(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 ^{1}H 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 ^{1}H 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. ^{1}H 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 ^{1}H NMR measurements.

Results and Discussion

^{1}H NMR Analysis. It is known that P copolymerizes with I by entering the chains mainly as the trans-1,4 unit.[3] ^{1}H 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 ^{1}H 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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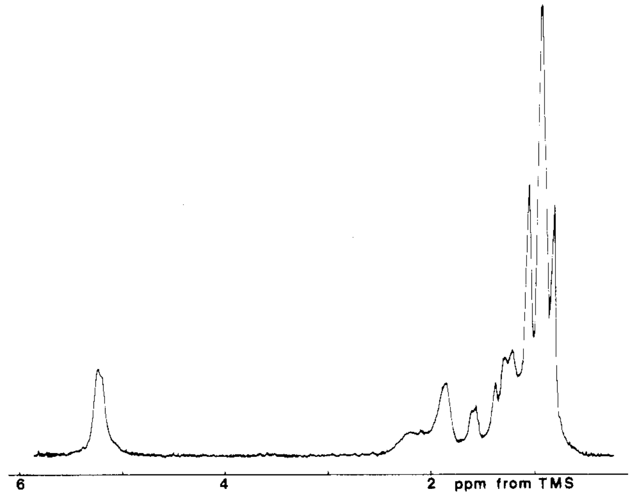


Figure 1. ^1H NMR spectrum of the I–P copolymer.

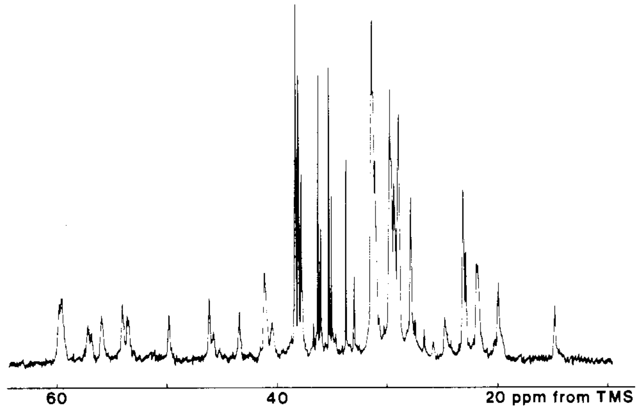


Figure 2. ^{13}C NMR spectrum of the hydrogenated I–P copolymer.

the evaluation of the triad data. In practice, ^1H NMR spectra are not useful in determining the monomer distribution.

The main signals of Figure 1, besides those discussed above, occur at ca. 1.4 (methylene of isobutylene), 2 (saturated and unsaturated protons of P), and 1.62 (weak doublet) ppm. The last signal, assigned to the methyl of P enchained as the 1.2 unit, suggests the presence of a small amount of this structural unit. Detailed information on the monomer distribution can be obtained from ^{13}C NMR spectra.

^{13}C NMR Analysis. Before we describe the ^{13}C NMR spectra of the I–P copolymers we emphasize that the spectrum of hydrogenated I–P copolymer is coincident with that of the corresponding hydrogenated isobutylene–isoprene (I_B–I_P) copolymer (apart from possible differences in the monomer distribution) when a regular trans-1,4 enchainment (i.e., head-to-tail) of the diene unit is assumed.

^{13}C NMR Spectra of the Hydrogenated I–P Cationic Copolymer. Figure 2 shows the ^{13}C NMR spectrum of the hydrogenated I–P copolymer containing 37 mol % P and dissolved in $CDCl_3$. Almost all the signals present in the spectrum of Figure 2 were previously discussed[2] when the hydrogenated I_B–I_P copolymer was investigated. Only the peak at 14.66 ppm, due to the hydrogenated 1,2 unit of P, is present besides those observed previously. Just this peak of the 1,2 unit is clearly evident because it occurs in a region completely free from other signals. Furthermore, since the methyl is the carbon atom most distant from the main chain, its signal is less influenced by the environment in which the structural unit is situated. Therefore, the signal is not split into several peaks under the influence of the possible sequences. The amount of 1,2 unit is about 15% of all P present in the copolymer. Apart from the signal discussed above, the ^{13}C NMR spectra of the hydrogenated I–P and I_B–I_P copolymers are essentially coincident. This situation confirms the regular 1,4 enchainment of the two dienes and the absence of inverse 4,1 addition of the P unit. The assignments of the spectrum have already been reported.[2] We said during the discussion of I_B–I_P copolymers that some signals of the spectra obtained from 1,2,4-trichlorobenzene solutions at 120 °C show fine structure due to long-range effects of the *gem*-dimethyl group of I_B. For I–P copolymers (see Figure 3) the region of the spectrum relative to the resonance of the isobutylene methylenes in the dyad II shows the tetrad signals split into other peaks assignable to hexads. In practice, it can be said that the *gem*-dimethyl group gives rise to a ζ effect on the chemical shifts of the methylene groups. However, such an effect is evident only when the *gem*-dimethyl group is beyond the analogous group in the β and δ positions. Conversely, if the *gem*-dimethyl group is in the ζ position with respect to a methylene from which is separated by a chain segment not containing *gem*-dimethyl groups, then the effect is negligible. In fact, the signal due to CH_2 of I in the tetrad IPIP is coincident with that of the tetrad PPIP, despite the presence, in the former case, of a *gem*-dimethyl group in the ζ position.

