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(31) Hydrogenation performed in the presence of 5% of Pd on charcoal, $T = 200$ °C, $P_{H_2} = 8$ atm, time = 8 h. The final product showed Cl content <10 ppm; Br number <0.5.

Cationic Copolymers of Isobutylene. 1. Nuclear Magnetic Resonance Investigation of the Structure and Monomer Distribution in Isobutylene–Butadiene Copolymer

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ABSTRACT: The structure of isobutylene (I)–butadiene (B) copolymers, obtained with a cationic catalyst, has been examined by ^1H and ^{13}C NMR spectroscopy. The spectra of these copolymers and their hydrogenated derivatives were investigated. From the assignment of these spectra, a detailed description has emerged of the sequence distribution of isobutylene and *trans*-1,4- and 1,2-butadiene units in the chain. The data for the triad fractions centered on isobutylene and *trans*-1,4-butadiene units show that the monomeric units are distributed in an essentially block manner. The great complexity of the I–B system does not allow us to describe it by the two-component copolymerization model.

New isobutylene copolymers have been synthesized recently in our laboratories. By means of coordination catalysts, we obtained isobutylene–butadiene copolymers which showed peculiar structural features.[1] Moreover, we studied the copolymerization of particular trienes (e.g., 1,3,5-hexatriene or 2,4,6-octatriene) with isobutylene in the presence of cationic initiators, obtaining macromolecules which contain conjugated double bonds.[2,3]

The structural characterization of these copolymers prompted us to study also the structure of isobutylene–butadiene (I–B) copolymers obtained in the presence of cationic catalysts. Their preparation has been known for a long time,[4] but their structural characterization is rather poor, since the resulting copolymers have mainly been studied from a technological point of view.[4]

The most recent studies on cationic I–B copolymers can be summarized as follows:[5] (1) Butadiene enters the copolymer chain mainly as the trans-1,4 unit; minor amounts (20–25%) of 1,2 units are also present. (2) The reactivity of butadiene is higher in an apolar, homogeneous medium than under polar, heterogeneous conditions. (3) The reactivity of butadiene with respect to isobutylene increases with the temperature. (4) At low temperature, the reactivity of butadiene (B) is extremely low compared to that of isobutylene (I). For instance, the reactivity ratios obtained for their copolymerization at −100 °C in CH_3Cl and in the presence of $EtAlCl_2$ were (Finemann and Ross method) $r_I = 43$ and $r_B \simeq 0$. (5) A random distribution of the monomeric units appears very likely and long sequences of butadiene units seem unlikely.

On the other hand, a critical examination of the data so far published indicates the great complexity of the I–B system. For instance, the content of 1,2-butadiene units (ca. 20%) suggests that the I–B copolymer is actually a terpolymer. The two-component copolymerization model cannot describe the copolymerization reaction and the

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actual structure of the resulting copolymer. Six reactivity ratios are necessary to account for all possibilities of enchainment among the three structural units.

A similar conclusion has been reached recently by Kennedy and Tüdos[6] after a reexamination of the copolymerization data concerning this system. It is worth noting that the butadiene content in I–B copolymers was usually determined by iodometric titration (Gallo's method[7]) and only recently has IR spectroscopy been employed. Since the accuracy of both methods is rather poor (it is necessary to make reference to appropriate model compounds to gain a good evaluation of the unsaturation content), we have reinvestigated the I–B system by using ^{1}H and ^{13}C NMR spectroscopy. This approach has noticeably improved the possibility of elucidating the structure of cationic I–B copolymers, both from a qualitative and quantitative point of view. In fact, ^{1}H and ^{13}C NMR spectroscopy have provided direct evidence for all the structural units present in the copolymer and also allowed quantitative determination of both the copolymer composition and the triad fractions.

Previous work[8] has showed that ^{1}H NMR allows an easy evaluation of the fraction of triads having isobutylene as the central unit. The fractions of triads containing *trans*-1,4-B as the central unit can be evaluated by ^{13}C NMR. These results were possible after studying the I–B copolymer obtained with coordination catalysts.[1] Also, the signals of some tetrads and pentads have been observed, and thus the knowledge of the overall structure of the I–B cationic copolymer has been improved markedly.

The interpretation of the ^{13}C NMR spectra of the original and hydrogenated cationic I–B copolymer and the information concerning the monomer distribution and its correlation with the copolymerization mechanism are the subjects of this paper. The study of other isobutylene–diene copolymers is in progress.

Experimental Section

1. **Materials.** Isobutylene and butadiene (Phillips Polym. Grade products) were dehydrated by passing them through two 1-m columns containing activated molecular sieves (4A). The monomers were stored at −78 °C and handled under dry nitrogen with precooled pipets. $Al(C_2H_5)Cl_2$ (Texas Alkyls product) was used as received and maintained under dry nitrogen atmosphere. *n*-Pentane and CH_2Cl_2 were purified and dried as reported elsewhere.[9]

Reference polymers, i.e., high molecular weight poly(isobutylene), hydrogenated 1,4-poly(4-methyl-1,3-pentadiene),[10] and hydrogenated I–B coordination copolymer were prepared as described in the references quoted.

2. **Procedure.** I–B copolymerizations were carried out in a three-necked flask by using a mixture of *n*-pentane and CH_2Cl_2 (1:1 by vol) as a solvent under an atmosphere of dry nitrogen at the temperature of −70 °C and with different molar ratios of the monomers (their total amount was kept constant at 3.3 mol/L). The copolymer obtained under these conditions was completely soluble, and hence the system was homogeneous. The initiator was $Al(C_2H_5)Cl_2$ (0.010–0.020 mol/L), and the reaction time was 15 min; the monomers conversion was <5%.

