

# Anionic polymerization of butadiene with organosodium soluble catalysts and structure of the resulting polymers

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The structure of liquid polybutadienes prepared by anionic catalysts with toluene as transfer agent was studied by  $^{13}\text{C}$  n.m.r. and information concerning initiation, propagation and transfer mechanism was obtained. A complete characterization of the fractions obtained by high vacuum distillation is also reported.

## INTRODUCTION

Low molecular weight polybutadienes can be prepared by means of different initiating systems (i.e. free radical, cationic, Ziegler–Natta, anionic initiators).

In particular the anionic polymerization may be carried out in two different ways: (a) by living systems; (b) in the presence of chain transfer agents. The organoalkali-initiated polymerizations of dienes have been the subject of intensive study in the last years<sup>1–5</sup>. High resolution n.m.r. studies have been carried out in order to obtain information on the polymerization mechanism by studying the propagating living species. In particular living polymers, dead (proton) and pseudoterminated (deuterobutadiene) polymers were compared by means of  $^1\text{H}$  n.m.r..

This paper deals with some aspects of initiation, propagation and transfer of butadiene polymerization by organosodium with toluene as transfer agent, in order to obtain liquid polymers.  $^{13}\text{C}$  n.m.r. is the technique employed for the analysis both of the raw polymer and of the fractions obtained by high vacuum distillation.

This technique allows information on the structure of the polymers to be obtained which is more detailed than that derived from  $^1\text{H}$  n.m.r. By  $^{13}\text{C}$  we can distinguish the signal from the last unit from internal ones, we can also determine the presence of the structural unit (1,2-1,4-*trans*-1,4-*cis*) in the chain and in the last unit.

Precise knowledge of these values and the study of the last living unit under similar conditions is the basis for a more detailed study of the influence of the polymerization parameters and therefore of the mechanism.

## EXPERIMENTAL

### *Monomer and solvents*

Polymerization grade butadiene obtained from Anic. Toluene was Esso chemical grade dried by azeotropic distilla-

tion ( $\text{H}_2\text{O} < 10$  ppm). THF was twice distilled before use, first from  $\text{LiAlH}_4$  and then from Na. Na was a C. Erba product powdered by usual techniques. *Trans*-stilbene was a pure product obtained from Fluka.

### *Catalysts*

Butyllithium was purchased from Fluka as 20% n-hexane solution. Na–tetraphenylethylene and Na–naphthalene were prepared according to refs 6 and 7, respectively. Na–stilbene dianion was prepared by reacting Na as powder with *trans*-stilbene (molar ratio 2:1). The reaction was carried out for 10 h. The quantitative determination of the dianionic species was made:

(a) by titration of soluble Na;

(b) hydrolysing the reaction mixture with  $\text{H}^+$  and measuring the bibenzylic species thus formed by gas chromatography (>95%).

### *Polymers and model synthesis*

Polymerization runs were carried out under a dry nitrogen atmosphere in a jacketed polymerization reactor of between 200 and 1000 ml. Solvent and catalyst were introduced in that order; butadiene was fed by means of a hypodermic needle while controlling the flow by a suitable valve.

After 30 min the polymerization mixture was quenched with a few ml of  $\text{CH}_3\text{OH}$  and the polymer solution was treated in a separating funnel with an equal volume of 3/97 w/w  $\text{HCl}/\text{H}_2\text{O}$  solution. The organic phase was collected and evaporated to dryness yielding a pale yellow polymer.

Oligomers contained in the fraction formed by  $\phi\text{CH}_2 + 1$  butadiene were distilled at  $10^{-3}$  mmHg and  $T = 40^\circ\text{C}$  with a 30 cm long Vigreux column. Oligomers contained in the fraction formed by  $\phi\text{CH}_2 + 2$  butadiene were distilled at  $10^{-3}$  mmHg and  $75^\circ\text{C}$  with a 5 cm Vigreux column.

