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Polymerization of Conjugated Dienes at High Pressures. X. Influence of Pressure upon the Microstructure of Anionic Polyisoprene

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ABSTRACT

The microstructure of polyisoprenes prepared in hydrocarbon solvents with *n*-butyllithium is very sensitive to pressure, whereas in oxygenated solvents the structure remains unchanged even in the highest pressure range. Thus in *n*-heptane the content of 1,4-*cis* units decreases with increasing pressure, leading to polymers with heterogeneous structure. It is assumed that electrostatic as well as steric effects must be taken into account together: pressure acts like a polar solvent; however, in the transition state, steric effects affect the 1,4-*cis* addition.

INTRODUCTION

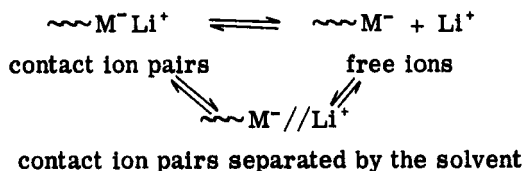
The influence of the reaction environment on the structure of the polymer formed during the anionic polymerization of isoprene has already been thoroughly investigated. Several parameters affecting

the structure have been examined: temperature [e.g., Refs. 1 and 2]; nature and initial concentration of the alkyllithium [2]; degree of polymerization [2]; impurities, especially lithium alkoxides [3]; and, above all, nature of the solvent in which the polymerization is carried out. The greatest structural modifications are induced by the solvent when it is able to solvate the propagating specie [e.g., Refs. 4 and 8].

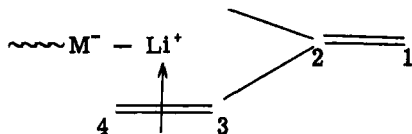
In a previous investigation we reported the effect of pressure on anionic polymerization [5]. We found that pressure is able to alter the structure of the polymer mainly by reducing the content of 1,4-cis units when the polymerization is performed in a hydrocarbon solvent, whereas this procedure yields nearly stereoregular polyisoprene at atmospheric pressure.

Before presenting our latest results, it may be worthwhile recalling the present state of knowledge concerning the mechanism of anionic polymerization of isoprene initiated by organolithium compounds.

Analysis of the ionic factors shows that the determining step in the mechanism governing the structure of the polymer is essentially the degree of interaction between the initiating ionic species and the growing chain. On the basis of the commonly adopted reaction scheme of Winstein [6],



Several authors [e.g., Ref. 7] have proved that in solvents allowing propagation through pure free ions, only the relative polarity of the four carbon atoms in the isoprene molecule determines the final structure of the polymer. In the case of propagation through contact ion pairs, a bond of the coordination type between the gegenion Li^+ and the double bond $\text{C}_3 = \text{C}_4$ is suggested [7]:



It is likely that the configuration of the complexed diene in the coordination complex controls the steric process of incorporation of the following monomer unit into the growing chain.

In hydrocarbons the well-known ability of the organic lithium compounds to form associated species or complexes with electron-donor

substances [8] is in good agreement with a mechanism involving a cationic attack of the monomer by the Li^+ cation before the anionic part [9], and therefore the structure seems to be principally determined by the associations of the growing chain (polyisoprenyllithium species) in which the C—Li bond is highly polarized. The addition of a polar solvent destroys the associations, produces selective solvations, and leads to intermediary structures with a progressive enrichment in 3,4-units. However, Schue et al. assume that the active species is rather a delocalized allylic form [10]. Finally, the presence of the methyl group in the molecule of isoprene may play an important role by modifying the configuration of either the anion or the attacking monomer.

Both effects, electrostatic and steric, must be involved to explain the final structure of the polymer obtained in the presence of n-butyllithium.

EXPERIMENTAL

Materials

Isoprene (purum from Fluka) was refluxed under argon atmosphere on sodium wire for several hours, condensed, and then prepolymerized in the presence of butyllithium.

Solvents were treated in the same way. N-Butyllithium (Fluka) was used as a clear solution in n-hexane without further purification and diluted to the required concentration.