The copolymerization was stopped by adding a few milliliters of methanol containing 5% of NH_4OH to the reaction mixture. The polymer solution was washed with acidic (HCl) water and then with deionized water to neutrality. Solvents were eliminated by evaporation under vacuum; the recovered polymer was redissolved in $CHCl_3$, coagulated from an excess of methanol, and dried in vacuum for 15 h at room temperature.

The copolymer homogeneity was tested by carrying out copolymerization runs at conversions higher than 5% and searching for the presence of I or B homopolymer by means of selective extraction (isopentane solvent at $T < 10$ °C). The copolymers investigated were always completely soluble. Furthermore, GPC analysis yielded symmetric, monomodal distribution curves, in agreement with an essentially homogeneous structure of the samples tested.

Table I
Cationic Copolymerization of Isobutylene (I) and Butadiene (B)[a]

run no.	% conversion	feed mol fract of B	composition[b] mol fract of B	$\overline{M}_n$
1	4	0.60	0.10	n.d.
2	5	0.75	0.31	15000
3	5	0.80	0.38	9200
4	2	0.80	0.31	n.d.
5	4	0.90	0.65	5400
6	5	0.94	0.77	n.d.
7	2	0.94	0.63	n.d.

[a] Experimental conditions: solvent = *n*-pentane + CH_2Cl_2 (1/1 v/v); I + B = 3.3 mol/L; $T = -70$ °C; [$AlEtCl_2$] = 0.01–0.02 mol/L; time = 15 min. [b] Determined by ^{1}H NMR.

I–B copolymer was hydrogenated by dissolving it in cyclohexane in the presence of Pd (5%) supported on charcoal. The reaction was performed in an autoclave equipped with a stirrer at 180 °C; H_2 pressure = 8 atm (at room temperature); time = 4 h. The recovered polymer was shown by NMR to be completely hydrogenated.

3. **Analyses.** GPC investigations were carried out on tetrahydrofuran copolymer solutions at 30 °C and with a Waters Associates instrument. The average number molecular weight ($\overline{M}_n$) was determined by means of a vapor pressure osmometer (Mechrolab. Model 502 instrument) using toluene solutions at 37 °C.

^{1}H NMR spectra were obtained with a Varian HA-100 instrument using copolymer solutions in $CDCl_3$ at room temperature. ^{13}C NMR investigations were performed with a Varian XL-100 instrument equipped with Fourier transform. Chemical shifts are reported in ppm from Me_4Si used as an internal reference.

The copolymer composition was determined by ^{1}H NMR analysis from the ratio of the area of the olefinic protons to the rest of the area in the spectrum. The presence of cyclized structures in the samples investigated would give rise to an overestimation of the isobutylene content. Significant amounts of these structures can be ruled out on the basis of the absence of a broad signal between 1.2 and 1.6 ppm in the ^{1}H NMR spectrum and of the base line linearity of the ^{13}C NMR spectrum.[21]

Results and Discussion

1. **Cationic Copolymerization of Isobutylene and Butadiene.** Table I shows the results obtained for a series of I–B copolymerization runs carried out at low conversion (<5%) with the aim of verifying the possibility of describing this system by two reactivity ratios, according to the classical copolymerization equation.

By treating the copolymerization data according to the method proposed by Kelen and Tüdos,[11] which refines the Finemann and Ross approach, it is possible to gain some information concerning the copolymerization mechanism. The limitations arising from the assumptions made in deriving the classical copolymerization equation are particularly evident when the conventional composition equation is applied to cationic copolymerizations, as has been discussed recently by Kennedy, Kelen, and Tüdos.[12] They have shown that the calculation of the reactivity ratios is meaningless for several monomer pairs, while the plot of parameter η vs. ζ, proposed by Kelen and Tüdos, allows one to check the reliability of the reactivity ratios obtainable in cationic copolymerization.

Figure 1 shows the results of Table I plotted in terms of the parameter η vs. ζ. Unfortunately, the dispersion of the experimental points and the analytical difficulties encountered in exploring a broad range of ζ values do not allow definite conclusions about the applicability of the two-parameter copolymerization model to the I–B system.

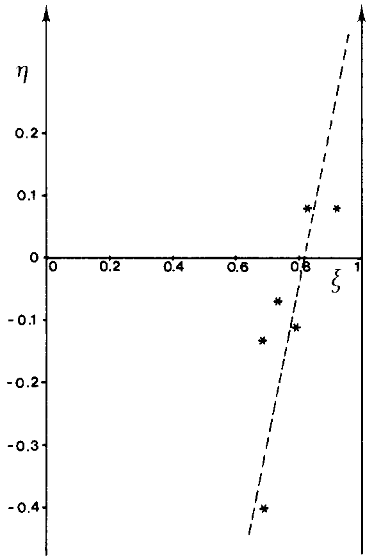


Figure 1. η vs. ζ plot for I–B cationic copolymerization.

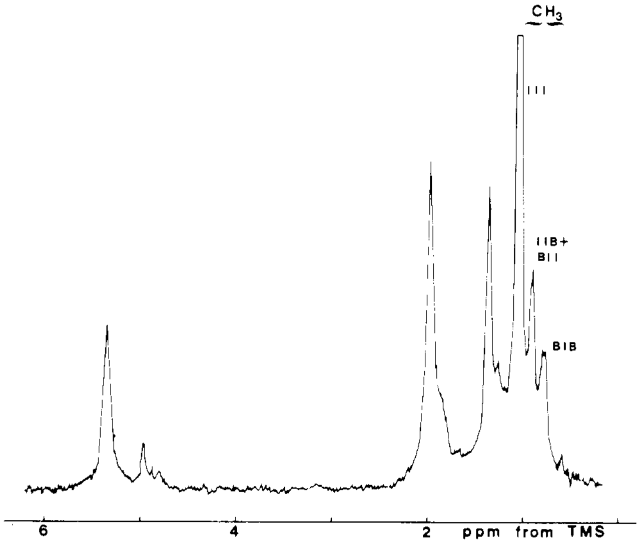


Figure 2. ^{1}H NMR spectrum of cationic I–B copolymer.

