09	$\alpha_G + \gamma_{4M} + \beta_t$
CH_2	 —C—C—C—C—C*—C—C—C—	$I_BI_BI_BI_B$	1	59.57	59.88	$2\beta_G + 2\delta_{\beta_G}$
	 —C—C—C—C—C*—C—C—C=	$I_BI_BI_BI_P$	2	57.21	57.47	$2\beta_G + \delta_{\beta_G} + \delta_{\beta_M}$
	 =C—C—C—C—C*—C—C—C—	$I_PI_BI_BI_B$	3	55.59	55.87	$2\beta_G + \delta_{\beta_G}$
	 =C—C—C—C—C*—C—C—C=	$I_PI_BI_BI_P$	4	53.32	53.45	$2\beta_G + \delta_{\beta_M}$
	 —C—C—C—C—C*—C=C—C—	/ I_B $I_BI_BI_P$ \\ I_P	3	55.59	54.57	$\beta_G + \beta_M + \delta_{\beta_M} + \alpha_t$
	 =C—C—C—C—C*—C=C—C—	/ I_B $I_PI_BI_P$ \\ I_P	5	51.65	50.56	$\beta_G + \beta_M + \alpha_t$
	 —C—C=C—C—C*—C—C—C—	I_B \\ $I_PI_BI_B$ / I_P	6	45.56	44.89	$\beta_G + \delta_{\beta_G}$
	 —C—C=C—C—C*—C—C—C=	I_B \\ $I_PI_BI_P$ / I_P	7	42.87	42.48	$\beta_G + \delta_{\beta_M}$

Table I (*Continued*)

carbon	structure	sequence	peak	chem shift exptl	chem shift calcd	substitution
	$-C-\overset{\vert}{C}=C-C-C^*-\overset{\vert}{C}=C-C-$	$\begin{array}{ccc} I_B & & I_B \\ \backslash & & / \\ & I_PI_P & \\ / & & \backslash \\ I_P & & I_P \end{array}$	8	39.69	39.58	$\beta_M + \alpha_t$
	$-C-\overset{\vert}{C}=C-C^*-C-\overset{\vert}{C}=C-C-$	$\begin{array}{ccc} I_B & & I_B \\ \backslash & & / \\ & I_PI_P & \\ / & & \backslash \\ I_P & & I_P \end{array}$	20	26.92	27.89	$\gamma_{2M} + \alpha_t$
	$-C-\overset{\vert}{C}=C-C^*-C-\underset{\vert}{\overset{\vert}{C}}-C-\underset{\vert}{\overset{\vert}{C}}-$	$\begin{array}{ll} I_B & \\ \backslash & \\ & I_PI_BI_B \\ / & \\ I_P & \end{array}$	21	23.23	23.98	$\gamma_{2G} + \epsilon_G + \alpha_t$
	$-C-\overset{\vert}{C}=C-C^*-C-\underset{\vert}{\overset{\vert}{C}}-C-\overset{\vert}{C}=$	$\begin{array}{ll} I_B & \\ \backslash & \\ & I_PI_BI_P \\ / & \\ I_P & \end{array}$	22	22.89	23.48	$\gamma_{2G} + \epsilon_M + \alpha_t$