Polymerization Procedure

The reaction tube consists in a flexible PTFE tube closed with slightly tapered PTFE stoppers. The tube was dried at 120°C under high vacuum for 1 day, then introduced into a stainless-steel container. The PTFE stopper was pushed into the tube by means of a screwed nut. After filling was carried out in a dry box, the tube was introduced into the compression vessel (18 kbar). After releasing the pressure, the polymer was dissolved in carbon tetrachloride under argon, precipitated with an excess of methanol, and then dried at 45°C under reduced argon pressure.

Spectroscopic Study

The microstructure of polyisoprenes was determined by NMR spectroscopy under the following conditions: Varian spectrometer

(60 Mc/sec), ambient temperature, with benzene or deuterated benzene as solvent. Calculations were performed from the integral curve given by a Varian integrator and checked by triangulation with an accuracy of 2 to 3%. We used the reference spectra studied in our laboratory [11]. The spectra were always run with polyisoprene samples obtained at nearly 100% yield and having a degree of polymerization (determined by viscometry) higher than 200, although we found that conversion and molecular weight have little influence on structure.

RESULTS

The polymerization rate is generally fast, especially at high pressures. Even in the presence of very low initiator concentrations, some 10 min under 10 kbar are sufficient to reach total conversion.

At ordinary pressure in heptane, the reaction mixture becomes progressively yellow as the reaction proceeds, at high pressures the medium is dark brown; the solution turns to pale yellow after addition of methanol. The red carmine coloration appearing in anisole is strongly enhanced under pressure. In *N,N*-dimethylaniline the solution is dark brown. These various colors are presumably connected with the existence of ionic or pseudo-ionic species in the reaction mixture.

Effect of Pressure on Anionic Polymerization in Pure Solvents

Table 1 shows the content of 1,4-*cis* units as a function of pressure and of the nature of the solvent.

In identical concentration conditions, the 1,2-addition does not appear in anisole and *N,N*-dimethylaniline. On the other hand, this type of addition exists when dioxane is used as the reaction solvent (0.15), but pressure has no effect in this case. In heptane as solvent, the content of 1,2-units varies from 0 to 0.10 when pressure is increased from 1 to 14,000 bar. The changes of 3,4- and 1,4-*trans*-additions are shown in Fig. 1.

In weakly polar solvents such as heptane, pressure induces deep transformations by reducing very significantly the percentage of 1,4-*cis* units. This diminution appears principally at low pressures (less than 3000 bar). Above this value the 1,4-*cis*-addition seems to tend to a limit. In solvents whose behavior with respect to the propagating species may be defined as intermediary between heptane and dioxane (anisole and *N,N*-dimethylaniline), the decrease is less accentuated, since it is only 10 and 5%, respectively, between 1 and 12,000 bar. In the case of dioxane, the 1,4-*cis*-units are absent in the whole pressure

TABLE 1. Effect of Pressure upon the Concentration of 1,4-cis Units in Anionic Polyisoprene

	Solvent			
	n-Heptane	Anisole	N,N-Dimethylaniline	Dioxane
$10^2 [C]_0^a$	1.80	1.06	1.06	1.80
$[M]_0^b$	7.80	5.00	5.00	5.00
Pressure (bar)				
1	0.78	0.48	0.52	0.00
1,000	0.62	-	-	-
3,000	0.55	0.40	0.49	0.00
6,000	0.54	0.40	0.49	-
9,000	0.50	0.38	0.49 ^c	0.00
12,000	-	0.38 ^c	0.47 ^c	0.00 ^c
14,000	0.44	0.38 ^c	-	-

^a $[C]_0$: Initial concentration of active n-butyllithium (moles/liter).

^b $[M]_0$: Initial concentration of isoprene (moles/liter).

^cReaction mixture probably solid.

range. The 1,4-trans- and the 3,4-additions are slightly increased by pressure. In this case, too, the major variations occur when the polymerization is carried out in heptane. In the other solvents the changes are less pronounced and disappear completely in dioxane (0.65 for 3,4-addition and 0.20 for 1,4-trans-addition at any pressure).

The absence or the low proportion of 1,2-units may be easily explained by the steric hindrance of the methyl group in C_2 . It seems that pressure is able to overcome this steric hindrance in the case of heptane, at least to a small extent (0.10 to 0.15), since no pressure effect on this type of addition is observed in the case of dioxane.