Therefore, we believe that a calculation of the reactivity ratios from the data of Table I is meaningless.

The evaluation of the monomer sequence distribution, reported in the next sections, allowed us to overcome the limitations encountered in studying the copolymer structure through the reactivity ratios evaluation and to obtain information concerning the complex behavior of this system.

2. ^{1}H NMR Analysis. The ^{1}H NMR spectrum of a typical cationic I–B copolymer containing 40% of B is shown in Figure 2. In the double-bond region, a signal is observed at 5.30 ppm characteristic of a $-CH=$ group and another signal at ca. 5.0 ppm typical of $CH_2=$ protons. Since IR and ^{13}C NMR spectra rule out the presence of significant amounts of cis double bonds in the copolymer, the composition of B units is 80% trans-1,4 and 20% 1,2.

In the upfield region there is evident the signal of methylene protons due to 1,4-B units at 2.0 ppm and that of methylene belonging to I units at 1.4 ppm.

The peaks at 1.1, 1.0, and 0.8 ppm are assigned to the methyl protons of triads III, IIB + BII, and BIB, respectively. The shift of methyl signals toward the upfield region, when the crowding of *gem*-dimethyl groups decreases, has been described previously[8] and observed also by us in previous work.[1] By measuring the area of the signals at 1.1, 1.0, and 0.8 ppm, the fractions of triads having isobutylene as the central unit can be calculated. The results will be discussed in the Calculation of the Triad Fractions section.

Table II
Experimental and Calculated Chemical Shifts of Carbon Atoms of Polyisobutylene

carbon	chemical shift exptl	chemical shift calcd
CH_2	59.6	54.32
C	38.2	36.37
CH_3	31.3	29.24

Table III
Substitution and Experimental Chemical Shift of Carbon Atoms of Hydrogenated 1,4-Poly(4-methyl-1,3-pentadiene)

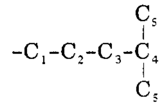
structural unit	atom	substitution	chemical shift
 $-C_1-C_2-C_3-\overset{C_5}{\underset{C_5}{C_4}}$	C_1 C_3	$\beta + \delta_2$	43.3
	C_2	$2\gamma_2$	18.4
	C_4	α	33.0
	C_5		27.3

Table IV
Substitution and Experimental Chemical Shift of Carbon Atoms of Coordination I–B Copolymer

carbon	substitution	chemical shift
CH_3		27.3
C	α	33.0
CH_2	β	42.2
	γ_2	24.2
	δ_2	30.9
	δ^+	29.9
	$2\delta_2$	31.9

The spectrum of Figure 2 and those of all I–B copolymers obtained by us are attributable to an essentially linear structure and do not show appreciable evidence of cyclized polybutadiene structures.

3. ^{13}C NMR Analysis. In order to improve the structural characterization of cationic I–B copolymers, ^{13}C NMR studies were carried out on both the original copolymers and their hydrogenated derivatives. ^{13}C NMR spectra have been interpreted by using the "off resonance" decoupling technique and making reference to the spectra of other polymers, namely polyisobutylene, hydrogenated 1,4-poly(4-methyl-1,3-pentadiene),[10] and the hydrogenated I–B coordination copolymer.[1] Also, chemical shifts have been calculated on the basis of additivity rules. As far as the last point is concerned, it is worth noting that the presence of "crowded" methyls gives rise to anomalous chemical shift values. Therefore, the agreement of the experimental values with those calculated according to the usual additivity rules[13] is not satisfactory. For instance, all the experimental chemical shifts of the carbon atoms of polyisobutylene (see Table II) are higher than the calculated ones, the difference being more than 5 ppm in the case of the methylene carbon.

In order to interpret ^{13}C NMR spectra, we have introduced a new set of substituent parameters. The hydrogenated copolymer can be considered as generated by methyl substitutions of the two methylene hydrogens in a polyethylene chain. The greek symbols (β, γ, etc.) reported in the following scheme indicate the substituent

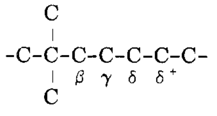
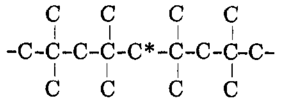
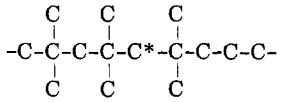
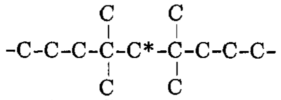
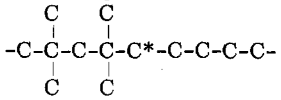
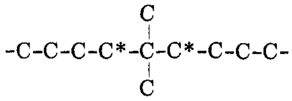
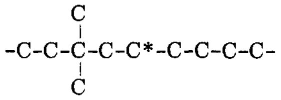
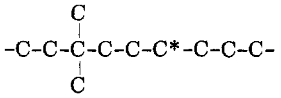
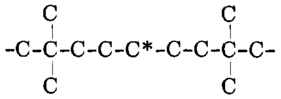

$$-C-\overset{C}{\underset{C}{C}}-\underset{\beta}{C}-\underset{\gamma}{C}-\underset{\delta}{C}-\underset{\delta^+}{C}-C-$$