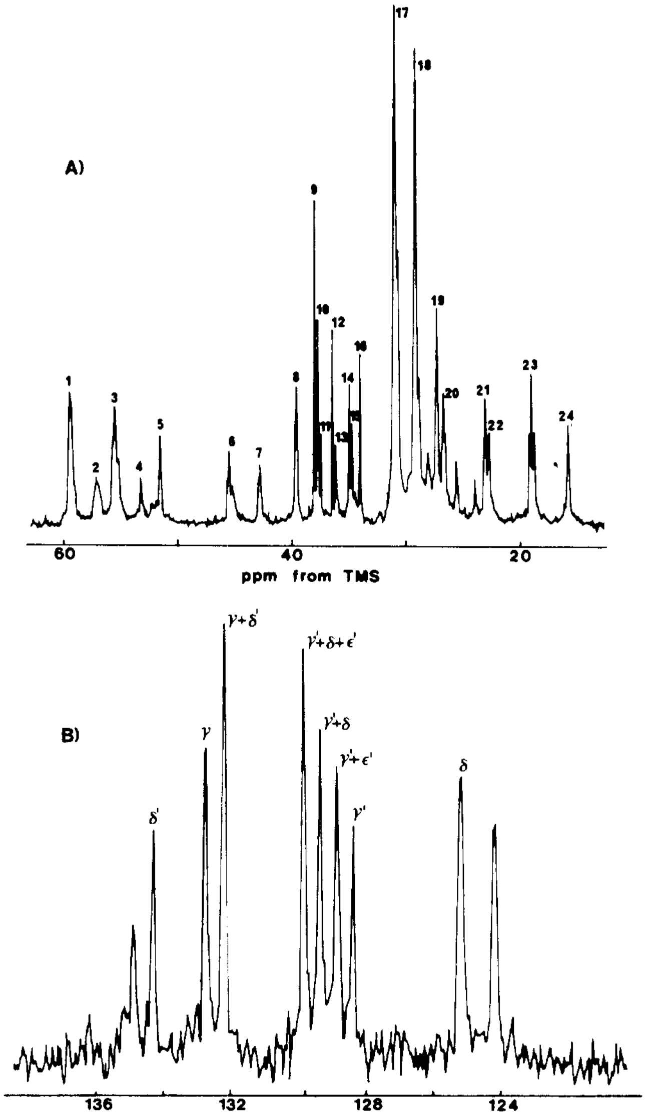


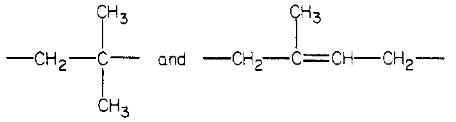
Figure 2. ^{13}C NMR spectrum of the I_B–I_P copolymer: (A) aliphatic region; (B) olefinic region.

Table II
^{13}C NMR Chemical Shifts (ppm) of the I_B-I_P Copolymer: Olefinic Region

carbon	sequence	chem shift	substitution
C	$I_PI_PI_P$	134.91	δ_M'
	$I_PI_PI_B$	134.32	δ_G'
	$I_BI_PI_P$	132.84	$\gamma_G + \delta_M'$
	$I_BI_PI_B$	132.29	$\gamma_G + \delta_G'$
CH	$\begin{array}{ll} & / I_P \\ I_BI_BI_PI_B & \\ & \backslash I_B \end{array}$	129.98	$\gamma_G' + \delta_G + \epsilon_G'$
	$\begin{array}{ll} & / I_B \\ I_PI_BI_PI_B & \\ & \backslash I_P \end{array}$	129.49	$\gamma_G' + \delta_G$
	$\begin{array}{ll} & / I_B \\ I_BI_BI_PI_P & \\ & \backslash I_P \end{array}$	128.99	$\gamma_G' + \delta_M + \epsilon_G'$
	$\begin{array}{ll} & / I_B \\ I_PI_BI_PI_P & \\ & \backslash I_P \end{array}$	128.51	$\gamma_G' + \delta_M$
	$I_PI_PI_B$	125.39	δ_G
	$I_PI_PI_P$	124.40	δ_M

values of the *gem*-dimethyl group agree with the results obtained in previous studies[1] of the anomalous effect of the $C(CH_3)_2$ group in chain segments with crowded methyls. The experimental values are compared in Table I with those calculated on the basis of the set of parameters listed above.