The hydrogenation of the fractions obtained was performed under 6 atm  $\text{H}_2$  at room temperature in a previously evacuated 200 ml autoclave, to which 0.4 mmol of Co-2-ethyl hexanoate, 0.4 mmol of poly(*N*-isopropyliminoalane) ( $\text{HAlN-iso-C}_3\text{H}_7$ )<sub>6</sub> in toluene, and the liquid polymer are added in that order, the latter had a weight of 2.15 g and a

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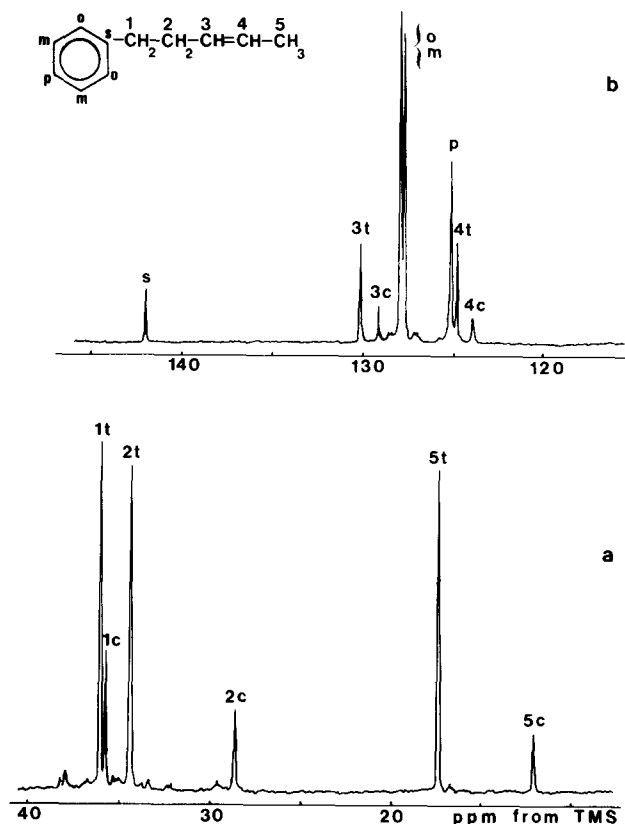


Figure 1 (a) Carbon spectrum of the first fraction (saturated region); (b) carbon spectrum of the first fraction (unsaturated region)

molecular weight of 250–300 g/mol equivalent to 30 mmol of double bonds. The polymer solution was extracted after 30 min and washed with dilute acid; the organic phase was then recovered and the solvent evaporated.

The preparation of benzene-4-pentenyl has been carried out by reacting  $\phi\text{CH}_2\text{Na}$  (1 mol) and  $\text{Br}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$  (1 mol) for 4 h at room temperature in a hydrocarbon solvent. The reaction mixture was filtered off and the solvent evaporated.

#### N.m.r. analyses

$^1\text{H}$  n.m.r. spectra have been recorded from  $\text{CCl}_4$  solution on a Varian HA 100-15D spectrometer, while the  $^{13}\text{C}$  spectra have been taken from  $\text{CDCl}_3$  solutions on a Varian XL 100-15 model equipped with Fourier transform facilities. Chemical shifts of  $^{13}\text{C}$  were recorded in ppm from TMS, used as the internal standard.

#### I.r. analysis

I.r. spectra obtained with a model 21 Perkin-Elmer spectrometer have been taken on polymer films using either coefficients calculated by us or the analytical method developed by Morero *et al.*<sup>8</sup> for solutions.

#### Gas chromatographic analysis

Gas chromatographic analysis of the fractions has been carried out on a Erba Fractovap Model C chromatograph and a column packed with 5% SE-30 on 60–80 mesh 'Chromosorb W'. The following conditions were employed: column temperature = 180°C, injector temperature = 220°C and He carrier gas with a flow rate = 1 ml/sec.

## RESULTS

Liquid polybutadienes were prepared by means of soluble organosodium compounds in toluene as chain transfer agent with a small amount of THF to make the whole polymerization system homogeneous.

A typical run employs 1 mmol soluble Na as catalyst, 250 mmol butadiene, 800 mmol toluene and THF in the range 25–100 mmol.