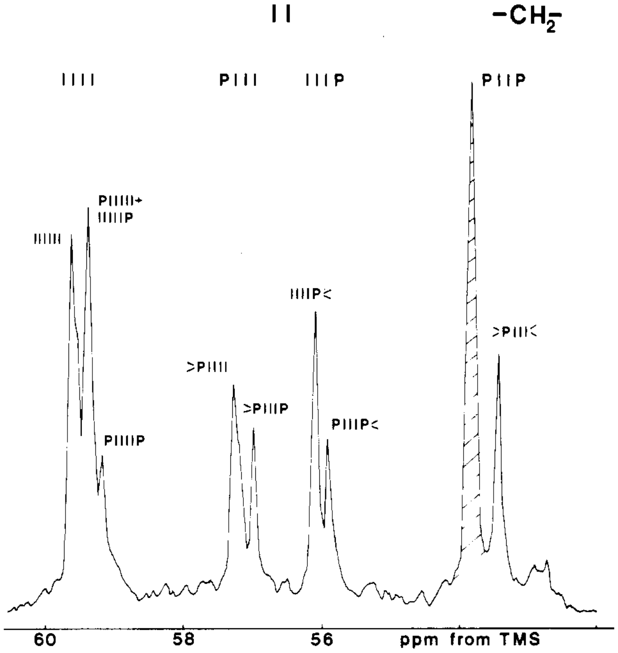


Figure 3. Hexad signals in the hydrogenated I–P copolymer.

A unique case of a long-range effect operating in chain segments uncrowded by *gem*-dimethyl groups will be discussed later. Therefore, the spectrum of the hydrogenated I–P copolymers sheds light on the type of enchainment of the monomers and, furthermore, gives information on the monomer distribution. The latter point allows more complete information to be obtained from the spectra of the original copolymers because data concerning the hexads and the percentage of all the pentads centered on both I and P can be derived.

^{13}C NMR Spectra of the Original I–P Cationic Copolymer. Figure 4A shows the olefinic region and Figures 4B and 4C show two parts of the aliphatic region of the spectrum of the original I–P copolymer. 1,2,4-Trichlorobenzene (at 120 °C) was used as solvent for the spectra of Figure 4B,C in order to obtain the best resolution of the

Table I
^{13}C NMR Chemical Shifts (ppm) for the Aliphatic Region of the I-P Copolymer

