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Study of Polyisoprene Microstructure by Flash Pyrolysis Gas Chromatography

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ABSTRACT

Flash pyrolysis of polyisoprene at 500°C in nitrogen atmosphere leads to four isomeric dimers of isoprene: dipentene, diprene, and 1,4-, and 2,4-dimethyl-4-vinyl-cyclohexenes. From systematic studies of various synthetic polyisoprenes of different microstructures, the four cyclic dimers have been assigned to specific diads of 4,1-4,3 or 1,2 units; for instance, dipentene and 2,4-dimethyl 4-vinyl cyclohexene are respectively characteristic of 4,1-4,1 and 4,1-4,3 diads. It has been possible to draw some correlations between the nature and the amount of the thermal degradation products and the distribution of the different kinds of units along the polymeric chain; anionic polyisoprenes obtained in the presence of alkali earth metals behave as random copolymers of 4,1 and 4,3 units, but Ziegler-Natta polyisoprenes show a definite tendency to alternate the same units.

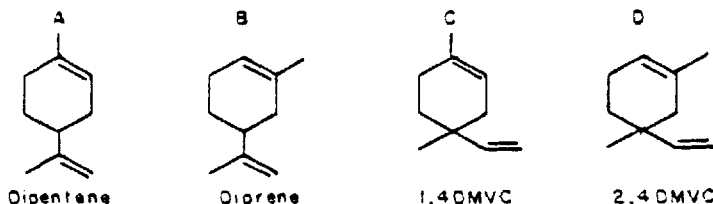
INTRODUCTION

In three previous communications [1-3] we were able to show that flash pyrolysis of various polyisoprenes in nitrogen atmosphere leads to three main thermal degradation products: monomeric isoprene, and two cyclic dimers dipentene (A) and 2,4-dimethyl-4-vinylcyclohexene (2,4-DMVC, C). It appeared that dipentene and 2,4-DMVC are respectively characteristic of 1,4 and 3,4 units, and that their yields are not only dependent on the average composition of polyisoprenes but also on the distribution of the different kinds of units along the polymeric chain.

The comparison of the thermal behavior of these different polyisoprenes and the results obtained on model compounds (dimer, trimer, and hexamer of 4,1 structure) and on random isoprene-methyl methacrylate copolymers [3] have led to the following conclusions:

1. Dipentene has to be correlated with the 4,1 unit content of the chain and more precisely to the 4,1-4,1 diad content. The pyrolysis of a copolymer containing as high as 27% isoprene but in which 95% of the isoprene occurs as isolated units leads to negligible amounts of dipentene.
2. 2,4-DMVC has to be correlated with the 4,3 unit content of the chain. Studies on model oligomers have shown that the presence of 4,3 unit is necessary for the formation for this dimer.
3. The presence of 1,2 units leads to a noticeable increase of the isoprene fraction.

In an independent investigation, Brock and Hackathorn [4] have recently obtained similar results. By using improved gas chromatography techniques, they were able to separate two other cyclic dimers among the degradation products of polyisoprene: diprene (B) and 1,4-DMVC (D) which are the isomers of dipentene and 2,4 DMVC, respectively.



Diprene was found in high amounts in the pyrolysis of some samples and its formation was assigned to adjacent vinyl or isopropenyl units.

Because of differences in pyrolysis techniques used in determining the structure of the polyisoprenes under study and in the methods of sample characterization, we have carried out a new investigation of most characteristic of our samples, and have tried to achieve gas chromatographic separation of the volatile products with the best possible efficiency.

EXPERIMENTAL

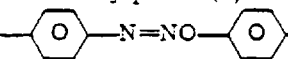
Polyisoprene Samples

The polyisoprenes studied are those previously described [3]. All the polymers were soluble in chloroform and do not contain any gel fraction. Their microstructure was determined by NMR spectrometry according to Chen [5], but the modifications of Kistler [6] and Pham Quang Tho [7] were taken into account.

Pyrolysis Gas Chromatography

We have systematically used the pyrolysis apparatus of Fisher from Prof. Simon (induction heating of the filament up to its Curie point in 30 msec) and we have selected the following experimental conditions: pyrolysis temperature, 500°C; pyrolysis time, 3 sec; and polyisoprene weight, 10 μ g (polymer sample deposited on the filament as a film from a chloroformic solution). Preliminary studies of the different parameters have shown that pyrograms obtained under such experimental conditions are quite reproducible and significant [3].