As a consequence, pressure leads to a structural heterogeneity of anionic polyisoprenes obtained in heptane and appears to act like a solvent such as dioxane where contact ion pairs are produced, probably by influencing the association equilibria of the growing chain.

Effect of Pressure on Anionic Polymerization in Dioxane-Heptane Mixtures

When studying the influence of the volumic ratio (heptane/dioxane) at constant pressure, we observed significant alterations of the structure

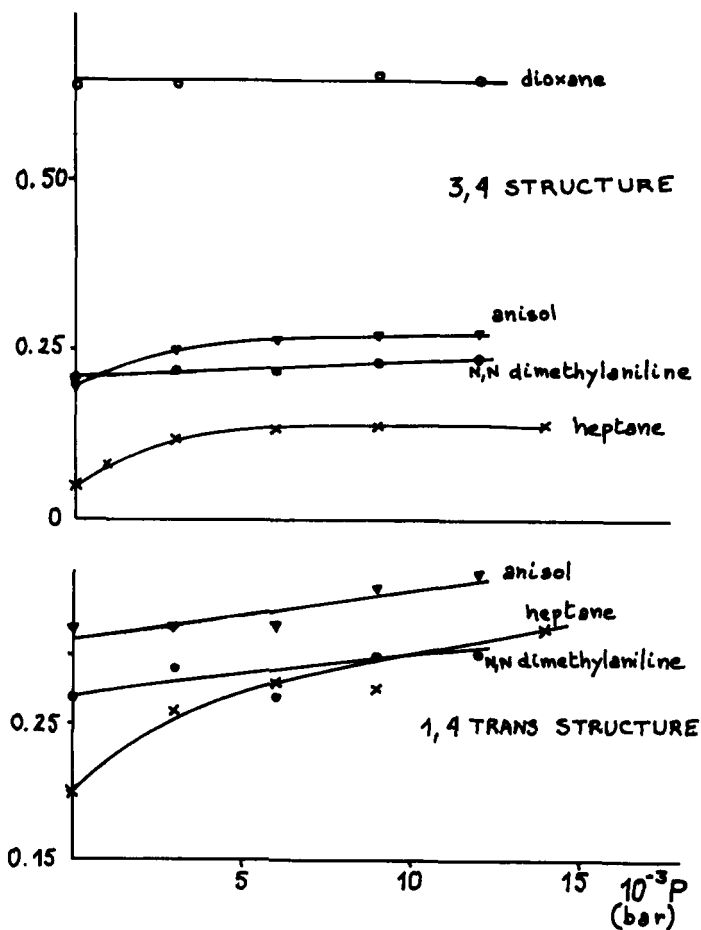


FIG. 1. Influence of pressure upon the concentrations of 1,4-trans and 3,4-additions in the anionic polymerization of isoprene. (The concentration in 1,4-trans units in dioxane is not indicated since it is not pressure dependent.)

which occur essentially when adding dioxane to the initial reaction mixture. Thus a low concentration of contact ion pairs is sufficient to produce a structure change affecting mainly the 1,4-cis- and 3,4-additions (Fig. 2).

The magnitude of these modifications is highest at low pressures.