This region of the spectrum is fully interpreted by assuming that I_P is present as trans-1,4 units and that both the monomers are joined head-to-tail, i.e.



$$-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}- \quad \text{and} \quad -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

Besides the resonances due to these structures, only very weak peaks, probably attributable to small amounts of I_P units other than 1,4, are present.[20] The study of the olefinic region and the analysis of the hydrogenated copolymer (see below) fully confirm the types of linkage suggested. As Table I shows, the spectrum exhibits signals assigned to triads of methyls of *gem*-dimethyl groups, to

Table III
^{13}C NMR Chemical Shifts (ppm) for Methyl, Methine, and Quaternary Carbons of the Hydrogenated I_B-I_P Copolymer

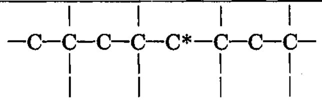
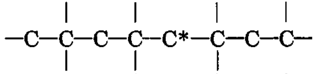
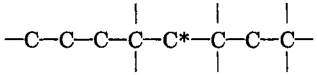
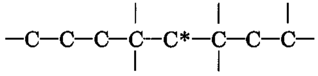
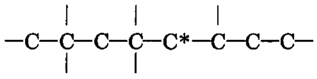
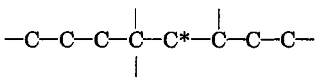
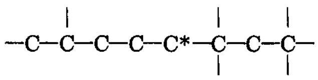
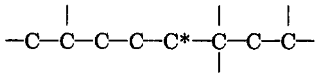
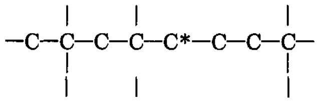
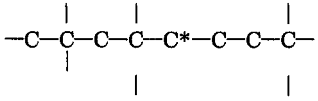
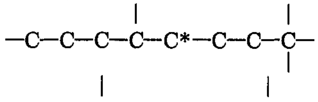
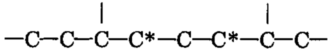
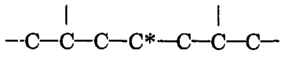
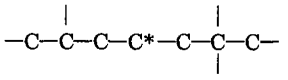
carbon	sequence	peak	chem shift		substitution
			exptl	calcd	
CH_3 (I_B)	$I_BI_BI_B$	20	31.25		
	$I_BI_BI_P + I_PI_BI_B$	21	29.63		
	$I_PI_BI_P$	23	27.73		
CH_3 (I_P)	I_B / I_BI_P \ I_P	25	23.02		
	I_B / I_PI_P \ I_P	27	19.80		
C	$I_BI_BI_BI_BI_B$	11	38.15	38.01	$\alpha_G + 2\gamma_{4G} + 2a_G$
	$I_PI_BI_BI_BI_B + I_BI_BI_BI_BI_P$	12	37.89	37.74	$\alpha_G + 2\gamma_{4G} + \epsilon_G$
	$I_PI_BI_BI_BI_P$	13	37.57	37.47	$\alpha_G + 2\gamma_{4G}$
	I_B / $I_BI_BI_BI_P$ \ I_P	14	36.11	36.10	$\alpha_G + \gamma_{4G} + \gamma_{4M} + \epsilon_G$
	I_B / $I_PI_BI_BI_P$ \ I_P	15	35.82	35.82	$\alpha_G + \gamma_{4G} + \gamma_{4M}$
	I_B \ $I_PI_BI_BI_B$ / I_P	16	35.11	35.51	$\alpha_G + \gamma_{4G} + \epsilon_G$
	I_B \ $I_PI_BI_BI_P$ / I_P	17	34.91	35.23	$\alpha_G + \gamma_{4G}$
	I_B I_B \ / $I_PI_BI_P$ / \ I_P I_P	18	33.58	33.59	$\alpha_G + \gamma_{4M}$
CH	I_B / I_PI_P \ I_P	19	32.83		α_M
	I_B / I_BI_P \ I_P	22	28.84		$\alpha_M + \gamma_{3G}$

pentads of quaternary carbons, and to tetrads of methylenes of both monomers. Selective decoupling experiments allowed the assignment of the three signals due to the methyls of I_B and also the discrimination of signals due to the methylenes of I_P (in α position to a double bond) from those of I_B. Furthermore, the latter signals could be ascribed to I_BI_B and I_PI_B dyads. The further distinction in terms of tetrads centered on the same dyad can be obtained from additivity contributions.