After pyrolysis, the thermal degradation products were separated and analyzed by gas chromatography (Perkin-Elmer model 900 apparatus) using a flame ionization detector; chromatographic separation was carried out at 115°C with liquid crystals as the stationary phase (4,4'-di-n-hexyloxyazoxybenzene

$C_6H_{13}O$ —— $O-C_6H_{13}$) deposited on chromosorb W (columns of 3 and 6 m length, 1,8 in. diameter; weight of phase, 0.508 and 1.000 g; and nitrogen flow rate, 27.5 ml/min).

RESULTS AND DISCUSSION

Efficiency of the Liquid Crystal Column for the Separation of the Different Isomers of Isoprene Dimers

Liquid crystals have been successfully used as stationary phases to separate isomers in gas chromatography [8]. We selected 4,4'-di-n-hexyloxyazoxybenzene because of its good efficiency in the separation of xylene isomers [9].

In Fig. 1 the variation of the specific retention volume (ml/g, on a logarithmic scale) is plotted vs the reciprocal of temperature for two isomeric cyclic dimers of isoprene, dipentene and diprene. This figure clearly shows three well-defined domains. The temperatures at the sharp discontinuities we have observed for the retention times are in good agreement with the temperatures of structural transitions of the liquid crystals: 82 and 129°C vs 81 and 127°C for smectic - nematic and nematic - liquid transitions, respectively, according to the literature [9].

The retention times are very short for the smectic phase, and dipentene and diprene cannot be adequately separated. This result does not agree with Dewar's finding for the xylene isomers [10].

In the temperature range of the nematic phase, where the retention times are drastically higher (increased by a factor of from 4 to 10), a good separation between dipentene and diprene has been observed.

The liquid phase is no more efficient for the separation of our two isomers.

The retention times are decreasing functions of the temperature for the nematic and liquid phase, except around the transition temperature where the phenomena are more complex.

Figure 2 is related to a typical pyrogram of anionic polyisoprene pyrolyzed at 500°C. The most important degradation products are monomer, isoprene ($\approx 66\%$), and dimers ($\approx 32\%$). The four cyclic dimers (dipentene, diprene, 2,4-DMVC, and 1,4-DMVC) are well separated (a capillary column of polyphenylether is efficient only for the two first isomers). They have been identified either by comparison of their retention times with those of pure model compounds (for dipentene and diprene) or by preparative gas chromatography and a study of their structure by IR, NMR, and mass spectrometry [2] (for the DMVC isomers). In both cases the

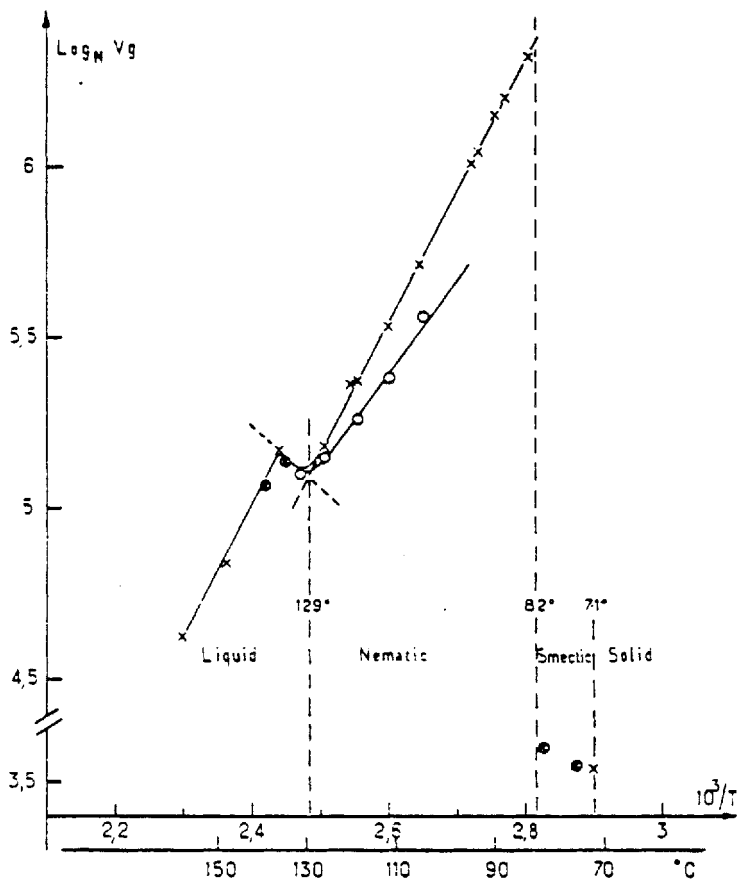


FIG. 1. Retention diagram for dipentene (x) and diprene (=) on 4,4-di-n-hexyloxyazoxybenzene (column, 3 m).

longer retention times correspond to the more symmetrical isomers.