atom	sequence[a]	no. of peak	substitution[b]	chem shift exptl	chem shift calcd
CH_2(I)	IIIIII	13	$2\beta_G + 2\delta_{\beta G} + 2\zeta_G$	59.57	59.80
	IIIIIP PIIIII	14	$2\beta_G + 2\delta_{\beta G} + \zeta_G$	59.36	59.54
	PIIIIP	15	$2\beta_G + 2\delta_{\beta G}$	59.25	59.28
	>PIIII	16	$2\beta_G + \delta_{\beta G} + \delta_{\beta M} + \zeta_G$	56.89	57.02
	>PIIIP	17	$2\beta_G + \delta_{\beta G} + \delta_{\beta M}$	56.60	56.76
	IIIIP<	18	$2\beta_G + \delta_{\beta G} + \zeta_G$	56.10	56.26
	PIIIP<	19	$2\beta_G + \delta_{\beta G}$	55.90	56.00
	>PIIP<	20	$2\beta_G + \delta_{\beta M}$	53.44	53.48
	≷>PIII	21	$\beta_G + \beta_M + \delta_{\beta G} + \zeta_G$	53.17	52.69
	≷>PIIP	22	$\beta_G + \beta_M + \delta_{\beta G}$	52.72	52.43
	≷>PIP<	23	$\beta_G + \beta_M$	49.42	49.15
CH_2(P)	IIIP≶	24	$\beta_G + \delta_{\beta G} + \zeta_G + \alpha_t$	48.86	49.21
	PIIP≶	25	$\beta_G + \delta_{\beta G} + \alpha_t$	48.53	48.95
	>PIP≶	26	$\beta_G + \alpha_t + \delta_{\beta M}$	45.98	45.67
	>PP<	27	$\beta_M + \alpha_t$	40.28	41.34
C	IIIII	28	$2\gamma_{4G} + 2\epsilon_G$	38.03	37.87
	PIIII + IIIIP	29	$2\gamma_{4G} + \epsilon_G$	37.74	47.62
	PIIIP	30	$2\gamma_{4G}$	37.44	37.37
	>PIII	32	$\gamma_{4G} + \gamma_{4M} + \epsilon_G$	35.95	36.12
	>PIIP	33	$\gamma_{4G} + \gamma_{4M}$	35.70	35.87
	IIIPI	34	$\gamma_{4G} + \epsilon_G + \eta_G$	35.55	35.68
	IIIPP + PIIPI	35	$\gamma_{4G} + \epsilon_G$ (or η_G)	35.31	35.44
	PIIPP	36	γ_{4G}	35.10	35.19
	>PIPI	37	$\gamma_{4M} + \eta_G$	34.06	33.94
	>PIPP	38	γ_{4M}	33.91	33.69
CH	PP	31		36.89	
	IP	39		33.36	
CH_3(I)	IIIII	40	$2\delta_G + 2\zeta_G$	31.03	30.98
	PIIII + IIIIP	41	$2\delta_G + \zeta_G$	30.83	30.78
	PIIIP	42	$2\delta_G$	30.63	30.58
	>PIII	43	$\delta_G + \delta_M + \zeta_M$	29.63	29.53
	>PIIP	44	$\delta_G + \delta_M$	29.37	29.33
	IIIP<	45	$\delta_G + \zeta_G$	29.01	29.21
	PIIP<	46	δ_G	28.86	29.01
	PIP	47, 48	δ_M	27.64–27.44	27.76
CH_3(P)	PI	49	δ_G	24.33	
	PI	50	δ_G	24.12	
	PP	51		20.04	
CH_3(1,2-P)		52		17.55	

[a] The indication < means that either a P or an I unit can follow the last unit. [b] The indexes G and M refer to the *gem*-dimethyl group and to the methyl group, respectively. For the other indexes, cf. text.

signals, whereas a $CDCl_3$ solution was used for Figure 4A because of interference from the aromatic solvent.

We discuss separately the assignments of the peaks in the aliphatic and olefinic regions of the spectrum.

Aliphatic Region. ^{13}C assignments are reported in Table I. The experimental chemical shifts are compared with the values calculated on the basis of additivity rules by considering the substituent effects listed in the fourth column of Table I.

As reported previously,[2] the index G refers to the *gem*-dimethyl group, the index M refers to the methyl group, the index 4 denotes that the substitution involves a quaternary carbon, α_t is the effect of a trans double bond, and δ_β denotes a substitution in the δ position after a *gem*-dimethyl substitution in the β position.

By means of a least-squares analysis we obtained the following set of parameter values (in ppm): (1) methylene carbon, $\beta_G = 11.41$, $\delta_{\beta G} = 3.28$, $\zeta_G = 0.26$, $\delta_{\beta M} = 0.76$, $\beta_M = 7.84$, $\alpha_t = 3.60$; (2) quaternary carbon, $\alpha_G = 3.11$, $\gamma_{4G} = 2.18$, $\epsilon_G = 0.25$, $\eta_G = 0.24$, $\gamma_{4M} = 0.68$; (3) methyl carbon, $\delta_G = 1.65$, $\zeta_G = 0.20$, $\delta_M = 0.41$. The base frequencies are 29.9 ppm (the resonance of the polyethylene) for the main-chain carbon atoms and 27.3 ppm (the resonance of an isolated *gem*-dimethyl group in a polyethylene chain)[1] for the methyls. The obtained values are in agreement with those found in I_B–I_P copolymers[2] and they are used to obtain the calculated chemical shifts reported in Table I. The assignments of the methylenes, and in particular peaks 23 and 24, whose calculated values are inverted with respect to the experimental chemical shifts, were confirmed by selective decoupling experiments which allowed the signals of the methylene of P, which is in an α position relative to the double bond, and the signal of the methylene of I to be distinguished.