From Table I, one can immediately assign the peak at 59.57 ppm to the methylene of the $I_BI_BI_BI_B$ tetrad. The other three signals, due to this methylene group in the remaining three tetrads centered on the dyad I_BI_B, are at 57.21, 55.59, and 53.32 ppm, as revealed by selectively decoupling the protons at 1.42 ppm. They are assigned to the tetrads $I_BI_BI_BI_P$, $I_PI_BI_BI_B$, and $I_PI_BI_BI_P$, respectively, by taking into account the fact that $\delta_{\beta_G} > \delta_{\beta_M}$ and both are greater than zero. The intensity of the signal at 55.59 ppm is greater than that of other signals in the decoupled spectrum obtained by irradiating the protons at 1.95 ppm. This means an overlapping of two resonances at 55.59 ppm, one of which is due to a methylene in the α position to a double bond. This carbon atom is the first methylene of I_P, i.e., $CH_2C(CH_3)_2C^*H_2C(CH_3){=}CHCH_2$, in some tetrads centered on the I_BI_P dyad. Another peak which is decoupled by irradiating at 1.95 ppm occurs at 51.65 ppm. On the basis of substituent effects, the signal at 55.59 ppm is assigned to tetrads $I_BI_BI_PI_P$ and $I_BI_BI_PI_B$, while the peak at 51.65 ppm is assigned to tetrads $I_PI_BI_PI_P$ and $I_PI_BI_PI_B$.

The resonances of the methylene of I_B in the tetrads centered on the dyad I_PI_B are upfield, i.e., that of tetrads $I_PI_PI_BI_B$ and $I_BI_PI_BI_B$ is at 45.56 ppm and that of tetrads $I_BI_PI_BI_P$ and $I_PI_PI_BI_P$ is at 42.87 ppm, the difference being a δ_G effect. Finally, the resonance due to the methylene of I_P marked by an asterisk, i.e., $CH_2C(CH_3){=}CHCH_2C^*H_2C(CH_3){=}CHCH_2$, in the four tetrads centered on the dyad I_PI_P is at 39.69 ppm. These are all the signals of methylene carbons observed in the downfield region.

Table IV
^{13}C NMR Chemical Shifts (ppm) for the Methylenes of the Hydrogenated I_B-I_P Copolymer

