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Optically Active Hydrocarbon Polymers with Aromatic Side Chains. 13. Structural Analysis of (*S*)-4-Methyl-1-hexene/Styrene Copolymers by ^{13}C NMR Spectroscopy

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ABSTRACT: The microstructure of copolymers of styrene with (*S*)-4-methyl-1-hexene, obtained in the presence of a Ziegler–Natta catalyst, has been investigated by ^{13}C NMR. Due to the heterogeneity of these materials, the investigation has been extended to copolymer fractions obtained by extraction with boiling solvents. The results obtained confirm a high degree of isotacticity for polymer fractions soluble in diethyl ether, cyclohexane, and chloroform. Computer analysis of the experimental spectra unequivocally demonstrates that these copolymer fractions are constituted by macromolecules containing long sequences of either one monomer linked through isolated units derived from the other comonomer. By contrast, fractions soluble in ethyl acetate are characterized by a quasi-random distribution of monomeric units and a lower tacticity degree. Implications for the polymerization mechanism have also been discussed.

Introduction

Since the first report in 1955 on the Ziegler–Natta catalyzed stereospecific polymerization of α-olefins,[1] an incredibly large number of papers have appeared dealing with catalyst structure and stereoregulation mechanism.[2-5] Most of the early controversies have been settled, even though a really complete understanding of the complex phenomena involved has not yet been reached.

Extensive studies of the chiroptical properties of stereoregular copolymers of α-olefins, particularly with styrene, have been very useful both for investigations on the stereochemistry of Ziegler–Natta polymerization and for studies on the conformations of macromolecules in solution.[6,7] The continuous refinement of techniques capable of giving information on the microstructure of macromolecules, however, has prompted a careful reinvestigation of the copolymerization of styrene (St) with (*S*)-4-methyl-1-hexene (4MH), carried out in the presence of a Ziegler–Natta catalyst based on $TiCl_4/Al(i\text{-}C_4H_9)_3$.

The mechanistic implications connected with the nonrandom distribution of monomeric units along the copolymer backbone, suggested by recent studies on chemical and spectroscopic properties of these copolymers,[8] made it necessary to gain a deeper insight concerning their molecular structure.

In the present paper we report the results obtained in an investigation of St/4MH copolymers by ^{13}C NMR, a technique that has proved to be the best suited to give quantitative information about polymer microstructure.[9]

Experimental Section

Copolymerization of styrene (St) with (*S*)-4-methyl-1-hexene (4MH) having $[\alpha]^{25}_D$ −2.82°, and optical purity 93.5%[10] was carried out in the presence of $TiCl_4/Al(i\text{-}C_4H_9)_3$ as previously reported. Copolymer samples were fractionated with boiling solvents in Kumagawa extractors,[1] using acetone, ethyl acetate, diethyl ether, cyclohexane, and chloroform in that order.[8] Data relevant to copolymerization experiments and to copolymer fractionation are summarized in Tables I and II, respectively.

^{13}C NMR spectra of polymer solutions in $CDCl_3$ were recorded at 50.28 MHz on a Bruker WP-200 spectrometer. The central peak of the $CDCl_3$ triplet (77.02 ppm from Me_4Si) was used as the standard. A 60° pulse was applied with a spectral width of 10 000 Hz and a relaxation delay of 3.0 s. Data were stored on a 32K memory. Typically the number of scans was 16 000.

The integrated intensities of overlapping resonances were evaluated by fitting the experimental pattern by computer simulation using the minimum number of Lorentzian-shaped lines, changing the chemical shifts, line widths, and integrated intensities as adjustable parameters. The Fortran program used was written for a Hewlett-Packard HP 21MX minicomputer equipped with a HP 721A digital plotter and is available on request. Decon-

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Table I
Copolymerization of Styrene (1) with (S)-4-Methyl-1-hexene (2) in the Presence of the Catalytic System Based on $TiCl_4/Al(i\text{-}C_4H_9)_3$

	polymerization conditions[a]			polymeric product		
run	styrene, mmol	molar ratio 1/2	conv,[b] %	monomeric[c] units from 1, mol %	$[\alpha]^{25}_D$,[d] deg	$[\eta]$,[e] dL/g
C1	34.7	9.00	11.6	87.2	+19	1.9
C2	108.0	3.00	17.8	68.7	+85	3.0
C3	74.3	1.00	22.8	41.4	+138	4.3
C4	75.0	0.30	31.7	15.4	+195	7.2
C5	4.1	0.11	63.2	8.8	+221	7.1