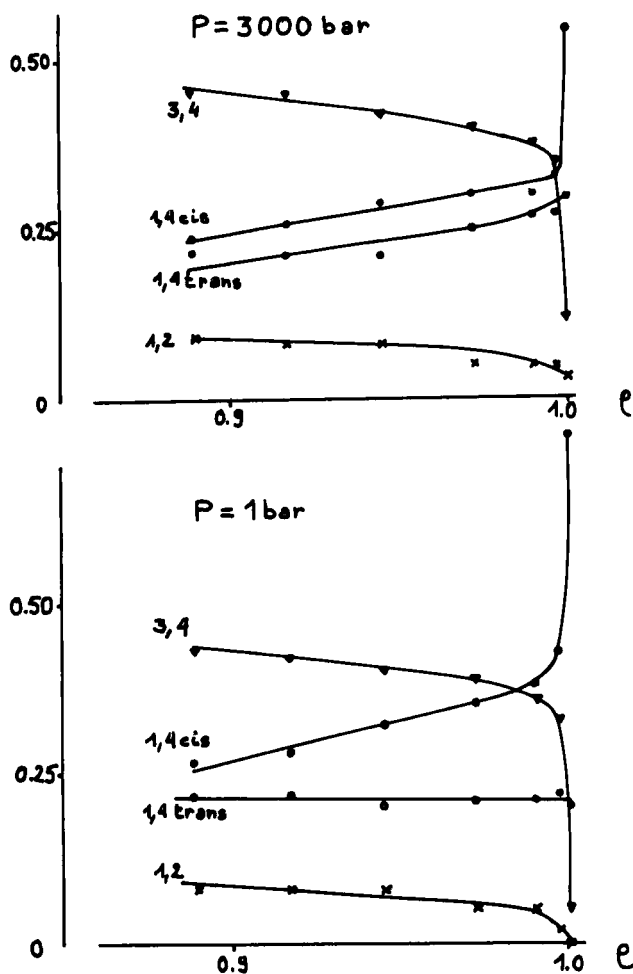


FIG. 2. Variations of the microstructure of anionic polyisoprene in heptane-dioxane mixtures as a function of ρ [$\rho = V_{\text{heptane}} / (V_{\text{heptane}} + V_{\text{dioxane}})$].

For a volumetric ratio $\rho = 0.997$, the concentration of 1,4-cis-units falls from 0.75 to 0.43 at 1 bar, whereas under 3000 bar the decrease is only from 0.55 to 0.33. The variations with ρ are less spectacular, but nevertheless observed in anisole-heptane mixtures [5b].

Discussion: The Effect of Pressure

The propagation steps of the four possible additions are characterized by overall propagation rate constants which are composite quantities, i.e., the sum of the rate constants for the different propagation steps corresponding to each type of ionic species and by an overall activation volume which may be split into two terms:

$$\Delta V^\ddagger = \Delta V_c^\ddagger + \Delta V_e^\ddagger$$

ΔV_c^\ddagger is the change in volume resulting mainly from changes in bond length, changes in the nonbonded interactions within the molecules, and changes in electron densities around nuclei. Thus ΔV_c^\ddagger is the change in volume resulting from modifications in the geometry of the molecules when the transition state is formed.

ΔV_e^\ddagger is an electrostatic term and represents the accompanying volume change due directly to the modified interaction between the surrounding molecules of solvent and the reacting molecules when they form the transition state.

It is obvious that in the presence of ionic species as they exist in anionic polymerizations, the solvent influences the value of ΔV_e^\ddagger and hence that of ΔV^\ddagger . Pressure thus seems to act as an intensifier of the electric field, and its apparent role is quite similar to that of a solvent; i.e., favoring the appearance of an electric dipole between the gegenion and the end of the growing chain.

In order to determine whether or not steric effects favoring 3,4- and 1,4-trans-additions may occur, we investigated the influence of pressure on the structure of the polymers obtained by polymerizing isoprene with an aqueous solution of hydrogen iodide [12]. The mechanism of this polymerization is believed to be pseudocationic. If this is true, the electrostatic effects in such a system should be much weaker than in anionic polymerizations. The pressure effect upon the structure of such polymers is shown in Fig. 3.

It is apparent that 1,4-cis-units fully disappear at sufficiently high pressures. It follows that, apart from electrostatic considerations, steric hindrance occurs in the transition state for the 1,4-cis-addition.

Finally we asked ourselves whether or not the structure changes induced by pressure really occur during the course of the reaction and if an isomerization, 1,4-cis \rightarrow 1,4-trans, could take place under high pressure.

A priori, this not impossible since the 1,4-cis-polymer has a lower density than the trans isomer. Hence pressure should influence the formation of the latter isomer positively. We therefore submitted samples of polyisoprenes containing high amounts of 1,4-cis-units to pressure with and without added n-butyllithium (BuLi) (Table 2).