structure	sequence	peak	chem shift exptl	chem shift calcd	substitution
 $-C-C-C-C-C^*-C-C-C-$	$I_BI_BI_BI_B$	1	59.58	59.88	$2\beta_G + 2\delta_{\beta_G}$
 $-C-C-C-C-C^*-C-C-C-$	$I_BI_BI_BI_P$	2	56.96	57.47	$2\beta_G\ \delta_{\beta_G} + \delta_{\beta_M}$
 $-C-C-C-C-C^*-C-C-C-$	$I_PI_BI_BI_B$	3	55.74	55.87	$2\beta_G + \delta_{\beta_G}$
 $-C-C-C-C-C^*-C-C-C-$	$I_PI_BI_BI_P$	5	53.34	53.45	$2\beta_G + \delta_{\beta_M}$
 $-C-C-C-C-C^*-C-C-C-$	$/I_B$ $I_BI_BI_P$ $\backslash I_P$	4	53.83	54.03	$\beta_G + \beta_M = \delta_{\beta_G}$
 $-C-C-C-C-C^*-C-C-C-$	$/I_B$ $I_PI_BI_P$ $\backslash I_P$	6	49.58	50.02	$\beta_G + \beta_M$
 $-C-C-C-C-C^*-C-C-C-$	$I_B\backslash$ $I_PI_BI_B$ $I_P/$	7	45.93	44.99	$\beta_G + \delta_{\beta_G} + \delta_M$
 $-C-C-C-C-C^*-C-C-C-$	$I_B\backslash$ $I_PI_BI_P$ $I_P/$	8	43.21	42.58	$\beta_G + \delta_{\beta_M} + \delta_M$
 $-C-C-C-C-C^*-C-C-C-$	$I_BI_PI_B$	9	40.93	40.93	$\beta_M + \delta^*_{\beta_G} + \delta_G$
 $-C-C-C-C-C^*-C-C-C-$	$I_BI_PI_P$	10	40.24	40.24	$\beta_M + \delta^*_{\beta_G} = \delta_M$
 $-C-C-C-C-C^*-C-C-C-$	$I_PI_PI_B$	nd		39.83	$\beta_M + \delta_G$
 $-C-C-C-C^*-C-C^*-C-C-$	$I_PI_PI_P$	13	37.57	39.14	$\beta_M + \delta_M$
 $-C-C-C-C^*-C-C-C-$	$I_B\backslash\ /I_B$ I_PI_P $I_P/\ \backslash I_P$	24	24.67	24.81	$2\gamma_{2M}$
 $-C-C-C-C^*-C-C-C-$	$I_B\backslash\ /I_B$ I_PI_B $I_P/\ \backslash I_P$	26	21.65	20.40	$\gamma_{2M} + \gamma_{2G}$

Two other signals due to the second methylene of I_P in the dyads I_PI_P and I_PI_B, i.e., $CH_2C(CH_3)=CHC^*H_2$, are expected, but they must occur upfield since they are subjected to negative substitutions.

In the region between 38.16 and 34.18 ppm eight peaks are present which can be assigned to the quaternary carbon of I_B. The first group of three signals observed downfield is due to pentads centered on the triad $I_BI_BI_B$. The difference between the three peaks is due to an ϵ_G effect. Two other pairs of peaks, the first at 35.56 and 36.27 ppm and the second at 35.08 and 34.88 ppm, are assignable to the pentads centered on triads $I_PI_BI_B$ and $I_BI_BI_P$. In this case the effect of the second lateral unit beyond an I_P unit is negligible because of the length (i.e., four carbon atoms) of the chain segment situated between the central unit and the second lateral unit. For this reason only one peak, due to the quaternary carbon of I_B present in the four pentads centered on the triad $I_PI_BI_P$, is observed. The spectrum shows also the three peaks of the methyls of I_B present in the four possible triads, which are easily assignable on the basis of selective decoupling experiments.

Two of the four remaining signals, namely, the peak at 26.92 ppm and the doublet at 23.23 and 22.89 ppm, are assigned to the second methylene of I_P in the dyads I_PI_P and I_PI_B, i.e., $CH_2C(CH_3)=CH^*CH_2CH_2C(CH_3)=CHCH_2$ and $CH_2C(CH_3)=CH^*CH_2CH_2C(CH_3)_2$, respectively. The last resonance, which occurs downfield being negative the γ substituent effect on a methylene and $|\gamma_G| > |\gamma_M|$, is split because it is influenced by the second lateral unit situated beyond the I_B unit. Finally, two peaks at 15.96 and 19.20 ppm are attributable to the methyls of I_P in the I_PI_P and I_BI_P dyads, respectively. This signal also shows a fine structure due to the effect of the second lateral unit situated beyond the I_B unit.