The particular catalytic systems used were Na stilbene mono- and diadduct, Na-naphthalene and Na-tetraphenylethylene. By changing the polymerization conditions, such as catalyst and transfer agent concentrations, rate of monomer addition, polymerization temperature etc., liquid polymers having  $MW$  between 400 and 4000 can be obtained.

The structure of the polymers was determined by means of  $^{13}\text{C}$  and  $^1\text{H}$  n.m.r. In a polymer of  $\bar{M}W = 1000$  the following microstructure was found:

$$1,2 (\%) = 77$$

$$1,4\text{-trans} (\%) = 14$$

$$1,4\text{-cis} (\%) = 9$$

The spectra show the following triad compositions:

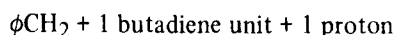
$$F_i = 22.4\%$$

$$F_h = 54.4\%$$

$$F_s = 23.2\%$$

from which we can deduce that the polymer is atactic.

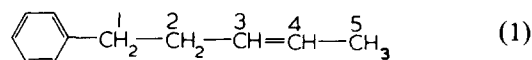
Owing to the polymer polydispersity which is in the range 1,5–2,5 as measured by g.p.c., high vacuum fractionation was carried out to analyse the oligomers structure. The first fraction, i.e. the one with the lowest molecular weight, comprises:



as revealed by gas chromatography-mass spectrometry.

The carbon spectrum of the first fraction shows two regions corresponding to saturated and unsaturated carbon atoms, which are reported in Figures 1a and 1b.

$^{13}\text{C}$  n.m.r. spectra correspond to the following structure:



In the aliphatic region (Figure 1a) of the spectrum the peaks at 17.9 and 12.7 ppm allow an easy identification of, respectively, the methyls in the  $\alpha$  position to a double bond with *trans* and *cis* configuration.

Peaks at 34.5 and 28.8 correspond to the two *trans* and *cis*  $\text{C}_2$  methylenes while those at 36.1 and 35.8 can be assigned to the two  $\text{C}_1$  methylenes again in the *trans* and *cis* configurations.

In the olefinic region (Figure 1b) it is possible to distinguish, apart from the four signals of the aromatic ring (at 142.3, 128.5, 128.3 and 125.8), four more signals, of which those at 130.7 and 125.0 ppm are more intense than the remaining ones at 129.7 and 124.6.

The chemical shifts agree with those of the two unsatu-



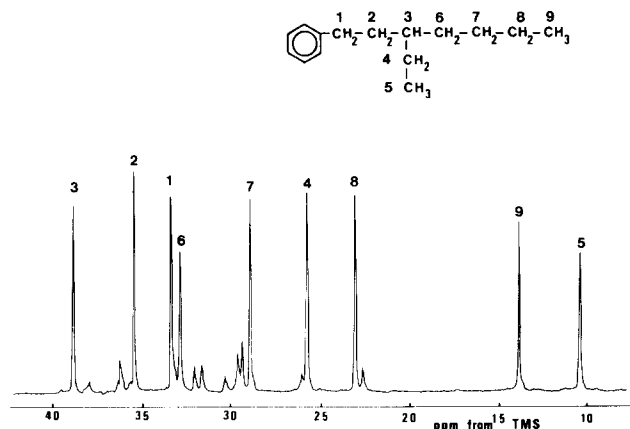
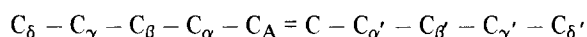


Figure 5 Carbon spectrum of the second fraction after hydrogenation

Assignments have been made on the basis of both 'off resonance' and 'selective' decoupling techniques, and of literature data reported in particular by Clague *et al.*<sup>9</sup> on polybutadiene and by Dorman *et al.*<sup>10</sup> on quantitative correlations of chemical shifts of carbon atoms of acyclic alkenes. In order to define the effect of the substituent for calculating the chemical shift of a carbon atom, both the notation and the values suggested by Dorman have been used; thus for the chain:



the effects induced on  $C_A$  by  $\alpha, \beta, \dots, \alpha', \beta'$ , and so on have been evaluated. On these grounds, spectra can be interpreted and assignments can be made by the following method. In the low field area (Figure 4b) assignments of five out of the six carbon atoms of the aromatic ring, that is those in the *ortho*, *meta*, and *para* positions with respect to substitution, can be written down immediately on the basis of the chemical shifts already found for the compound having a single butadiene unit.