[a] At room temperature in *n*-heptane, molar ratio comonomers/$Al(i\text{-}C_4H_9)_3$ = 9.1 and Al/Ti = 3.3; [1] + [2] = 1.5 mol L^{-1}. [b] Evaluated as (weight of polymer/weight of comonomers) × 100. [c] Evaluated by ^1H NMR and UV spectroscopy. [d] In chloroform. [e] In tetrahydronaphthalene at 120 °C.

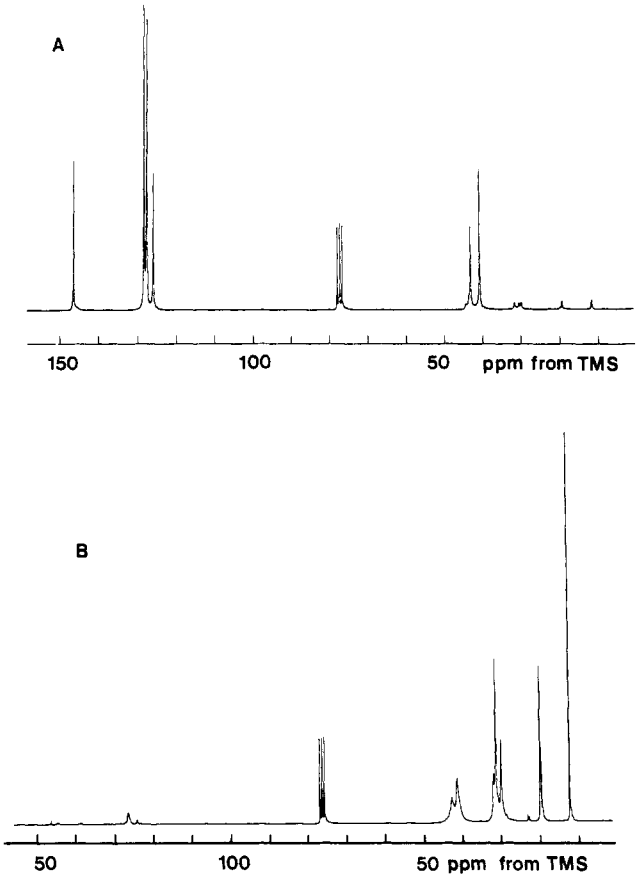

Figure 1. ^{13}C NMR spectra of copolymers of styrene with (S)-4-methyl-1-hexene: (A) fraction extracted in chloroform; (B) fraction extracted in cyclohexane.

volution data relevant to the different fractions of sample C3 are reported in Table III.

Results and Discussion

Copolymers of (S)-4-methyl-1-hexene and styrene, prepared in the presence of a $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst, were fractionated with boiling solvents into five fractions, soluble respectively in acetone, ethyl acetate, diethyl ether, cyclohexane, and chloroform.[8] Due to their negligible amounts, acetone extracts were not investigated further.

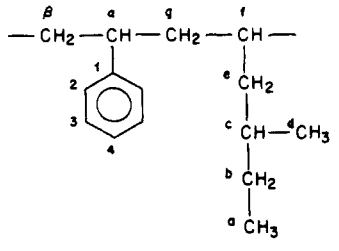

Table II
Styrene Content[a] (mol %) of Different Fractions of Copolymers of Styrene (St) with (S)-4-Methyl-1-hexene

	fraction[b]				
sample	I	II	III	IV	V
C1	91	52			96
C2	81	49	5	3	96
C3	72	39	3	1	95
C4	41	28	4	2	
C5		22	3	2	

[a] Determined by ^1H NMR. [b] Extracted with acetone (I), ethyl acetate (II), diethyl ether (III), cyclohexane (IV), and chloroform (V), respectively.