The region of the quaternary carbons (39–33 ppm) shows some anomalies. The hypothesis adopted for the assignment of the peaks in all the spectra of isobutylene–diene copolymers so far studied is that no contribution arises from the substituents situated beyond the monomeric units having four carbon atoms in the chain. In the case of the pentads centered on the triad IIP the situation is different and three peaks are observed. Their relative intensity depends on the copolymer composition in a way quite analogous to the variation of the three peaks due to the pentads centered on the triad III. Consequently, the peak downfield (35.55 ppm) is assigned to the pentad having two I units at the extremities, the central peak (35.31 ppm) to the two pentads having one I unit and one P unit at the

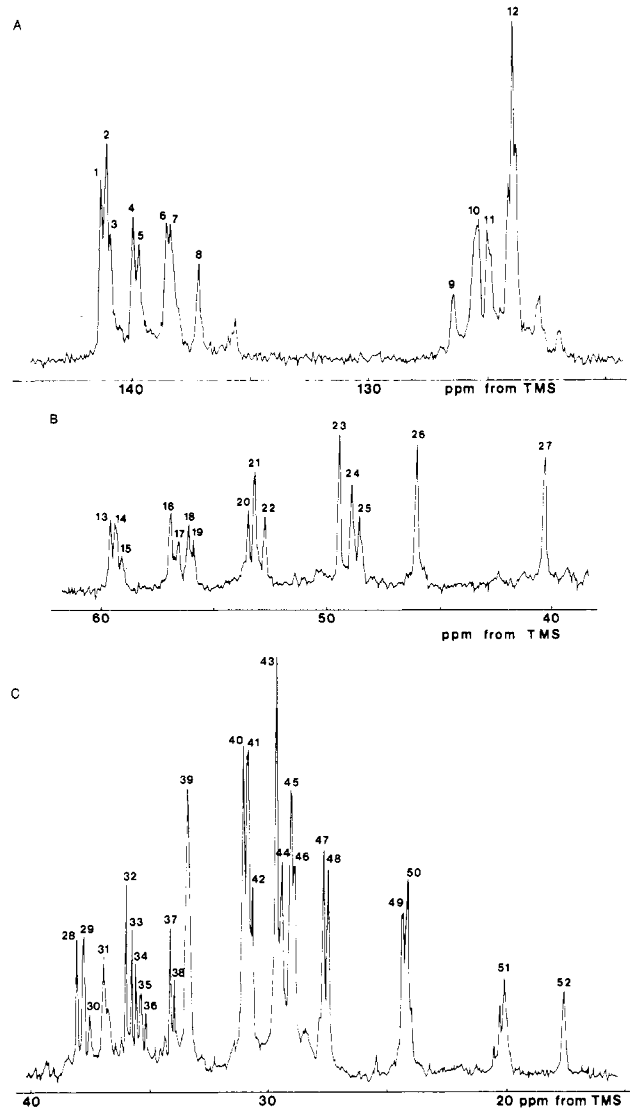
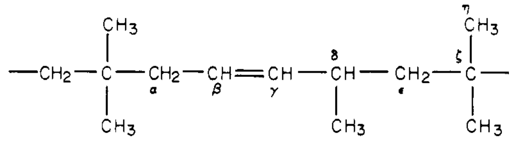


Figure 4. ^{13}C NMR spectrum of the I–P copolymer: (A) olefinic region; (B) methylene region; (C) region for other carbons.

extremities, and the peak upfield (35.10 ppm) to the pentad containing two P units at the extremities. That means that a positive η effect is exerted on the quaternary carbon of I by the *gem*-dimethyl group situated beyond one P unit in sequence A, in which the double bond is in the β position and the isolated methyl is linked at the δ position. Conversely, the η effect becomes negligible either in the opposite sequence, i.e., when the methyl is in the β position and the double bond is in the γ position or when the inserted monomer unit is isoprene or hydrogenated P.


$$-CH_2-C(CH_3)_2-\underset{\alpha}{CH_2}-\underset{\beta}{CH}=\underset{\gamma}{CH}-\overset{\delta}{CH}(CH_3)-\underset{\epsilon}{CH_2}-\overset{\zeta}{C}(\overset{\eta}{CH_3})(CH_3)-$$

A

The assignments of the doublet at 34.06 and 33.91 ppm are a consequence of the previous discussion. It is worth noting that also the signal of methyls of I (Figure 4A) is influenced by the long-range effect due to the *gem*-dimethyl group. In fact, the signal of the methyls of the triad PIP is split into a doublet; this splitting vanishes when the hydrogenated I–P copolymer and the I_B–I_P copolymer are examined.