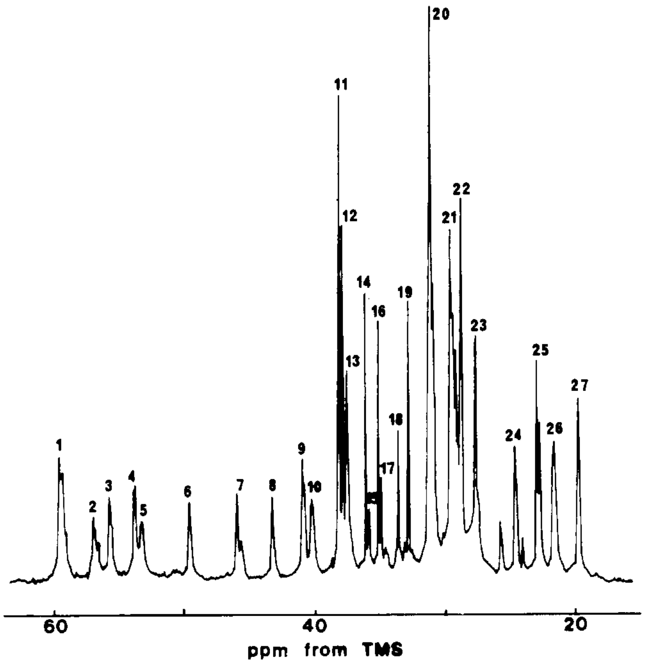
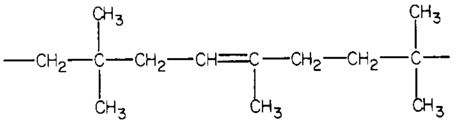


Figure 3. ^{13}C NMR spectrum of the hydrogenated I_B–I_P copolymer.

The analysis of the olefinic region of the spectrum (Figure 2B) fully confirms the hypothesis of a regular linkage of the monomeric units.[21] In fact, ten signals are evident in this region and the four downfield are assigned to carbon atoms linked to the methyl groups. The remaining six upfield signals are assigned to —CH= carbons on the basis of off-resonance decoupling. Table II shows the assignments. Two signals, assigned to the $I_PI_PI_P$ triad, occur at the extremes of this region, i.e., the signal at 134.93 ppm due to the >C= carbon and that at 124.41 ppm due to the —CH= carbon. Therefore, the substitution of an I_P unit by I_B shifts the resonance of >C= upfield and that of —CH= downfield. It can be concluded, in agreement with the predicted sign of the additive contributions (positive values of γ' and δ and negative values of γ and δ') and with previous findings,[1] that >C= is the first carbon (C_1) of the double bond while —CH= is the second carbon (C_2). In fact, if I_P were irregularly linked, the signal of =C< in the triad $I_BI_PI_B$, i.e.



$$-CH_2-C(CH_3)_2-CH_2-CH{=}C(CH_3)-CH_2-CH_2-C(CH_3)_2-$$

would be shifted downfield, compared to the same resonance of the triad $I_PI_PI_P$, because of the positive value of γ' and δ, while the signal of —CH= would be shifted upfield since the values of γ and δ' are negative. Actually, the olefinic region of the spectrum does not show peaks of appreciable intensity downfield from 134.93 ppm and upfield from 124.41 ppm. According to Table II the —CH= carbon shows an ϵ_G' effect (not evident in the case of the I_B-butadiene copolymer[1]) whose value is positive, while the value of ϵ_G is practically negligible.

^{13}C NMR Spectra of the Hydrogenated I_B–I_P Copolymer. The spectrum of a typical sample of the hydrogenated I_B–I_P copolymers is shown in Figure 3. In this case selective decoupling allows only the identification of the type of carbons, i.e., primary, secondary, etc., while the assignments to the different sequences can be obtained by comparison with the spectra of the original copolymer and by consideration of additive contributions.

Tables III and IV list the assignments of all the carbons other than methylenes and all the possible types of methylenes, respectively. The experimental values are compared with calculated values obtained using the parameters listed in the previous section. An inspection of Table III shows that the chemical shifts of methyls and quaternary carbons are very close to the values obtained for the original copolymer. The largest difference concerns the values of the three signals assigned to the quaternary carbons of the pentads centered on triads $I_BI_BI_P$ and $I_PI_BI_P$. The difference stems from a β_t effect of a trans double bond in the β position relative to the quaternary carbon which, of course, is not present in the hydrogenated copolymer.