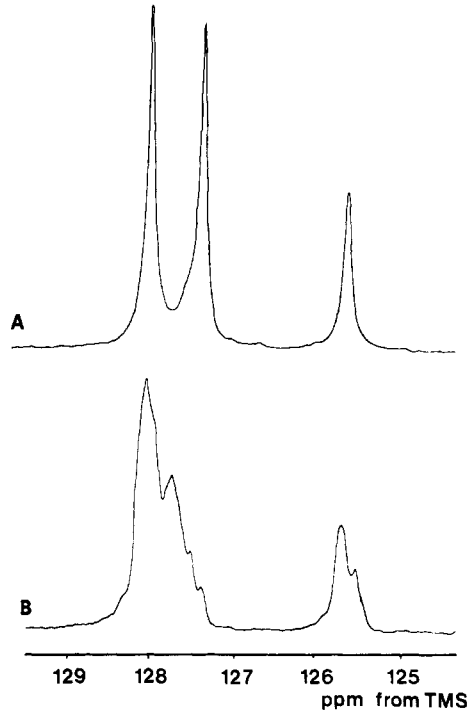

Figure 2. ^{13}C NMR spectrum in the region of ortho, meta, and para aromatic arbon atoms: (A) fraction of poly(St-*co*-4MH) extracted in chloroform; (B) atactic polystyrene.

^{13}C NMR spectra of crude copolymer samples exhibit, in addition to the signals expected for the corresponding isotactic homopolymer mixtures[11-13] (Table IV), a series of new resonances that can be tentatively attributed to junctions between 4MH and St monomeric units. In order to clarify this point, the spectra of fractions soluble in chloroform and in cyclohexane (Figure 1), mainly constituted by St and 4MH units respectively (Table I), have been investigated in some detail.

In styrene-rich fractions only the peaks at 127.5 and 128.2 ppm are present (Figure 2A), whereas extra reso-

Table III
Fitting of the Resonances of the ^{13}C NMR Spectra of Different Fractions of a Styrene/(*S*)-4-Methyl-1-hexene Copolymer Sample[a] (Run C3)

ethyl acetate			diethyl ether			cyclohexane			chloroform		
δ	LW	I	δ	LW	I	δ	LW	I	δ	LW	I
127.53	9	65	127.68	15	41	127.68	15	1	127.53	7	357
127.68	15	130	127.82	20	82	127.82	15	81	127.64	25	267
127.82	15	100	127.94	20	55	127.94	15	113	128.82	7	375
127.94	15	80	128.14	30	822	128.14	30	806			
128.14	30	500				128.22	9	1			
128.22	9	120									
29.55	15	10	29.55	15	20	29.55	15	20	29.47	12	175
29.73	15	65	29.73	15	170	29.73	15	199	29.59	8	75
29.87	30	150	29.87	25	140	29.87	25	81	29.87	30	158
30.43	30	70	30.43	25	10	30.43	25	12	30.17	10	145
30.51	30	70	30.63	25	40	30.63	25	36	30.35	30	75
30.63	30	110	31.05	12	360	31.05	12	364	31.06	35	175
31.05	20	180	31.42	15	10	31.42	15	4	31.27	15	202
31.42	15	10	31.64	25	100	31.64	25	61			
31.64	30	100	31.76	18	150	31.76	18	223			
31.76	25	240									
			18.82	30	57	18.82	28	68	19.02	12	518
	n.d.		19.43	20	943	19.43	20	932	19.16	18	150
									19.41	18	286
									19.64	18	45
			10.73	16	30	10.73	16	31	11.15	8	220
	n.d.		11.03	16	42	11.03	16	39	11.24	16	317
			11.39	10	928	11.39	9	930	11.39	16	462

[a] Chemical shifts are in ppm ±0.01 ppm; line widths (LW) are in Hz ±1 Hz; integrated intensities (I) are normalized to 1000 ± 5 by groups of resonances.

Table IV
Assignment of the Resonances in the ^{13}C NMR Spectra of Isotactic Polystyrene and Poly[(*S*)-4-methyl-1-hexene][11-13]

carbon	chem shift, ppm	carbon	chem shift, ppm
C_α	43.20	C_a	11.47
C_β	40.92	C_b	31.10
C_1	146.34	C_c	31.72
C_2	128.22	C_d	19.47
C_3	127.46	C_e	41.19
C_4	125.80	C_f	29.62
		C_g	42.70

nances appear between these two peaks on increasing the 4MH content. In samples containing more than 95% of 4MH units, only a broad composite signal is present in this spectral region (Figure 3A). The ^{13}C NMR spectrum of polystyrene exhibits in this same region only two resonances at 127.5 and 128.2 ppm in the case of isotactic samples, some extra signals being present in the case of atactic ones (Figure 2B). Therefore, the two resonances at 127.5 and 128.2 ppm can be assigned to styrene units inserted in isotactic St sequences and their relative intensity affords a quantitative measure of the content of isotactic styrene blocks in the copolymer. On the contrary, it is not possible to unequivocally assign the extra peaks, as they could arise both from triads of different composition, such as 4MH–St–4MH and 4MH–St–St, and from steric irregularities of the polymer backbone.