Table V
Experimental Chemical Shifts in the Hydrogenated Cationic I-B Copolymer (Sequences Containing Units I and T)

atom	structure	sequence	no. of peaks	substitution	chemical shift
CH_3		III	10		31.3
		IIT + TII	n.d.		
		TIT	12		27.3
C		III	6	$\alpha + 2\gamma_4$	38.2
		IIT + TII	7	$\alpha + \gamma_4$	35.3
		TIT	9	α	33.0
CH_2	 $\mathrm{-C-\overset{C}{\underset{C}{C}}-C-\overset{C}{\underset{C}{C}}-C^{*}-\overset{C}{\underset{C}{C}}-C-\overset{C}{\underset{C}{C}}-C-}$	IIII	1	$2\beta + 2\delta_\beta$	59.6
	 $\mathrm{-C-\overset{C}{\underset{C}{C}}-C-\overset{C}{\underset{C}{C}}-C^{*}-\overset{C}{\underset{C}{C}}-C-C-C-}$	IIIT + TIII	2	$2\beta + \delta_\beta$	55.8
	 $\mathrm{-C-C-C-\overset{C}{\underset{C}{C}}-C^{*}-\overset{C}{\underset{C}{C}}-C-C-C-}$	TIIT	n.d.	2β	
	 $\mathrm{-C-\overset{C}{\underset{C}{C}}-C-\overset{C}{\underset{C}{C}}-C^{*}-C-C-C-C-}$	IIT + TII	3	$\beta + \delta_\beta$	45.8
	 $\mathrm{-C-C-C-C^{*}-\overset{C}{\underset{C}{C}}-C^{*}-C-C-C-}$	TIT	4	β	42.2
	 $\mathrm{-C-C-\overset{C}{\underset{C}{C}}-C-C^{*}-C-C-C-C-}$	IT + TI	15	γ	24.2
	 $\mathrm{-C-C-\overset{C}{\underset{C}{C}}-C-C-C^{*}-C-C-C-}$	ITT + TTI	n.d.	δ	(30.9)[a]
	 $\mathrm{-C-\overset{C}{\underset{C}{C}}-C-C-C^{*}-C-C-\overset{C}{\underset{C}{C}}-C-}$	ITI	n.d.	2δ	(31.9)[a]
	-C-C-C-C-C*-C-C-C-C-	TTT	11		29.9

[a] Reported in ref 1.

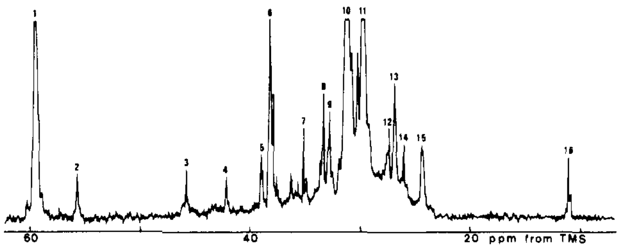
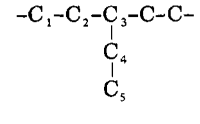


Figure 3. ^{13}C NMR spectrum of hydrogenated cationic I-B copolymer.

effects due to *gem*-dimethyl groups. Their values can be obtained from the spectra of the model polymers mentioned above. Tables III and IV report the substitutions and the chemical shift of hydrogenated 1,4-poly(4-methyl-1,3-pentadiene) and of hydrogenated I-B coordination copolymer, respectively. In the last copolymer, the minimal distance between two *gem*-dimethyl groups is five methylenes, as described previously,[1] and the $2\delta_2$ carbon is the central methylene in the triad IBI. In Tables III and IV the index of γ and δ indicates that, according to the addition scheme proposed by Lindeman and Adams, each type of carbon atom, i.e., primary, secondary, tertiary, and quaternary, has its own set of γ and δ parameters, namely $\gamma_{1,2,3,4}$ and $\delta_{1,2,3,4}$. Since ν_E = 29.9 ppm is the polyethylene resonance, the data of Tables III and IV allow us to calculate the following best values of the substituent parameters: $\alpha = 3.1$; $\beta = 12.3$; $\gamma_2 = -5.7$; and $\delta_2 = 1.0$ ppm. For polyisobutylene, the resonances of the methylene and quaternary carbon are $\nu_{CH_2} = \nu_E + 2\beta + 2\delta_2$ and $\nu_C = \nu_E + \alpha + 2\gamma_4$, respectively. In the last case, from the values of ν_C, ν_E, and α reported above, we obtain $\gamma_4 = 2.6$ ppm, i.e., a positive value for γ_4, which is in agreement with the results of Lindeman and Adams. The values of β and δ_2 could be used to calculate the methylene resonance of polyisobutylene, but the agreement between the experimental (59.6 ppm) and the calculated value ($\nu_E + 2\beta + 2\delta_2 = 56.5$ ppm) is not satisfactory. However, it is worth noting that in polyisobutylene the δ substituent is preceded by a β substituent, whereas in the other cases there are no substituent groups between the *gem*-dimethyl group and the carbon atom considered. Therefore we introduce two types of δ contribution, the former (δ) not influenced by an intermediary β substitution and the latter (δ_β) involving an intermediary β substitution, as suggested in another case.[14] The polyisobutylene spectrum allows us to calculate the δ_β contribution, but it is preferable to discuss first the spectrum of cationic I-B copolymer and then to calculate the δ_β value which permits the best agreement between calculated and experimental chemical shifts.