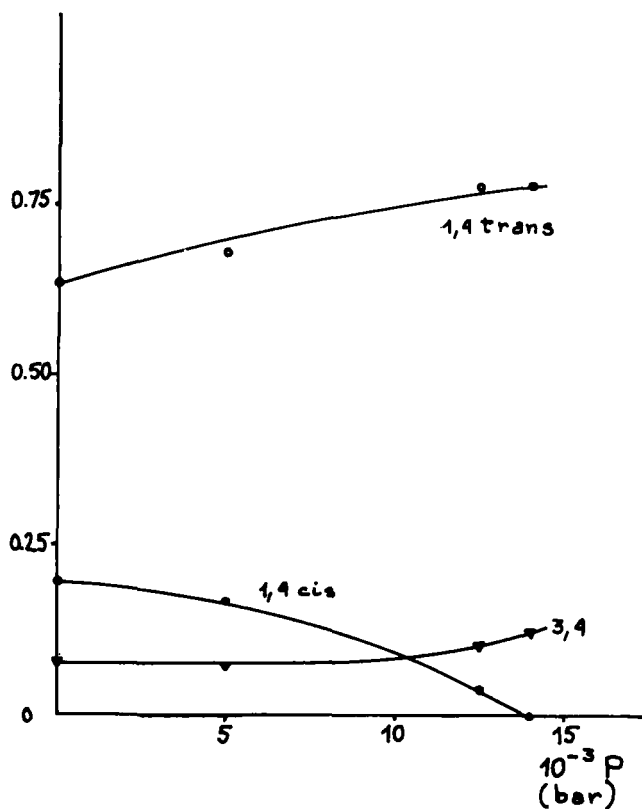


FIG. 3. Influence of pressure on the polymers formed in the polymerization of isoprene with an aqueous solution of HI (in bulk or in any solvent). (The concentration in 1,2 units (0.08) is independent from pressure.)

The initial structure remained unchanged after these compression tests. Obviously there is no isomerization from 1,4-cis into 1,4-trans, and *n*-butyllithium does not act as an isomerization catalyst. Consequently, structural changes are induced by pressure exclusively during the polymerization reaction.

TABLE 2. Compression of Solutions of cis-Polyisoprenes (isomerization attempts at 20°C)^a

Pressure (bar)	Catalyst	Solvent ^b	Time (hr)
1	BuLi	Toluene	24
10,000	None	Toluene	1
10,000	BuLi	Toluene	1

^aInitial structure: 0.78 (1,4-cis), 0.14 (1,4-trans), 0.08 (3,4), and 0.00 (1,2).

^bThe same attempts have also been carried out in tetrahydrofuran. The polymer became insoluble.

CONCLUSION

It appears that pressure probably affects the separation and the delocalization of the ionic charges in the polymerization of isoprene initiated by n-butyllithium. Pressure presumably enhances the ionic character of the reaction and allows the formation of contact ion pairs even in nonsolvating solvents such as heptane. On the other hand, steric effects are revealed by the reduction of the 1,4-cis-addition. From this point of view, pressure produces its effect during the formation of the transition state, since the structure of the polymer is determined as soon as it is formed and is insensitive to further pressure variations.

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REFERENCES

- [1] C. Rogers, *Amer. Chem. Soc., Div. Polym. Chem.*, **2**, 75 (1961).
- [2] H. Hsieh, *J. Polym. Sci., A-1*, **3**, 181 (1965).
- [3] D. Worsfold and S. Bywater, *Can. J. Chem.*, **42**, 2884 (1964).

- [4] A. Tobolsky and C. Rogers, J. Polym. Sci., **40**, 73 (1959).
- [5] (a) G. Jenner, Bull. Soc. Chim. Fr., **1966**, 3133. (b) G. Jenner, J. Hitzke, and M. Millet, Ibid., **1970**, 1183.
- [6] S. Winstein and R. Robinson, J. Amer. Chem. Soc., **80**, 169 (1958).
- [7] A. Essel and Quang Tho Pham, J. Polym. Sci., **A-1**, **10**, 2793 (1972).
- [8] M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Wiley-Interscience, New York, 1968, p. 476.
- [9] J. Kennedy and A. Langer, Advan. Polym. Sci., **3**, 508 (1964).
- [10] F. Schué, D. Worsfold, and S. Bywater, Macromolecules, **3**, 509 (1970).
- [11] J. Kistler, G. Friedmann, and B. Kaempfer, Bull. Soc. Chim. Fr., **1967**, 4759.
- [12] H. Abdi-Oskoui, G. Jenner, and C. Brun, Makromol. Chem., **164**, 149 (1973).

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