Considering the ring carbon atom from which the chain starts, a partial overlapping of its signal and of the signal from the unsaturated CH of the vinyl group has been observed. The assignment of the peak at 142.73 to the ring carbon atom and of the peak at 142.60 to the vinyl CH group has been decided on the basis of the 'off resonance' decoupled spectrum.

In the low field region, the peak at 114.70 is due to the vinyl  $CH_2$  group and the 126.29, 124.70 peaks denote the CH group in the  $\alpha$  position with respect to the methyl ( $C_8$ ) in the *trans* and *cis* configurations respectively. The latter values agree very well with the 126.22 and 124.63 values calculated from the chemical shift of the  $C_2$  carbon of 2-hexene (124.0 for the *cis*, and 125.1 for the *trans* configurations, i.e. values converted from original data by assuming  $\delta_c^{CS2} = 193.7$ ) and by adding the  $\gamma'$  *cis* (0.63) and  $\gamma'$  *trans* (1.12) contributions<sup>10</sup>.

Finally, the peak at 129.18 can be made to correspond to the  $C_7$  carbon atom in the *trans* configuration, since this chemical shift agrees very well with the 129.16 value obtained from literature data, starting from the chemical shift of the carbon 5 of the 3-ethyl-1-*trans*-5-octadiene<sup>9</sup> and subtracting the  $\beta'$  *trans* effect ( $\beta'$  *trans* = 2.16 ppm)<sup>10</sup>. The absence of the  $C_7$  carbon peak in the *cis* configuration is likely to be due to the overlapping of this signal with one of the two rather intense signals coming from the *meta* and *ortho* carbon atoms of the aromatic ring. As a matter of fact, the

*cis* correction is about 1 ppm and therefore the estimated value lies around 128 ppm, i.e. just in the region of the two signals mentioned above.

In the aliphatic region (Figure 4a) the 'off resonance' decoupled spectrum allows assignment of the peak at 43.70 ppm to the methine carbon ( $C_3$ ), as well as confirmation of the *cis* and *trans* methyl groups. Further, from literature data<sup>9</sup> the peaks at 38.33 and 32.26 ppm can be assigned to the *trans* and *cis*  $C_6$  carbon atom, in good agreement with the 38.3 and 30.6 values for the corresponding carbon in the polybutadiene, relative to the diads 1,2-1,4 *trans* and 1,2-1,4 *cis*.

The two remaining peaks at 35.95 and 33.52 should be assigned to the 2 and 1 carbons, respectively. The latter assignment comes out easily by analysing the 'selective' decoupled spectrum obtained by irradiating at the proton resonance frequency of the methylene group substituted in the  $\alpha$  position with respect to the aromatic ring (253 Hz from TMS).

Besides the peaks mentioned above, a few low intensity peaks are also present in the spectrum, such as a weak signal at 30.33 and another one at 36.04, that can be assigned to a compound formed by  $\phi CH_2 + 2$  butadiene + H, both 1,4.

The presence of this product may be anticipated by considering that the composition found for the high molecular weight polymers, i.e. for the internal chain units, includes about 80% of 1,2 units, with the remainder being made up of 1,4 units.

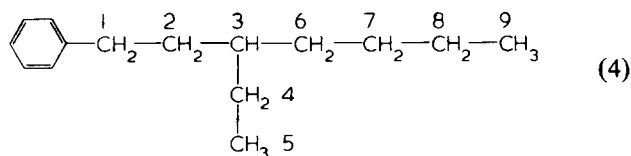
It is therefore probable that the  $\phi-CH_2 + 2$  butadiene component consists of 80% 1,2-1,4 diads and 20% 1,4-1,4 diads.