a. ^{13}C NMR Spectra of Hydrogenated I-B Cationic Copolymer. Figure 3 shows the ^{13}C NMR spectrum of the hydrogenated I-B cationic copolymer containing 40% butadiene. The assignments of the main peaks are listed in Tables V and VI. Table V reports the sequences containing isobutylene (I) and hydrogenated 1,4-B (T) units while Table VI reports the structure containing T

Table VI
Experimental Chemical Shifts of the Structure Containing Hydrogenated 1,2-B Unit

structure	carbon	no. of peaks	chemical shift
 $-C_1-C_2-C_3(-C_4-C_5)-C-C-$	C_1	13	26.8
	C_2	8	33.3
	C_3	n.d.	
	C_4	14	25.9
	C_5	16	10.9

and 1,2-B (V) units. In view of the complexity of the spectrum, we carried out the analysis in two phases. First, we neglected 1,2-B units and considered only the signals of the triads containing I and T units. The assumption made is that isobutylene is enchained regularly, i.e., head-to-tail. Second, we identified the peaks due to the triad carrying T as a side unit and V as a central unit. Peaks due to triads containing I and V units were not identified since their intensity was low.

As far as the sequences containing units I and T are concerned, three signals are expected for the methyls belonging to triads III, IIT + TII, and TIT. The first is at 31.3 ppm. The third occurs at 27.3 ppm on the basis of the assignments made for I-B coordination copolymers.[1] The assignment is confirmed by off-resonance decoupling. Another signal, due to triads IIT + TII, is expected at 29.3 ppm, in a region intermediate between the two previous peaks. It is not clearly visible in Figure 3, probably because it is overlapped by other peaks occurring between 29 and 30 ppm. Among them, the signal at 29.9 ppm is very large. This peak is assigned to methylenes distant more than four bonds from a *gem*-dimethyl group, i.e., to polyethylene sequences derived from the hydrogenation of 1,4-B units. Three signals are also expected from quaternary carbons. The first peak, due to the triad III, is evident at 38.2 ppm. The second peak occurs at 33.0 ppm and is assigned to triad TIT on the basis of the assignments made for the coordination I-B copolymer.[1] The third signal, due to the TII + ITT triads, is identified, on the basis of the off-resonance decoupled spectrum, at 35.5 ppm. As expected, its position is almost intermediate between that of the other two signals.

On the basis of these assignments, the ^{13}C NMR spectra could also permit us to calculate the fractions of triads centered on isobutylene. However, the results are less accurate than those obtained from the ^1H NMR spectra because of the complexity of the ^{13}C NMR spectra.

More interesting is the study of signals due to methylenes. The signal of the homopolymeric tetrad is downfield (59.6 ppm). At 42.2 ppm, the signal of methylene is subject only to the β contribution (triad TIT). This peak was identified in the study of the hydrogenated I-B coordination copolymer. Two other peaks are present between 42.2 and 59.6 ppm, namely at 55.8 and 45.8 ppm, and hence they are almost equidistant from the peaks limiting the range considered. They can be assigned to the methylenes undergoing $2\beta + \delta_\beta$ and $\beta + \delta_\beta$ substitution, i.e., to tetrads IIIT + TIII and to the triads IIT + TII. From these data, the value of $\delta_\beta = 3.7$ ppm and results much higher than the δ value (1.0 ppm) are obtained.

Conversely, no signal attributable to tetrad TIIT appears in the spectrum of Figure 3. The absence of the peak expected at ca. 54 ppm ($\nu_E + 2\beta$) agrees with the fact that the signals at 45.8 and 55.8 ppm have practically the same intensity. In fact, it is evident that the signal due to the methylene of triad IIT (and also to the corresponding methylene of triad TII) is the sum of signals due to tetrads IIIT + TIIT (and also of the corresponding methylenes of tetrads TIII + TIIT). Since the intensity of the signals due to IIT triad and IIIT tetrad is equal, it is evident that the intensity of signal due to tetrad TIIT is negligible. As far as other signals listed in Table V are concerned, that due to γ_2 substitution occurs at 24.2 ppm,[1] while the two peaks due to methylenes undergoing δ_2 and $2\delta_2$ substitution are not clearly evident because of the existence of several signals near 29.9 ppm. Finally, Figure 3 shows some peaks that can be assigned to hydrogenated 1,2-B units. From the analysis of cationic I-B copolymers richer in butadiene and from literature data concerning hydrogenated polybutadienes[15] and branched polyethylenes,[16,17] the signals at 10.9 and 25.9 are assigned to the methyl and methylene carbons, respectively, of ethyl branches arising from the hydrogenation of vinyl groups. The signals observed at 33.3 and 26.8 ppm are assigned to the two methylenes in β and γ positions, respectively, relative to the ethyl branches.

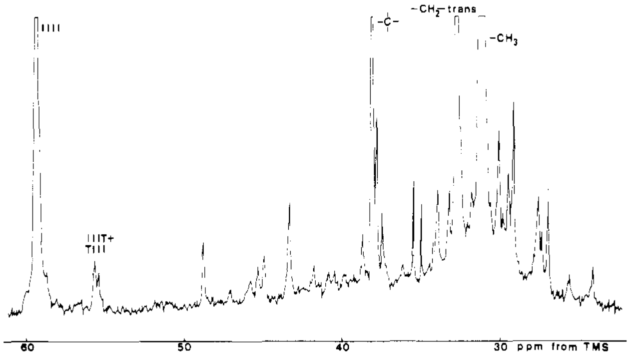


Figure 4. ^{13}C NMR spectrum of cationic I–B copolymer (aliphatic region).