In Table IV, three types of δ substitution are taken into account, namely, δ, $\delta_\beta{}^*$, and δ_β. The substitutions δ and δ_β have the usual meaning, while the second one refers to a δ substitution beyond a β-methyl substitution. From a quantitative standpoint, i.e., the evaluation of the sequence fractions, it can be observed that the spectra of the original copolymers allow the calculation of more precise values of the pentads centered on I_B because any overlapping of signals due to quaternary and methylene carbons is absent. Conversely, the analysis of the spectra of hydrogenated copolymers allows the separation of the signals of some tetrads which overlap in the spectra of the original copolymers.

Conclusions

Detailed interpretation of the ^{13}C NMR spectra of the I_B–I_P copolymers and their hydrogenated derivatives yields the useful information that the linking of the monomeric units is substantially regular.[21] The spectra also allow the calculation of the triad, tetrad, and pentad fractions, the values of which elucidate the monomer distribution and the copolymerization statistics.[8]

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(10) When 1,2,4-trichlorobenzene was used as solvent at high temperature (120 °C), the tetrad peaks of the methylene carbons showed a fine structure and signals assignable to hexad sequences were revealed. The analysis in this case must be restricted to the aliphatic region of the spectrum because of the interference of the solvent in the olefinic region. The study of the fine structure and of the possibility of identifying long-range contributions due to the *gem*-dimethyl group is in progress.
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(19) The base frequencies used for calculation were ν_{CH_2} = 29.90 ppm (resonance of linear polyethylene) and ν_C = 33.00 ppm (quaternary carbon of the *gem*-dimethyl group present in a polymethylene chain).

(20) Units arising from the opening of the 3,4 double bond of I_P were ascertained in ^{13}C NMR spectra of cationic polyisoprene and I_B–I_P copolymers containing high amounts of I_P, i.e., >50 mol %.

(21) Regular enchainment means in the context the essential head-to-tail insertion of the monomers. They arise from the 1,2-I_B addition and trans-1,4 (not trans-4,1) I_P addition to the carbenium ion of the chain growing end.

Cationic Copolymers of Isobutylene. 3. Nuclear Magnetic Resonance Investigation of the Structure of Isobutylene–*trans*-1,3-Pentadiene Copolymer

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ABSTRACT: The structure of isobutylene–*trans*-1,3-pentadiene (I–P) copolymers, obtained in a homogeneous medium with a cationic catalyst, has been studied by ^1H and ^{13}C NMR spectroscopic techniques. The spectra of these copolymers and their hydrogenated derivatives were investigated. Both I and P enter the copolymer chain head-to-tail; the diene enters mainly as the trans-1,4 unit but a minor amount (15% for typical samples) is incorporated as the 1,2 unit. A detailed description of the sequence distribution up to the hexad level emerged from the assignments of these spectra. The data for the triad, tetrad, pentad, and hexad fractions show that the distribution of the monomeric units deviates slightly from the randomness toward the alternation.

Pursuing previous investigations in which we studied the structure of isobutylene–butadiene[1] and isobutylene–isoprene[2] copolymers, we have now taken into account the cationic copolymers of isobutylene (I) with *trans*-1,3-pentadiene (P). The aim of our work was the extension of the information obtained with butadiene and isoprene copolymers to new diene monomers, i.e., *trans*- and *cis*-1,3-pentadienes, in order to establish their influence on the process of copolymerization with isobutylene and on the monomer distribution. The introduction of a methyl group in position 4 of the conjugated diene system modifies the electron distribution of the entire system and stabilizes the carbenium ions formed during the copolymerization process. Both effects influence the monomer reactivity[3] and hence are expected to regulate the distribution of the monomeric units in the chains. As far as the relative reactivity of *cis*- and *trans*-1,3-pentadienes is concerned, the trans isomer was found to be more reactive than the cis isomer in the cationic copolymerization with isobutylene, but in that work[3] it was impossible to evaluate the reactivity ratios concerning the diene monomers. In this paper the structure of I–P copolymers is investigated by ^1H and ^{13}C NMR spectroscopic techniques. Several monomer sequences have been identified and their fractions have been calculated. The copolymerization of *cis*-1,3-pentadiene with isobutylene gives rise to a more complex system that will be discussed in a forthcoming paper.