Since, however, 4 isomers are possible for this diad, that is *cc*; *ct*, *tc* and *tt*, the reason why signals are in practice so weak is now clear.

Gas chromatographic analysis of this fraction also shows, near to a strong peak, a number of less intense peaks where the area ratio is about 80/20.

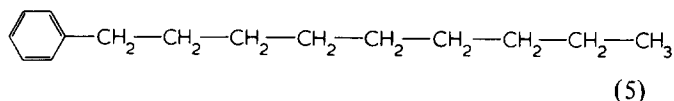
In order to evaluate the percentage of these units this fraction was hydrogenated prior to spectroscopic analysis.

The <sup>13</sup>C n.m.r. spectrum of the aliphatic part is reported in Figure 5 and the assignments, made as usual on the basis of 'off resonance' and 'selective' decouplings as well as by literature data, are shown in the following table by assuming the following compound:



Carbon	Chemical shift
$C_1$	33.36
$C_2$	35.40
$C_3$	38.73
$C_4$	25.90
$C_5$	10.83
$C_6$	32.87
$C_7$	29.03
$C_8$	23.27
$C_9$	14.22

The percentage of this product with respect to compound (5)



can be obtained by measuring the peak areas corresponding to the C<sub>5</sub> and C<sub>9</sub> methyl groups. The ratio between the two products (branched and linear, respectively) is 84/16. This ratio represents in practice the 1,2/1,4 ratio existing between the dimer internal units and is in good agreement with the composition found for the high molecular weight polymers; that is, in practice, in agreement with the percentage of chain internal units. From the analysis of this fraction it can therefore be concluded that it consists of compound (3) (~85%) and  $\phi\text{CH}_2 + 2$  butadienes (1,4) + 1H. These results are quite different from the ones reported by Kume *et al.*<sup>11</sup>.

No evidence of terminal vinyl units has been found. It should however be noticed that the identification of a compound whose concentration would in any case be about 1% is not easy, due to the marked complexity of this fraction as well as to its low level of purity.

The spectra of all the fractions examined showed that the benzyl group was the initiating species. This was confirmed by comparing the osmometric molecular weights of a series of samples with those computed on the basis of the ratio between aromatic protons and chain protons, on the assumption that all chains are initiated by a benzyl group. The results are reported in *Table 1*.

The good agreement between the two series of values gives support to the view that in the case of polybutadienes prepared by Na-stilbene in toluene the percentage of chains not initiated by the benzyl group is practically negligible.

Good agreement between osmometric and n.m.r. molecular weights can also be found with commercial samples prepared with the use of different catalytic systems (with Li as the counterion) and by using toluene as transfer agent (Lithene P). From the foregoing results a dependence of the 1,2 content on the molecular weight of the oligomers was observed due to the effect on the composition of the presence of a 1,4 terminal unit.

If  $P_{1,2}$  is assumed to be the probability that the internal unit is of the 1,2 type and  $n$  is the number of chain units, the polymer composition in terms of percentage of 1,2 units ( $F_{1,2}$ ) as a function of  $n$ , can be written as follows:

$$F_{1,2} = P_{1,2} \frac{n-1}{n}$$

In *Figure 6*, the experimental values of  $F_{1,2}$  are given as a function of the molecular weight computed by n.m.r. and compared with the curve of  $F_{1,2}$  vs.  $MW_{\text{n.m.r.}}$  ( $MW = n54 + 92$ ) for the  $P_{1,2} = 0.8$ . This value minimizes the root mean square deviation between experimental and calculated values and results in a good agreement between the calculated curve and the experimental points. It should also be pointed out that although the *trans/cis* ratio of the terminal unit is 85/15, high molecular weight polymer has the following composition: 1,2 = 77%; 1,4 *trans* = 14%; 1,4 *cis* = 9% i.e. a *trans/cis* ratio of 59/41.