Flash Pyrolysis of Various Natural and Synthetic Polyisoprenes

The samples of natural and synthetic polyisoprenes studied are the same as those previously described [3]. Most of them

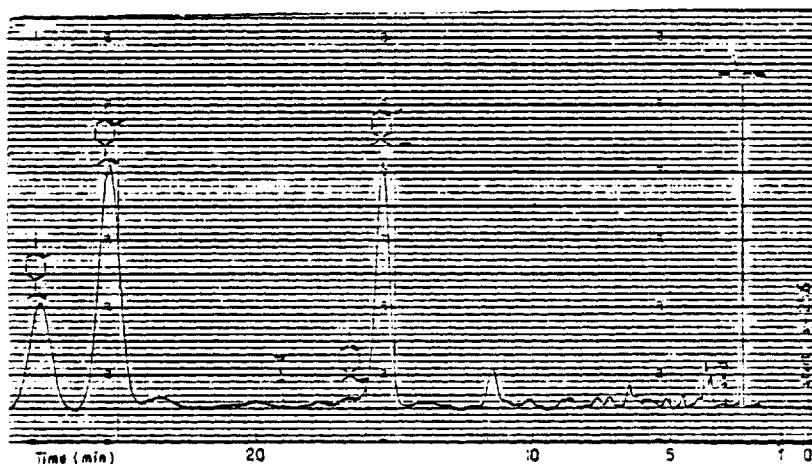


FIG. 2. Gas chromatogram of pyrolysis products at 500°C from anionic polyisoprene P₂ (column, 6 m).

were prepared by anionic polymerization and, according to recent results on the mechanism of the propagation step [11, 12], it seems more accurate to speak of 4,1 and 4,3 structures instead of 1,4 and 3,4 structure. This is important for the different kinds of diads.

The polymers investigated may be arranged in four main classes, characterized respectively by

1. A very high content of 4,1 units and a lack of 1,2 units.
2. Increasing content of 4,3 units and a lack of 1,2 units for a homogeneous series of anionic polyisoprenes polymerized by alkali earth metals, either in bulk or in heptane solution.
3. A still higher content of 4,3 units and a lack of 1,2 units for Ziegler-Natta polymers.
4. The most complex microstructure containing the three kinds of units.

The pyrolysis results obtained with these various samples are reported in Table 1. All the data related to isoprene, dipentene, and 2,4-DMVC are in good agreement with our previous results [3]. On the other hand, 1,4-DMVC is obtained in negligible amounts in

all our samples. Finally, diprene formation occurs in a significant way only in the presence of 1,2 units. In particular, a high 4,3 unit content does not necessarily lead to diprene formation. This is in contradiction with Brock's findings [4].

Reaction Mechanisms for Dimer Formation

We have previously [3] assumed the possibility of a Diels-Alder reaction between the isoprene evolved during the pyrolysis and pendent vinyl or isopropenyl groups of 1,2 or 4,3 units. This process, which leads to diprene and 2,4-DMVC, respectively, cannot be completely excluded, but its contribution is probably very low. It may obviously have a greater importance when secondary processes arising from bad thermal conductivity, slow heating rate, and slow diffusion of the volatile products through a thick polymer film take place, as in the pyrolysis techniques which involve large amounts of polymer and the Joule effect as the heating mode (Pyromatik Fisher, for instance). Our flash pyrolysis apparatus allows us to avoid these phenomena and it seems quite justified for us to neglect secondary degradation effects.

It is better to visualize reaction mechanisms which possibly account for the formation of thermal degradation products of polyisoprene according to the following simple rules:

1. As suggested by Bolland [13] and Madorsky [14], thermal degradation occurs by random chain-scission at a carbon β with respect to the double bond. Isoprene may be produced either by a 1,4 depolymerization step or by two successive chain scissions.
2. The presence of 1,2 units introduced into the chain as quaternary carbon atoms may act as preferential scission points. This accounts for the increase in the amount of monomer observed when the polymer contains 1,2 units in appreciable amounts. By analogy with the behavior of poly- α -methylstyrene, of polymethyl methacrylate, and of polymethacrylonitrile, we may assume that 1,2 blocks depolymerize to isoprene in a nearly quantitative way.
3. Dimer formation may take place by reaction of a radical on the double bond of the antepenultimate unit according to Markovnikov's rule. In some cases it is necessary to assume previous isomerization of the allylic radical in order to build a six carbon atom ring.