Olefinic Region. An inspection of the assignments of the unsaturated carbons listed in Table II shows that the signals of C_1 and C_2 belonging to homopolymeric sequences are the two most internal in the range considered. As expected on the basis of the signs of the additional contributions (γ and δ' are negative while γ', δ, and the long-range effects are positive), the signal of C_2 is shifted downfield and that of C_1 upfield when P is substituted by I. Fine structure (pentads) is evident for the four signals due to the triads of carbon C_2, but analogous fine structure is not present in the four peaks of carbon C_1. It can be said that ϵ' and ζ effects are not equal to zero, while ϵ and ζ' effects are practically negligible. For the assignments of the triads IPP and PPI we have considered $\gamma'_G > \gamma'_M + \delta_G$ and $|\gamma_G| > |\delta_G + \gamma_M|$ for both C_1 and C_2, in agreement with previous findings concerning γ'_G and γ_G.[4] However, the exchange of signals of the two triads is without consequence on the calculation of the sequence fractions because their intensity is equal. Two weak peaks, at 135.84 and 123.16 ppm, are due to the *trans*-1,2-P unit.

Table II
^{13}C NMR Chemical Shifts (ppm) for the Olefinic Region of the I-P Copolymer

atom	sequence	no. of peak	substitution	chem shift
C_2	IIPII	1	$\gamma_G' + \delta_G + \epsilon_G' + \zeta_G$	141.45
	PIPII + IIPIP	2	$\gamma_G' + \delta_G + \epsilon_G'$, $\gamma_G' + \delta_G + \zeta_G$	141.24
	PIPIP	3	$\gamma_G' + \delta_G$	141.06
	IIPP<	4	$\gamma_G' + \epsilon_G'$	140.10
	PIPP<	5	γ_G'	139.86
	>PPII	6	$\delta_G + \gamma_M' + \zeta_G$	138.68
	>PPIP	7	$\delta_G + \gamma_M'$	138.52
	>PPP<	8	γ_M'	137.34
C_1	IPI	12	$\gamma_G + \delta_G'$	124.15
	IPP	11	γ_G	125.12
	PPI	10	$\delta_G' + \gamma_M$	125.60
	PPP	9	γ_M	126.58

In conclusion, the analysis of the spectrum has shown the *gem*-dimethyl group to produce long-range effects on the chemical shift of carbon atoms situated several linkages distant from it. Consequently, our 25.14-MHz instrument can detect signals of hexads. These effects are observed, however, only when homopolymeric sequences of I are present, i.e., in chains crowded by methyl groups. Very likely, these long-range effects are indirect, as suggested by previous studies on stereospecific polypropylene,[5] since they would not originate from real contributions arising from very distant groups but from variations of the value of closer contributions (e.g., β, γ, δ) when sterically hindered structures are taken into account. The long-range effects would have a conformation origin according to this hypothesis.

Quantitative Analysis. According to the discussion reported in the previous sections, ^{13}C NMR spectra allow calculation of the values of the sequence fractions up to the hexad level. Tables III and IV show the values obtained for two I–P copolymers having different compositions. The experimental results are compared with values calculated for a random distribution of both monomers.

The values listed in Tables III and IV were reckoned by using almost all the signals of the spectrum. In fact, the peaks of the methyls of the *gem*-dimethyl groups were employed for determining the triad fractions centered on I, while the fractions of the corresponding pentads were obtained from the peaks of the quaternary carbons. The triad fractions centered on P were calculated from the signals of carbons C_1 and the corresponding pentads from the signals of carbon C_2. Finally, the tetrad and hexad fractions were obtained from the signals of methylenes.

Table III
Sequence Fractions in the I-P Copolymer[a]