For all the copolymer samples the region around 40 ppm is of little diagnostic value, due to the severe overlap of the signals from both 4MH and St units (carbon atoms g, e, α, and β). Three more groups of signals are present at about 30, 20, and 10 ppm, and particularly in samples having a low 4MH content, many extra resonances are present, as compared with the spectrum of poly(4MH) (Figures 4 and 5). None of these extra signals can be attributed to carbon atoms α or β to a phenyl group because of the high value of the additive contribution for a phenyl group.[14] These signals have therefore been assigned

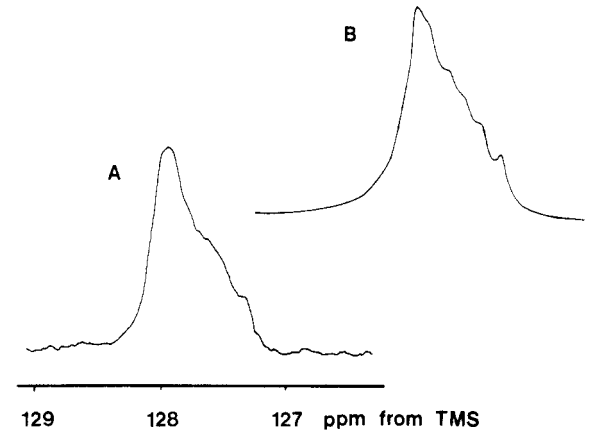

Figure 3. Experimental (A) and simulated (B) ^{13}C NMR spectrum in the region of ortho, meta, and para aromatic carbon atoms of the cyclohexane extract of poly(St-*co*-4MH).

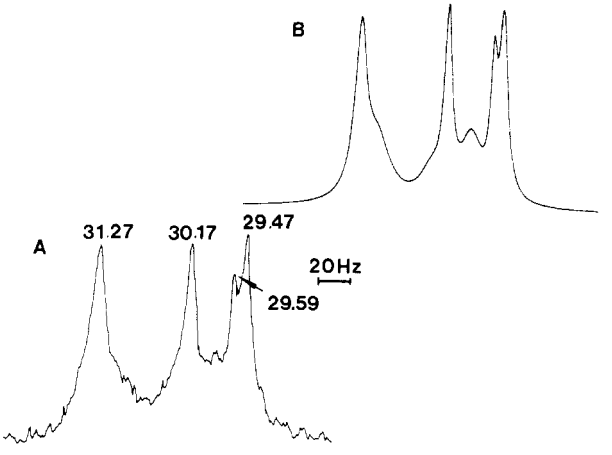

Figure 4. Experimental (A) and simulated (B) ^{13}C NMR spectrum in the 29–32 ppm region of the chloroform extract of poly(St-*co*-4MH).

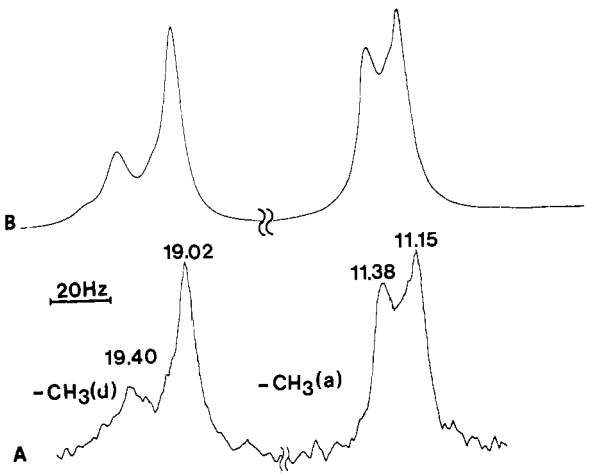

Figure 5. Experimental (A) and simulated (B) ^{13}C NMR spectrum in the methyl group region of the chloroform extract of poly(St-*co*-4MH).