It has been previously stated that almost all the chains are initiated by benzyl groups deriving from toluene. In fact, if *d*<sub>8</sub>-toluene is used as solvent, only a very weak signal is observed in the aromatic region of the <sup>1</sup>H n.m.r. spectrum. This weak signal, has an intensity higher than the known isotopic purity of toluene, and has been attributed to the presence of chains initiated by benzyl groups deriving from

stilbene. That this may occur has been supported by the fact that various analytical techniques such as u.v., <sup>1</sup>H and <sup>13</sup>C n.m.r., have detected in the oligomer mixture prepared in pure THF aromatic compounds that cannot be ascribed either to stilbene or to diphenyl ethane, the <sup>13</sup>C n.m.r. spectrum exhibits neither the characteristic peak at 137.44 ppm of the stilbene quaternary atom, nor the signal at 141.81 ppm corresponding to the quaternary carbon atom of the aromatic diphenylethane ring nor the saturated CH<sub>2</sub> at 37.94 ppm.

Further, since in a typical polymerization reaction gas chromatographic analysis shows that the amount of free diphenylethane is negligible and since Na/stilbene 2:1 does not appreciably metallate toluene, it may be concluded that the diphenylethane group must somehow be bound to the polymer.

Lastly, the molar ratio of Na/stilbene 2:1 to toluene is about 1:800 under these experimental conditions so that almost all the chains are initiated by benzyl groups derived from toluene.

## DISCUSSION

The following results have been established.

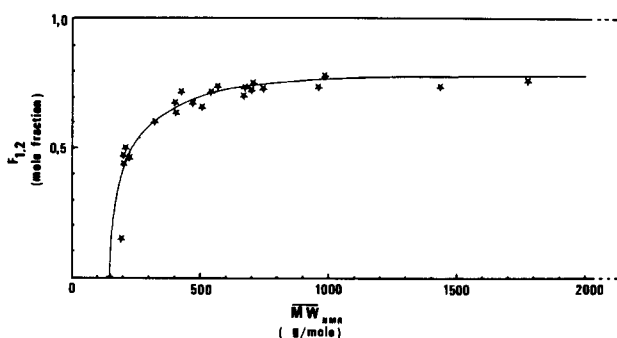
- (1) Nearly all the chains contain benzyl groups.
- (2) The configuration of the end unit is essentially 1,4.
- (3) About 80% of the internal units show a 1,2 configuration.
- (4) The 1,4 configuration shows a *cis* to *trans* ratio of 15:85 for the end units and 40:60 for the internal ones.

As far as the first point is concerned it appears that a small amount of butadiene is initiated by Na-stilbene, until proton transfer with toluene yields a benzylic anion which

*Table 1* Comparison of the osmometric molecular weight with n.m.r. molecular weight of some liquid polybutadienes

Catalyst	$MW_{\text{osm.}}$ (g/mol)	$MW_{\text{n.m.r.}}$ (g/mol)
Stilbene-Na	770	802
Stilbene-Na	1050	1184
Stilbene-Na	890	1169
Stilbene-Na	520	577
Stilbene-Na	365	400
Stilbene-Na	600	679
Stilbene-Na	600	645
Stilbene-Na	960	1050
Stilbene-Na	10150	n.d.*
Naphthalene-Na	840	805
Benzyl-Na (Nisseki)	1100	1129
Butyl-Li (with promoter) (Lithene PL)	720	761

\* Not determined because of high molecular weight



*Figure 6* Plot of  $F_{1,2}$  (fraction of 1,2 units in the polymer) against n.m.r. molecular weight

Table 2 1,4-Configuration ratio in the terminal and internal units for some polybutadienes prepared under different experimental conditions