TABLE I. Molar Percent of Monomer and Dimers Obtained from Flash Pyrolysis of Various Polyisoprenes of Different Microstructures

Sample	Polymeri- zation conditions	Structure							Dipen- tene		
		%1,4, total	cis	trans	%3,4	%1,2 prene	2,4- DMVC	1,4- DMVC			
Hevea		97.8	97.8	0	2.2	0	67.4	2	-	0.3	30.3
Synthetic polyisoprene	Li	95.5	95.5	0	4.5	0	69	3.6	0.4	0.3	26.7
Balata		98.7	0	98.7	1.3	0	67	1.5	-	0.2	31.3
Ba 2	Ba, n-heptane, 40°C	79	67	12	21	0	66	8	0.5	1	24.5
4	Ba, n-heptane, 40°C	72	72	0	28	0	66	9	1	1	23
6	Ba, toluene	70	70	0	31	0	65.5	9	0.5	0.5	24
Sr 8	Sr, 40°C	65	53	12	35	0	65.5	11.2	1.3	0.5	21.5
9	Sr, n-heptane 30°C	56	56	0	40	0	66	12.2	1.3	1	19.5
Zn 1	Ziegler-Natta catalyst	48	48	0	52	0	66.6	28.2	0.3	0	5

Zn 3	Ziegler-Natta catalyst	40	40	0	60	0	66.5	29.1	0.4	0	4
P ₂	BuLi, THF, 25°C	46.7		50.4	2.9	71.5	13.7	0.3	8.7	5.8	
P ₃	Radical	89.6		3.9	6.5	72	3.5	0.5	7	17	
(1,2-3,4) _n	CoX ₂ /RMgX, HMT ^a	24.1		42.2	33.6	86	4.5	0	2.3	1.7	

We have shown in Table 2 some possible cyclization processes leading to the four identified dimers, and in Table 3 some of the possible cyclization products arising from different diads according to the previously assumed mechanisms. Obviously, all these reactions do not occur with the same probability. By comparison with experimental results it seems possible, however, to determine the main processes occurring during thermal degradation.

Dipentene is mainly produced from *cis*- or *trans*-4,1-4,1 diads according to the generally accepted mechanism by attack of the radical on the double bond of the antepenultimate unit. On the other hand, it may also be formed from 4,3-4,3 diads (or blocks).

Since for 1,2-1,2 diads (or blocks) depolymerization to monomer is preferred over dimer formation, we may conclude that 2,4-DMVC is formed from 4,1-4,3 diads. It is necessary to assume isomerization of the allylic radical prior to the attack of the double bond.

1,4-DMVC, always obtained in very low amounts (smaller than 1.3%), cannot be correlated with a precise diad in a definite way; 4,1-1,2 diad would lead to this isomer but this diad is less probable than 1,4-1,2 [15] diad which should lead to dipentene. Moreover, 1,4-DMVC may occur in the absence of 1,2 units.

Diprene may be produced from 4,3-1,2 diads or from added 1,4-4,1 diads. According to Brock et al. [4], diprene is produced from vinyl or isopropenyl diads, whatever their nature is. This is partly in contradiction with our previous mechanism. Moreover, as the maximum yield of diprene is obtained for a radical polyisoprene which has a largely predominant 4,1 structure it seems necessary to assume a contribution from some added 1,4-4,1 diads in its formation. It has been shown by theoretical calculations that such odd diads may be present in polyisoprenes [16].

Qualitative Analysis of Anionic Polyisoprene Microstructure

Because the mechanisms for dipentene and 2,4-DMVC formation seem to be quite certain, it is possible to study in a semiquantitative manner the distribution of the various units in polyisoprenes lacking 1,2 units.