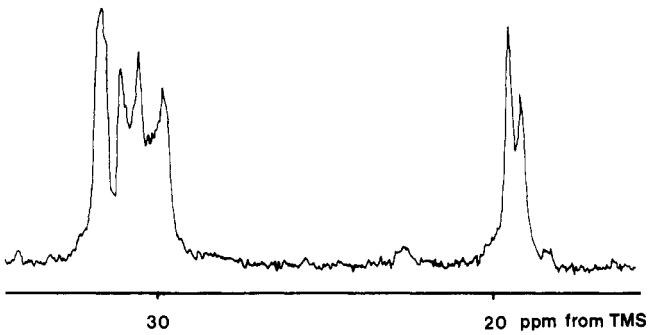

Figure 6. ^{13}C NMR spectrum in the 15–35 ppm region of the ethyl acetate extract of poly(St-*co*-4MH) (run C3).

to 4MH units next to St units (junctions) and/or to steric irregularities.

No signal is present in the region around 50 ppm where defects such as head-to-head linkages are expected to give resonances on the basis of the ^{13}C chemical shift additivity in vinyl polymers.[15]

As preliminarily reported above, most of the experimental spectra are constituted by strongly overlapping resonances and in order to make a quantitative evaluation of their individual components it was necessary to deconvolute them. In principle this can be done either without fixing the chemical shift values, i.e., leaving the fitting process open to find the "correct" chemical shifts, or by assuming "fixed" values of the possible chemical shifts, thus leaving the fitting process free to evaluate the relative intensities and line widths. This last procedure was adopted, since some of the peaks had quite clear and invariant chemical shifts. Data relevant to the deconvolution of spectra of the different fractions of sample C3 are reported in Table III. Similar results were obtained for the other copolymer samples, apart from obvious variations in the intensities of the individual components for fractions soluble in ethyl acetate in which the chemical composition changes in the different runs.

Fractions Extracted in Ethyl Acetate. The content of 4MH units increases from 49% to 86% by increasing the amount of 4MH in the polymerization feed. Correspondingly, in the ^{13}C NMR spectra the relative intensities of the peaks attributable to sequences of 4MH and St units respectively increase and decrease. However, the most pronounced feature of the spectra of these fractions is the large number of overlapping resonances (Figure 6). Even if it has not been possible to unequivocally assign all the

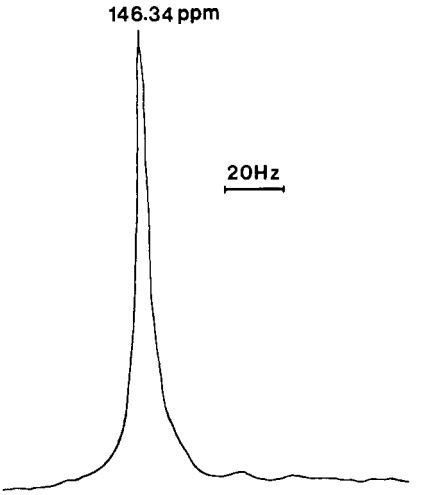

Figure 7. Quaternary aromatic ^{13}C resonance of the chloroform extract of poly(St-*co*-4MH).

lines present, it is, however, evident that a substantial number of St–4MH junctions is present, very likely accompanied by a rather low degree of isotacticity.

Fractions Extracted in Diethyl Ether and in Cyclohexane. No significant difference is observed either in the chemical composition or in the profile of ^{13}C NMR spectra of these two fractions. The St content in these fractions never exceeds 5% and their ^{13}C NMR spectra are almost identical with those of the corresponding fractions of isotactic poly(4MH).[11] This demonstrates that the fractions are characterized by long isotactic sequences of 4MH units, minor tacticity differences probably giving rise to different conformations in solution, analogous to what is observed for poly(4MH).[12]