Catalyst	Solvent	T (°C)	$\overline{MW}$ n.m.r. (g/mol)	1,2 (%)	Ratio 1,4 <i>cis/trans</i> in chain	Ratio 1,4 <i>cis/trans</i> last unit
Stilbene-Na	THF and toluene 2/18 V/V	-20	2264	87.0	18/82	< 10/90
Stilbene-Na	THF and toluene 2/18 V/V	6	1111	77.8	36/64	16/84
Stilbene-Na	THF and toluene 2/18 V/V	20	740	77.8	38/62	15/85
Stilbene-Na	THF and toluene 2/18 V/V	50	376	62.7	37/63	17/83
Stilbene-Na	THF and toluene 2/18 V/V	20	n.d.*	74.8	41/59	n.d.*
Benzyl-Na (Nisseki 1000)	a	b	1120	63.6	43/57	25/75
Butyl-Li (Lithene PL)	a	b	761	33.1	35/65	34/66

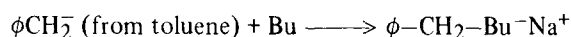
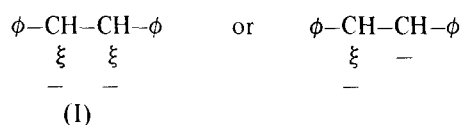
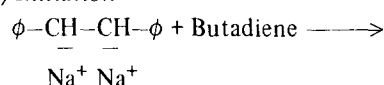
\* Not determined because of high molecular weight

a Toluene, as chain transfer

b Unknown

then becomes the major initiator of polymerization. A probable polymerization mechanism is the following:

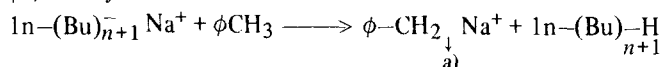
(a) Initiation



(b) Propagation



(c) Transfer



Points (2) and (3) are in agreement with all the data reported on the organoalkali metal polymerization of dienes. Living diene polymers and their products obtained after hydrolysis and pseudotermination (with deuterobutadiene) have been studied by n.m.r. spectroscopy<sup>1</sup>. In all cases the negative charge of the living end is located essentially on the primary carbon atom ( $\alpha$  carbon), although in polar solvents it exists in the more delocalized allylic form with considerable charge density on the  $\gamma$  carbon atom.

Recently, new explanations concerning the mechanism of the anionic propagation of polydienes have taken into account possible interaction between the living chain end, the counterion and the nature of the solvent used. It has been asserted<sup>4,5</sup> that in hydrocarbon media the 1,4 propagation stereospecificity is the consequence of coordination of the counterion with both double bonds of the diene molecule. Conversely, the 1,2 configuration in a donor solvent is the consequence of competition between diene and solvent. In the present system the type of attacking reagent (proton or butadiene) clearly plays a very important role: the proton from toluene almost uniquely reacts with the more basic primary  $\alpha$  carbon, whereas butadiene adds predominantly to the secondary  $\gamma$  carbon; in the latter case coordination might be an important factor<sup>6,7</sup>. The small amount of THF present is evidently enough to complex the major part of the Na counterion of the growing chains in competition with butadiene in such a manner that polymeri-

zation proceeds as in polar solvents. Regarding point (4) it must first be noted that the *cis* to *trans* ratio in the last unit does not depend on the source of the proton involved (toluene, methanol, or hydrogen chloride).

In Table 2 the 1,4 configuration ratio of the terminal and internal units for different temperatures and solvents is shown. At low temperatures ( $-20^\circ\text{C}$ ) the *trans* content is higher both for terminal and internal units. The *trans* content of the internal units does not change from toluene to hexane.

Finally the difference in the *cis* to *trans* ratio for terminal and internal unit is present also in commercial samples made using Na-benzyl as catalyst and toluene as transfer agent, while it is not present in the samples made with Li-alkyl in toluene.

## CONCLUSIONS

The study of  $^{13}\text{C}$  n.m.r. spectroscopy of low molecular weight polybutadienes prepared by sodium stilbene in toluene and of pure fractions obtained by high vacuum distillation gives precise information about the structure of these polymers in terms of configuration of the terminal unit, of the chain unit and of the initiator.

New information about the polymerization mechanism may be obtained by studying the living chain end by  $^{13}\text{C}$  n.m.r. and evaluating whether the hydrolysis affects the configuration of the terminal group or not<sup>12</sup>.

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