In Fig. 3A we have drawn the calculated variations of the 4,1-4,1 (Curve 1), 4,3-4,3 (Curve 2), and 4,1-4,1 + 4,3-4,3 (Curve 3) diad

TABLE 2. Possible Cyclization Processes

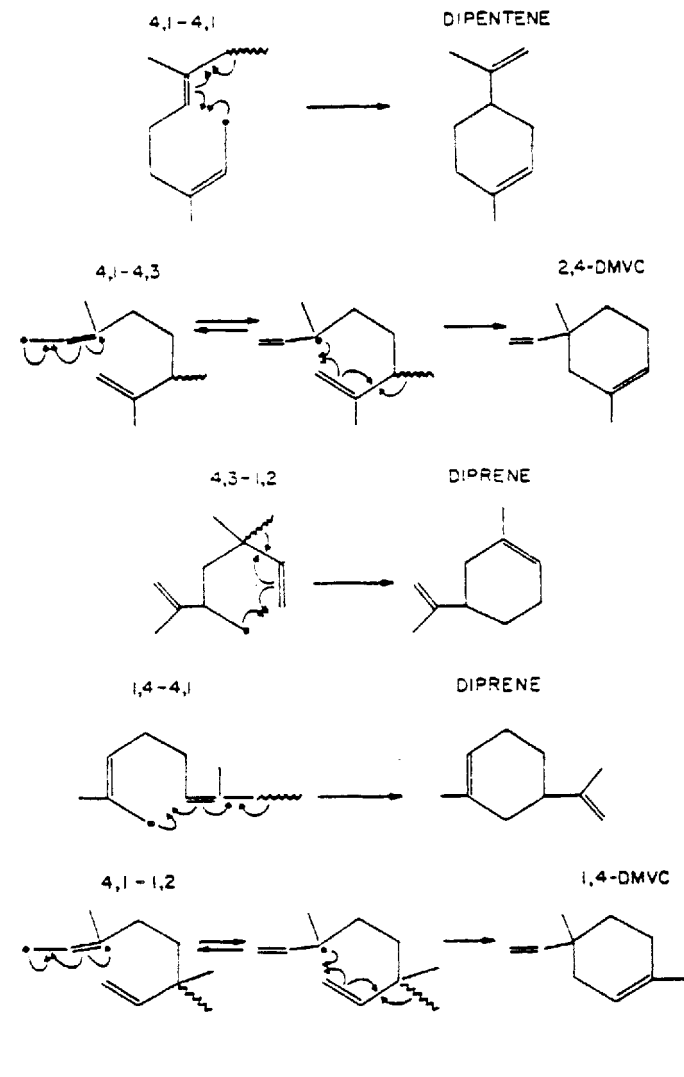


TABLE 3. Possible Cyclization Products from Different Diads

Dimer	Cyclization by attack of a radical, without or with allylic isomerization, on the penultimate double bond	
	(1)	(2)
4,1-4,1	Dipentene	-
4,3-4,3	Dipentene	-
1,2-1,2	2,4-DMVC	-
4,1-4,3	-	2,4-DMVC
4,3-4,1	-	-
4,1-1,2	-	1,4-DMVC
1,2-4,1	-	-
1,4-1,2	-	Dipentene
1,2-1,4	-	-
4,3-1,2	Diprene	-
1,2-4,3	Dipentene	-
4,1-1,4	-	-
1,4-4,1	Diprene	-

fractions vs the content in 4,1 units, assuming a Bernoullian distribution of the two kinds of units along the chain. In the same figure we have plotted the experimental points related to the dipentene fraction (percent of the total dimers) vs the same content in 4,1 units. Curve B is drawn in a similar way and is related to the 4,1-4,3 diad fraction and the 2,4-DMVC fraction.

This procedure is, in fact, a rough approximation which takes into account neither the fact that only a fraction of the diads considered can be cyclized in a random process [17] nor the