In the aromatic region only a broad structured band constituted by 4–5 overlapping resonances is observed, whereas the peaks at 127.5 and 128.2 ppm, typical of isotactic St sequences, are completely missing (Figure 3). The presence of isotactic 4MH–St–4MH triads, that should give rise to only two resonances, cannot account for the observed multiplicity, and therefore we have to assume either that the insertion of a St unit between sequences of 4MH units occurs without steric control or that St–St–4MH triads are present in significant amounts. This last assumption, however, does not seem very likely on the basis of both chemical composition and spectroscopic properties of these extracts.[8]

Fractions Extracted in Chloroform. These fractions contain more than 95% of St units and the presence in their ^{13}C NMR spectra of only two intense bands at 127.5 and 128.2 ppm demonstrates that St units are present in long isotactic sequences. An analysis of the quaternary carbon atom resonance (Figure 7) shows that the isotacticity is very high (larger than 95%).

In the 29–32 ppm region, deconvolution of the experimental spectra shows that at least seven signals are present. Due to the very low content of 4MH units, it has not been possible to unequivocally assign these peaks by off-resonance experiments; however, an isotactic St–4MH–St triad is expected to give rise to only three resonances in this region. Therefore, the larger number of signals observed can be attributed either to sequences of the type 4MH–4MH–St, which is not very likely on the basis of chemical composition, or to St–4MH–St triads having different tacticity (steric defects). This last hypothesis is partially confirmed by the shape of the signals in the 18–20 and 10–12 ppm range, which are attributed to d and a carbon atoms, respectively (Figure 5). In fact,

the multiplicity of these peaks and the relative intensities of their components, even if they do not allow unequivocal assignments, strongly support the presence of sequences of St units linked to isolated 4MH units without any steric control. In particular, the intensity distribution of the signal relevant to the methyl d, that is known to be tacticity sensitive,[16] would imply the presence of either long syndiotactic sequences of 4MH units or 4MH units isolated between St sequences. By considering that long syndiotactic placements in the polymerization of 4MH by a Ziegler–Natta catalyst are very unlikely,[17] the second hypothesis appears to be more reasonable, considering the chemical composition of the chloroform extracts.

We have to stress that the signals relevant to the minor component present in fractions III–V cannot arise from contamination with fractions having a large content of this same component. In fact, in this case their chemical shifts should correspond to those of units in sequence, contrary to what has been observed.

Concluding Remarks

Copolymer samples obtained by fractionation with boiling solvents of the polymeric products obtained by anionic coordinate polymerization of mixtures of styrene (St) and (*S*)-4-methyl-1-hexene (4MH) have been analyzed by ^{13}C NMR.

Deconvolution of the experimental ^{13}C NMR spectra and, whenever possible assignments of the individual resonances, substantiate a nonrandom distribution of monomeric units along the macromolecular chain, as already indicated by other spectroscopic techniques.[8] The results obtained can be summarized as follows.

Copolymer samples soluble in chloroform are constituted by long, highly isotactic St sequences linked through an isolated 4MH unit. The opposite situation, isolated St units inserted in long isotactic 4MH sequences, is found in fractions soluble in diethyl ether and in cyclohexane.

The insertion of isolated units of both kinds very likely occurs with an almost complete loss of stereoregularity.

Fractions soluble in ethyl acetate are characterized by a rather low stereoregularity and a quasi-random distribution of the monomeric co-units. It is interesting to recall that, as already reported,[7] only the composition of the ethyl acetate extracts reflects the composition of the polymerization feed, whereas the major structural features of the other fractions are practically independent of feed composition.

The reported results indicate, in accordance with some recent studies on Ziegler–Natta catalysts,[9,18,19] that the polymerization process occurs, at least in the present case, on catalytic sites having intrinsically different activity: (a) one low selectivity site yielding polymers with low stereoregularity, where the ethyl acetate fraction is formed and (b) two highly dissymmetric sites capable of polymerizing almost exclusively one of the two monomers and giving rise to macromolecules containing more than 95% of either 4MH or St units. These two sites show an extremely high stereospecificity in controlling the polymerization process of the preferred monomer, whereas this control is partially lost during the insertion of the other monomer.

At present, studies are in progress to clarify if these last two sites are intrinsically different, or if their differentiation occurs only after the insertion of the first monomeric unit. However, the observation that whenever a "wrong" monomeric unit is inserted into the growing macromolecule, the polymerization of the "right" monomer is immediately resumed, makes the first hypothesis more reasonable.

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