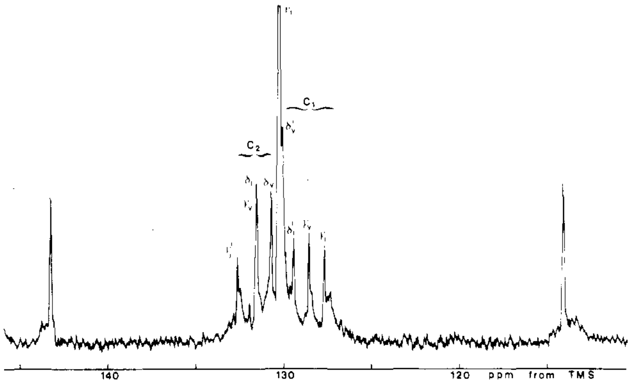


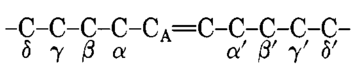
Figure 5. ^{13}C NMR spectrum of cationic I–B copolymer (olefinic region).

b. ^{13}C NMR Spectra of the I-B Cationic Copolymer. The aliphatic region of ^{13}C NMR spectra of the original cationic I-B copolymers does not give any information not obtainable from the hydrogenated copolymer. Figure 4 shows the spectrum of the same copolymer as in Figure 3 before hydrogenation and the main assignments which can be made by referring to the spectra of hydrogenated samples. It is worth noting that the aliphatic region of the spectrum is no simpler than that of the hydrogenated copolymer. The presence of a double bond reduces the number of saturated carbon atoms, but the hydrogenation introduces a symmetry which is lacking in the original copolymer. Conversely, it is useful to study the olefinic region of the spectra (Figure 5) in order to determine the fractions of triads having *trans*-1,4-B as central units. In this region there are two signals, at 114.70 and 142.60 ppm, due to CH_2= and –CH=, respectively, of the vinyl branch and the signals of the two carbon atoms C_1 and C_2 of the

Table VII
Substitution and Experimental Chemical Shifts of the Carbon Atoms of Unit T in the Triads with Unit V

triad	carbon	substitution	chemical shift
VTV	C_1	$\gamma_V + \delta'_V$	n.d.
	C_2	$\gamma'_V + \delta_V$	n.d.
VTT	C_1	γ_V	128.44
	C_2	γ'_V	131.37
TTV	C_1	δ'_V	129.94
	C_2	δ_V	130.53
TTT	C_1 and C_2		130.08

unit *trans*-1,4-B (T) in all the possible triads with 1,2-B unit (V) and isobutylene (I). The assignments of C_1 and C_2 carbons can be made following the scheme proposed by Dorman et al.[18] to define the contributions of different substitutions to the chemical shift of the unsaturated carbons. By referring to the following chain:



$$-\underset{\delta}{C}-\underset{\gamma}{C}-\underset{\beta}{C}-\underset{\alpha}{C}-C_A=\underset{\alpha'}{C}-\underset{\beta'}{C}-\underset{\gamma'}{C}-\underset{\delta'}{C}-$$

the effects upon C_A are indicated by the different substitutions. In this case we denote by α_V, β_V, etc., and by α_I, β_I, etc., the substituent effect due to the vinyl group and *gem*-dimethyl group, respectively.

The substitution and the experimental chemical shifts of the two unsaturated carbons of unit T in the four possible triads with unit V are listed in Table VII. The base resonance of C_A is the resonance of the carbon belonging to a trans double bond, i.e., $\nu_t = 130.08$ ppm. The peaks are identified on the basis of the spectra of copolymers having different compositions.

In order to make assignments, we use the following values of parameters from the literature:[15] $\gamma_V = -1.74$, $\gamma'_V = 0.84$, $\delta_V = 0.30$, and $\delta'_V = -0.15$ ppm. They are the average of contributions to unsaturated carbons belonging to both cis and trans double bonds. In a more recent paper,[19] the single contributions due to the cis and trans configuration have been calculated. For the trans form the values are: $\gamma_V = -1.66$, $\gamma'_V = 0.46$, $\delta_V = 1.25$, and $\delta'_V = -0.19$ ppm.

In this last work the assumption has been made that $\delta > \gamma'$ in contrast with the majority of other literature data. According to the more widely accepted hypothesis, i.e., $\gamma' > \delta$, the assignments reported in Table VII are obtained.

The values of the substituent parameters are: $\gamma_V = -1.64$, $\gamma'_V = 1.29$, $\delta_V = 0.45$, and $\delta'_V = -0.14$ ppm, which are quite close to the values quoted above, apart from the exchange between the γ' and δ values.

In the spectrum of Figure 5 the signals of the triad VTV are not evident. This fact will be discussed further.

Other signals present in Figure 5 are due to triads containing T as the central unit and I or T as side units. The chemical shifts of C_1 and C_2 carbons in these triads have been previously reported.[1] A partial overlapping of the signal due to C_2 present in the triad VTT with the signal of the same carbon present in triad TTI occurs at 131.37 ppm. However, the assignment scheme can follow that reported in Table VII by substituting the index of the vinyl group (V) by the symbol of the *gem*-dimethyl group (I).