triads			pentads			tetrads			hexads		
	exptl	calcd		exptl	calcd		exptl	calcd		exptl	calcd
III	0.353	0.397	IIIII	0.118	0.157	IIII	0.132	0.157	IIIIII	0.043	0.062
			IIIIP + PIIII	0.180	0.186				PIIIII + IIIIIP	0.063	0.073
			PIIIP	0.068	0.054				PIIIIP	0.026	0.022
PII	0.264	0.233	>PIII	0.168	0.147	PIII	0.100	0.093	>PIIII	0.063	0.058
			>PIIP	0.100	0.086				>PIIIP	0.037	0.035
IIP	0.209	0.233	IIIPI	0.078	0.093	IIIP	0.087	0.093	IIIIP<	0.060	0.058
			IIIPP + PIIPI	0.101	0.108				PIIIP<	0.027	0.035
			PIIPP	0.031	0.032	PIIP	0.058	0.054	>PIIP<	0.058	0.054
						>PII	0.154	0.147	≥>PIII	0.100	0.093
PIP	0.174	0.137	>PIP<	0.156	0.137				≥>PIIP	0.054	0.054
IPI	0.439	0.397	IIPII	0.110	0.157	>PIP	0.103	0.086	≥>PIP<	0.103	0.086
	0.43		PIPII + IIPIP	0.176	0.186						
			PIPIP	0.096	0.054	IIP<	0.139	0.147	IIIP<≤	0.084	0.093
									PIIP<≤	0.055	0.054
IPP	0.235	0.233	IIPP<	0.125	0.147	PIP<	0.120	0.086	>PIP<≤	0.120	0.086
			PIPP<	0.133	0.086						
PPI	0.225	0.233	>PPII	0.139	0.147						
			>PPIP	0.138	0.086	>PP<	0.107	0.137	≥>PP<≤	0.107	0.137
PPP	0.101	0.137	>PPP<	0.083	0.137						

[a] Copolymer composition 63:37 I/P.

Table IV
Sequence Fractions in the I-P Copolymer[a]

triads			pentads			tetrads			hexads		
	exptl	calcd		exptl	calcd		exptl	calcd		exptl	calcd
III	0.186	0.260	IIIII	0.016	0.067	IIII	0.048	0.067	IIIIII	0.012	0.017
			IIIIP + PIIII	0.102	0.130				PIIIII + IIIIIP	0.027	0.034
			PIIIP	0.075	0.063				PIIIIP	0.009	0.016
PII	0.262	0.250	>PIII	0.114	0.127	PIII	0.067	0.065	>PIIII	0.034	0.033
			>PIIP	0.114	0.123				>PIIIP	0.033	0.032
IIP	0.236	0.250	IIIPI	0.062	0.065	IIIP	0.052	0.065	IIIIP<	0.029	0.033
			IIIPP + PIIPI	0.115	0.125				PIIIP<	0.023	0.032
			PIIPP	0.075	0.060	PIIP	0.053	0.063	>PIIP<	0.053	0.063
									≥>PIII	0.076	0.650
PIP	0.316	0.240	>PIP<	0.297	0.240	>PII	0.131	0.127	≥>PIIP	0.055	0.062
IPI	0.346	0.260	IIPII	0.063	0.067	>PIP	0.134	0.123	≥>PIP<	0.134	0.123
			PIPII + IIPIP	0.151	0.130						
			PIPIP	0.084	0.063	IIP<	0.132	0.127	IIIP<≤	0.058	0.065
									PIIP<≤	0.074	0.062
IPP	0.265	0.250	IIPP<	0.119	0.127	PIP<	0.184	0.123	>PIP<≤	0.184	0.123
			PIPP<	0.144	0.123						
PPI	0.240	0.250	>PPII	0.126	0.127	>PP<	0.199	0.240	≥>PP<≤	0.199	0.240
			>PPIP	0.190	0.123						
PPP	0.149	0.240	>PPP<								

[a] Copolymer composition 51:49 I/P.

As reported in the Experimental Part, the experimental FT conditions ensure a complete relaxation of all the carbon atoms, while no special precaution was made with respect to the NOE. However, each set of values of sequence fractions was obtained by measuring peaks of the same type of carbon atoms. Furthermore, the sequences fractions were deduced from the signals of all the carbon atoms considered. These two facts ensure a sound quantitative analysis.

The analysis of the results obtained and the comparison of the experimental and calculated values show that the cationic I-P copolymer displays a slight deviation from the random structure and a small, constant tendency toward the alternating distribution of the monomers. In fact, the calculated values for the fractions of all the homopolymeric sequences are consistently higher than the experimental values and, correspondingly, higher values of the experimental data for sequences containing an alternation of the monomers are observed.

Conclusions

The study of the structure of I-P copolymers by ^{13}C NMR spectroscopy allows identification of monomer sequences up to the level of hexad. The unusual long-range effect of the *gem*-dimethyl group is probably related to the peculiar structure of the homopolymeric sequences of isobutylene which are crowded by methyl groups. The evaluation of the sequence fractions clearly shows a distribution of the monomeric units which deviates slightly from the randomness toward the alternation.

References and Notes

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