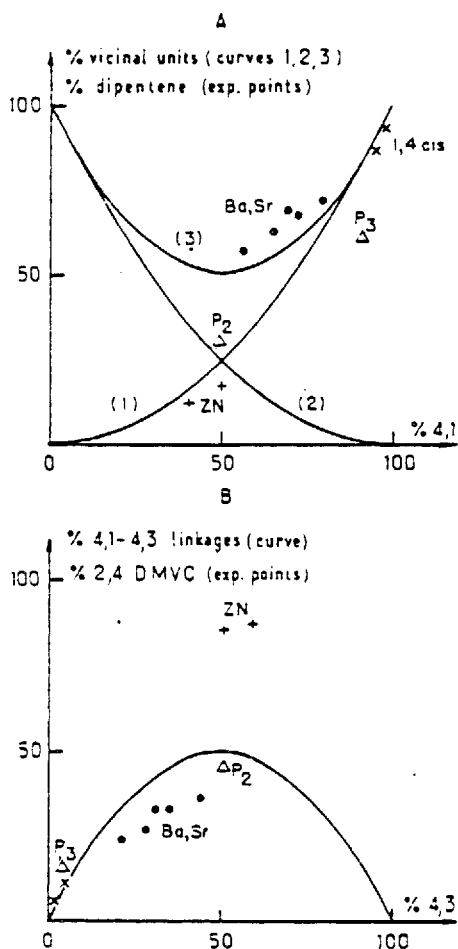


FIG. 3. A: Correlation of percent dipentene from pyrolysis products with percent 4,1-structure (experimental points). Curves (1), (2), and (3) are related to the variations of percent 4,1-4,1, 4,3-4,3, and 4,1-4,1 - 4,3-4,3 linkages vs the 4,1-units content, respectively assuming Bernoullian distribution of the two kinds of units along the polymeric chain. B: Correlation of percent 2,4-DMVC from pyrolysis with percent 4,3-structure (experimental points). The curve is related to the variation of percent 4,1-4,3 linkages vs the 4,3-units content according to the same assumption used in A.

nonequivalence of the 4,1-4,3 and 4,3-4,1 diads in our reaction mechanism. Nevertheless, the comparison appears interesting and clearly shows the great difference between alkali-earth polymerized polyisoprenes and Ziegler-Natta samples. Taking into account the previous assumptions concerning the formation mechanism of dipentene and 2,4-DMVC, and the position of the experimental points with respect to theoretical curves A-3 and B, we may conclude that the microstructure of the first series is not very different from that of a random "copolymer," which is not necessarily a Bernoullian copolymer. On the other hand, Ziegler-Natta polyisoprenes definitely behave as alternating copolymers. This structure obviously affords a maximum content of 4,1-4,3 diads and thus leads to a drastic increase of 2,4-DMVC and a drastic decrease of dipentene.

Brock et al. [4] have obtained good agreement between their experimental results and the theoretical curves A-1 and B for the systems dipentene/4,1-4,1 diad and 2,4-DMVC/4,1-4,3 or 1,2 diad. They have concluded that their "experimental lithium polymers" are characterized by a random distribution of 4,1 and 4,3 units. Nevertheless, we want to point out that for some samples under study, 4,3-4,3 diads or longer blocks cannot be neglected as the source of dipentene, and it is thus better to consider the possible agreement of the experimental results with Curve A-3 relative to the total amount of 4,1-4,1 and 4,3-4,3 diads. Moreover, it seems misleading to take into account 4,3 and 1,2 units in the same way, as is clearly shown by our examination of the possible cyclization processes.

Finally, our results are not large enough to establish a clear correlation between diprene formation and the chain microstructure.

CONCLUSION

The use of a liquid crystal column at a well chosen temperature in vapor phase chromatography has enabled us to carry out a single step quantitative separation and evaluation of the four cyclic dimers of isoprene which appear in various yields in the flash pyrolysis of polyisoprenes.

Careful examination of the experimental results obtained with a large variety of samples and model compounds has shown that dipentene and 2,4-DMVC may each be correlated to a specific diad; 4,1-4,1 and 4,1-4,3, respectively, in good agreement with

Brock's findings. This enables us to study the simpler case of the lack of 1,2 units and offers insight into the distribution of the different kinds of chemical units along the polymeric chain. Thus for 4,1 and 4,3 units, Ziegler-Natta polyisoprenes show a definite tendency to an alternating microstructure whereas alkali-earth polyisoprenes behave as random copolymers. On the other hand, diprene and 1,4-DMVC formation still remain to be clarified.

In this first approach we have obviously neglected some parameters such as branched or cyclic structure, tacticity of vinyl blocks, and possible thermal cyclization of lateral double bonds, but these factors seem to be of minor importance.

We think that the study of a wider range of synthetic polyisoprenes and, in particular, of model compounds for 4,3 and 1,2 blocks and for 4,3-1,2 or 4,1-1,4 diads would lead to very interesting results and could allow a better selection in the reaction mechanisms.

Flash pyrolysis appears as a quite powerful technique in this complex field of polyisoprene microstructure. Its coupling with some other methods, such as quantitative analysis of the ozonolysis or, better, of the olefin-polymer metathesis products [18], may be of great value in obtaining quite definite results.

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