We now discuss the spectrum of Figure 5. Three signals occurring downfield, namely at 131.37, 132.26, and 133.53 ppm and due to C_2 of triads TTI, ITT, and ITI, respectively, are coincident with the values found in the coordination I–B copolymer.[1] Conversely, two of the three peaks present upfield and assigned to C_1 of triads ITI and ITT show chemical shifts a little higher than the corresponding values observed in the coordination I–B copolymer. The latter peaks are present also in Figure 5, but their intensity is very low. Such a result can be attributed to an ϵ_I contribution, i.e., to the contribution of the *gem*-dimethyl group present in the ϵ position. In practice, the signals of Figure 5 occurring at 127.55 and 126.69 ppm are assigned to pentads IITTI + IITTT and IITII + IITIT, respectively, while those observed at 127.19 and 126.34 ppm are assigned to pentads TITTI + TITTT and TITII + TITIT, respectively. It is evident that, because of the block character of cationic I–B copolymers (which will be defined quantitatively below), the former pentads are likely in the cationic copolymer, while they are not present in the coordination copolymer since they implicate two adjacent I units.[1]

Table VIII
Substitution and Calculated Chemical Shift of the Carbon Atoms of Unit T in the Triad with Units I and V

triad	carbon	substitution	calcd chemical shift
VTI	C_1	$\gamma_V + \delta'_I$	127.64
	C_2	$\delta_V + \gamma'_I$	132.58
ITV	C_1	$\gamma_I + \delta'_V$	127.04
	C_2	$\delta_I + \gamma'_V$	132.22

Therefore, only the signals due to the last three pentads (among the eight series written above) are expected in the spectra of the coordination I–B copolymer. From the spectrum, the contribution $\epsilon_I = 0.33$ ppm can be calculated. Finally, in the olefinic region, the signals of the triads ITV and VTI, analogous to that of the triad VTV mentioned above, are not clearly evident. Table VIII shows the substitutions and the calculated chemical shifts obtained for these triads on the basis of the contributions reported above. The presence of the signals listed in Table VIII cannot be excluded since the olefinic region is complicated by the presence of several signals having low intensity. Such an abundance of weak signals introduces some difficulties and inaccuracy in calculating the fractions at the monomers sequence, as will be evident in the next section.

4. Calculation of the Triad Fractions. The triad fractions having I as the central unit can be calculated from ^{1}H NMR spectra (cf. part 1 of this section), while the ^{13}C NMR spectra allow us to obtain (with some inaccuracy) the triad fractions centered on T units. Table IX shows the values of the triad fractions centered on I for a series of copolymers having different compositions but synthesized under the same conditions. These values are compared with the calculated data obtained for a "Bernoullian" copolymer. The large difference existing between the two series of values is clearly evident. In particular, the homopolymeric III sequence is always prevalent while the fractions of triads IIB and BII are always very low.

For four samples of Table IX, calculation of the fractions of the triads centered on T units has been carried out on the basis of the ^{13}C spectra. Triads VTV, VTI, and ITV have been neglected because their signals are not detectable. Calculations were based on the assignments reported above and by taking into account that the area of the signal occurring at 131.37 ppm and due to carbon C_2 in two different triads has to be divided into two parts on the basis of the ratio obtained for carbon C_1 in the same two triads. Table X collects the results obtained which are compared with the data calculated by assuming a Bernoullian copolymerization of B and I.

Table IX
Fractions of the Triads Centered on Unit T Determined by ^{1}H NMR

			triad fractions					
	feed mol fract of B	composition mol fract of B	F_{III}		$F_{\text{IIB+BII}}$		F_{BIB}	
run no.			exptl	calcd	exptl	calcd	exptl	calcd
1	0.94	0.77	0.37	0.053	0.26	0.354	0.37	0.593
2	0.94	0.63	0.52	0.137	0.26	0.466	0.23	0.397
3	0.90	0.65	0.56	0.122	0.22	0.455	0.22	0.423
4[a]	0.80	0.44	0.72	0.313	0.17	0.493	0.11	0.194
5	0.80	0.37	0.78	0.397	0.14	0.466	0.08	0.137
6	0.80	0.31	0.75	0.476	0.16	0.428	0.09	0.096
7	0.75	0.31	0.81	0.476	0.13	0.428	0.06	0.096
8[b]	0.60	0.14	0.88	0.740	0.09	0.240	0.03	0.020
9	0.60	0.10	0.83	0.810	0.13	0.180	0.04	0.010

[a] Conversion = 15%. [b] Conversion = 21%.

Table X
Fractions of the Triads Centered on Unit T Determined by ^{13}C NMR

	F_{TTT}		$F_{\text{ITT+TTI}}$		F_{ITI}		$F_{\text{VTT+TTV}}$		$F_{\text{VTV+VTI+ITV}}$	
run no.	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
4	0.39	0.11	0.27	0.37	0.03	0.31	0.31	0.07		0.14
5	0.38	0.08	0.27	0.35	0.08	0.40	0.27	0.05		0.12
8	0.31	0.01	0.37	0.17	0.06	0.74	0.26	0.01		0.07
9	0.27	0.01	0.45	0.14	0.12	0.81	0.16	0.00		0.04

Independently of the limitations introduced in elaborating the experimental data and due also to the inaccuracy of measurements, it is evident in Table X that there is a large deviation of the experimental data from the values calculated for a random copolymer. In fact, it is evident that the fractions of the triads of B, i.e., F_{TTT} and $F_{\text{VTT+TTV}}$, are always much higher than the calculated values. This result confirms the block character of the cationic I–B copolymer.