Experimental Part

Materials. Isobutylene (Phillips, polymerization-grade product), solvents (*n*-pentane and CH_2Cl_2), and the catalyst ($C_2H_5AlCl_2$) were purified and handled as described elsewhere.[1] *trans*-1,3-Pentadiene (Fluka AG) was distilled under an inert atmosphere and stored at 0 °C (VPC purity >99%).

Procedure. Copolymerization runs were carried out under dry N_2 as reported previously.[1] A mixture of *n*-pentane and CH_2Cl_2 (1:1 by volume) was used as a solvent (homogeneous system). $C_2H_5AlCl_2$ (10–40 mmol/I in *n*-pentane) was added to the solution of monomers and the mixture was maintained at −70 °C. The copolymerization reaction was carried out for 15 min and stopped with methanol containing 5% NH_4OH. The copolymer was recovered by coagulating the reaction solution with an excess of methanol. A typical copolymer for spectroscopic analysis was prepared according to the following conditions (I = isobutylene, P = *trans*-1,3-pentadiene): [I] = 1.9 mol/L, [P]/[I] = 0.47, [$C_2H_5AlCl_2$] = 0.030 mol/L, conversion = 30%, P content of the copolymer = 37 mol %, [η] = 0.11 dL/g (in cyclohexane at 30 °C).

The hydrogenation of the I–P copolymer was carried out in cyclohexane at 180 °C, as described previously.[1]

Analyses. ^1H and ^{13}C NMR spectra were obtained at 25 °C for copolymer solutions in $CDCl_3$ and at 120 °C for copolymer solutions in 1,2,4-trichlorobenzene with a Varian XL-100 spectrometer. Experimental FT conditions were the same as those described in a previous work[2] except that a pulse delay of 9.2 s was used for samples subjected to quantitative analysis. No precaution was adopted with respect to differences in nuclear Overhauser effect (NOE), as it was assumed that no difference would occur for these copolymer spectra. Selective decoupling experiments were carried out as described previously.[2]

The ^{13}C NMR area measurements were made by cutting out and weighing each peak in a xerocopy of the spectrum. Chemical shifts are reported in parts per million from Me_4Si. For spectra recorded at 120 °C the chemical shifts were obtained from HMDS and referred to Me_4Si by assuming that ν_{HMDS} = 2.00 ppm. The copolymer composition was evaluated by ^1H NMR measurements.

Results and Discussion

^1H NMR Analysis. It is known that P copolymerizes with I by entering the chains mainly as the trans-1,4 unit.[3] ^1H NMR spectra do not give accurate data on the monomer distribution because it is impossible to utilize the signals of the *gem*-dimethyl group for calculating the triad fractions centered on I, as for other copolymers containing isobutylene.[1,2,4] In fact, in the region between 0.8 and 1.1 ppm of Figure 1, which shows the ^1H NMR spectrum of a typical I–P copolymer containing 37 mol % P, there are three signals due to the methyls of I belonging to triads III (1.09 ppm), IIP + PII (0.97 ppm), and PIP (0.85 ppm). Unfortunately, there is also present at about 0.9 ppm the signal of the methyl of P which overlaps the peaks of the methyls of I and mainly those of triads IIP + PII. Therefore, it is necessary to take into account the contribution of the methyl of P for calculating the triad fractions and this correction introduces an inaccuracy in

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