Conclusions

Interesting information has been obtained on the structure of cationic I–B copolymers by means of ^{1}H and ^{13}C NMR analyses. The monomer distribution calculated as triad fractions from the spectroscopic data rules out the possibility of describing these copolymers as random. This conclusion is in contrast with that deduced from the reactivity ratios reported in the literature[5] which appear meaningless on the basis of our work. A similar conclusion was reached by other authors on the basis of a critical analysis of the experimental data so far collected.[6] In fact, the cationic I–B system shows great complexity due to the occurrence of different events which complicate the copolymerization process. First, butadiene is present as 1,2 and trans-1,4 units; therefore, the system is actually ternary. Consequently, six reactivity ratios are necessary to describe the propagation reactions. There are also other factors involved in the mechanistic complications observed. In particular, there is a very large difference in reactivity between isobutylene and butadiene. Such a situation has been shown by Kennedy et al.[12] to give rise to meaningless reactivity ratio values when the classical two-parameter copolymerization equation is used. Furthermore, it is very likely that the reactivity ratios change with the feed composition during the course of copolymerization in agreement with the fact that the reactivity of butadiene depends on the solvent polarity.[5]

Concerning the cyclized structures, it is well known that they are present in the cationic homopolymerization[20] of conjugated dienes. For I–B copolymers, it has been reported previously (cf. Experimental Section) that significant amounts of these structures can be ruled out on the basis of spectroscopic analysis, at least in the composition range investigated.[21]

It must be noted that the presence of cyclized units will cause a decrease of the homopolymeric triad fraction and strengthen our conclusion concerning the block distribution of the monomeric units. The presence of butadiene block sequences in cationic I–B copolymer despite its low reactivity may be explained by a preferred solvation exerted by the diene on the propagating species when it is in the form of the allylic cation. Preferential solvation phenomena have often been invoked in cationic copolymerization systems.[10]

From the spectroscopic point of view, particular note should be taken of the difference in the contribution to the methylene chemical shift by a *gem*-dimethyl group situated in the δ position beyond a β substitution with respect to a simple δ contribution. Such a difference may be attributed to conformational effects.

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Quantum-Chemical Study of the Reactivity in Anionic Polymerization. 1. The Effect of the Polarity of Medium and Alkali Metal Cations on the Rate of Propagation Reaction

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ABSTRACT: The effect of counterion and solvent polarity on the activation energy of the propagation reaction of styrene anionic polymerization has been studied by a semiempirical quantum-chemical method. The structures of ion pairs of the polymer anion with cation and of the activated complex have been estimated. The effects of solvent polarity and of various counterions on these structures have been investigated and changes in activation energies evaluated. The theoretical properties found are in qualitative agreement with the experimental data available.

Much attention has recently been devoted to processes taking place during anionic polymerization.[1-5] Research carried out in this field led to the conclusion that the reactivity (either in initiation or in propagation reactions) is markedly affected by ion-pair formation between reacting anions and present cations. During the propagation reaction, a living polymer anion may form ion pairs with the present cations, usually alkali metal cations. Ion pairs compared with free living anions show different reactivity with respect to monomer. This has been confirmed by observations that the rate of the propagation reaction of styrene polymerization is influenced by the quality of counterion and solvent polarity (see review by Szwarc[3]). However, the detailed structure of the individual species is not known. The purpose of this paper is to study the above-mentioned effects, i.e., the effect of the quality of counterion and the effect of solvent polarity, on the activation energy of the propagation reaction from the theoretical point of view. The semiempirical quantum-chemical calculations of model structures in the propagation reaction of styrene show the possibilities of applying the theoretical methods aiming at acquiring further knowledge on the mechanism of the propagation reaction of ionic polymerization.

Calculations

In the quantum-chemical study of the propagation reaction of anionic polymerization two problems have to be overcome: (i) choosing the proper quantum-chemical method able to well define the ion-pair formation between anion and alkali metal cation and the solvent effect; and (ii) choosing a simple model of the initial state and activated complex because the polystyrene anion reacting with the monomer of styrene in the presence of cations in polar medium represents a very complicated system in view of the quantum-chemical calculation.

As to the first problem, in calculations of the systems similar to those considered here, current all-valence methods fail.[6,7] The Pariser–Parr–Pople method in π approximation has recently been modified by us;[8] the method enables consideration of alkali metals. Since the method was successfully applied to the study of ion pairs between radical anions and cations,[9] we have used it also in the present paper. All details concerning this method have been described previously.[8,9]

A simplified model system was chosen (Figure 1) to evaluate theoretically the effect of counterion and solvent in the propagation of anionic polymerization. The activated complex was considered as a symmetrical system, where $r_{C_1-C_2} = r_{C_2-C_3} = 1.53 \times 10^{-10}$ m and the position of the cation Me$^+$ varied according to the axis of symmetry in the plane of complex corresponding to the model proposed by Szwarc.[1] We did not take account of the activated complex proposed by Szwarc later[3] since the energy of the asymmetrical complex was higher than that of the symmetrical one. Calculations centered mainly on evaluating the interaction of alkali metal. Therefore in the structures shown in Figure 1 we changed the position of cations in the directions outlined and looked for the energetically most stable structure. The distance r_{Me} varied between 1.5×10^{-10} and 6.5×10^{-10} m.

The stability of the individual structures is influenced not only by the electronic structure itself but also by the solvation energy. Regarding the charged systems under study the decisive solute–solvent interaction will likely be of electrostatic character. This part of the solvation energy can be expressed by the relation,[10]

$$E_{\text{solv}} = -\tfrac{1}{2}\sum_{\mu}\sum_{\nu} Q_{\mu} Q_{\nu} \gamma_{\mu\nu}\left(1 - \frac{1}{\epsilon}\right) \qquad (1)$$

where Q_μ and Q_ν are the net charges on the atoms μ and ν of solute molecule, calculated by quantum-chemical method, $\gamma_{\mu\nu}$ is the electron-repulsion integral, and ϵ is the dielectric constant of the medium.

By adding E_{solv} to the total energy of the system of ion pair or activated complex, we obtain the summary energy describing the energetic state of the system in solvent.

Results and Discussion

Figure 2a shows the results of calculations of the total energy for ion pair (initial state) without solvation energy as a function of r_{Me} and Figure 3a shows the results for the activated complex.

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