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POLYMERIZATION KINETICS OF ISOPRENE INITIATED BY 1,1′-DIPHENYL-*n*-HEXYL-LITHIUM

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Abstract—The kinetics of the anionic polymerization of isoprene in *n*-hexane and benzene initiated by 1,1′-diphenyl-*n*-hexyl-lithium have been studied. The propagation step is shown to be of first order with respect to monomer and of order 1/4 with respect to the total polyisoprenyl-lithium. It has been shown also that there exists an equilibrium between monomeric and associated species of poly-*iso*prenyl-lithium. The energy of activation for the propagation is about 19 kcal/mol. The microstructure of the resulting polyisoprene has been studied by NMR; these polymers are basically copolymers of the structural units *cis*-1,4 and *trans*-1,4, predominantly the first; the nature of the polymers is similar to that of natural rubber.

INTRODUCTION

THE POLYMERIZATION of isoprene in hydrocarbon solvents with organolithium compounds as initiators has received considerable attention in the past few years, particularly from a kinetic point of view. The initiation and propagation steps have been studied, mainly the latter.(1–12) The kinetics in both steps are complicated by the presence of alkyl-lithium in the form of agglomerates $(RLi)_n$ in which the monomeric units RLi are strongly bonded.(13–15) This may give rise to similar propagation and initiation rates, as happens when *n*-butyl-lithium is used as initiator. In this case either spectrophotometric(5,6) or gas chromatographic techniques(2) can be employed to study separately both polymerization steps. Another method has been the addition of a living polymer of low mol. wt. to the monomer.(4,7,16) This "seeding" technique must secure the total conversion of the initiator into low mol. wt. polymer. Otherwise, the results obtained could possibly be ambiguous, as in the case of Morton's work(3,4,15) according to Szwarc.(15)

The association occurs also for the living polymer in hydrocarbon solvents, complicating the propagation step. The rate of propagation follows the law

$$-\frac{d(M)}{dt} = k_a(RLi)_0^r(M),$$

$(RLi)_0$ being the total concentration of all the poly(isoprenyl-lithium) species present in the system, (M) is the concentration of monomer after time t, and k_a and r are constants.

There is almost complete agreement on the interpretation of this result by accepting an equilibrium

$$(RLi)_n \rightleftarrows n\ RLi$$

between the associated and monomeric forms of the polyisoprenyl-lithium, the latter

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being the only active species from a kinetic viewpoint. The equilibrium written above limits the rate of propagation in a way such that $r = 1/n$. On the other hand, as the degree of association in hydrocarbon solvents is independent of these solvents, agreement would be expected among the values of r. But this is not the case therefore the existence of dimers(3,4,6,16) trimers and hexamers(17) and tetramers(2,5,7) has been accepted.

In the present work, the initiator has been 1,1′-diphenyl-*n*-hexyl-lithium (DPHLi), which shows weak association owing to the presence of benzene groups, so allowing the study of the propagation independently of the initiation step. Two solvents have been used, viz. *n*-hexane (aliphatic) and benzene (aromatic). Special attention has been paid to the determination of r by a statistical method. Finally, the influence of reaction conditions on the microstructure of the polymer has been examined.

EXPERIMENTAL

Solvents and monomers were carefully purified. Benzene and *n*-hexane (Merck A.R.) were kept in conc. sulphuric acid for 1 week, with stirring. After several washings and drying, they were rectified in a fractionating column, and collected on calcium hydride. The reservoir was connected to the high vacuum line. The solvents were degassed and kept in contact with butyl-lithium. They were distilled immediately before use from this reservoir.

Isoprene (Fluka) was twice fractionally distilled at normal pressure to separate the inhibitor; it was dried initially on calcium hydride, and was kept in contact with fresh *n*-butyl-lithium at room temperature for 0·5 hr each time.

The initiator was prepared from *n*-butyl-lithium. The latter was prepared by reaction of Li metal, *n*-butyl chloride in hexane and 1,1′-diphenyl-ethylene (Fluka).(18) The resulting compound was purified by vacuum distillation on a sodium mirror. Further partition of the initiator solution either in *n*-hexane or in benzene was carried out by means of an apparatus similar to that already described.(19) Analysis was carried out following Gilman's method(20) by potentiometric titration; in other cases, the method followed was addition of CH_3I and titration of the resulting LiI by Volhard's method.

The experimental technique for polymerization was an improvement over that previously reported:(19) silicone joints were practically eliminated and replaced by direct glass sealing and breakable ampoules. The pyrex glass, from which the high vacuum line and related reservoirs (bulbs and reaction vessels) were made, was conveniently cleaned by conventional means before using. Then the glass vessels were submitted to high vacuum (10^{-5} mm Hg) for at least 6 hr before use. The inner walls of the vessels were then carefully washed with a conc. solution of *n*-butyl-lithium in *n*-hexane.

Kinetic experiments were carried out by dilatometry. The dilatometer was a modification of Pepper's type.(21) After filling and degassing the contents, the dilatometer was cut off the line and placed in a thermostated bath controlled to better than ± 0·01°. The contraction was followed by means of a precision cathetometer.

The microstructure of the polymers was determined by NMR spectroscopy (Perkin–Elmer instrument operating at 60 MHz). The polymers were dissolved in benzene.

RESULTS AND DISCUSSION

The kinetic experiments were carried out at 30° for both solvents, *n*-hexane and benzene. Initiation starts immediately and is complete in 3–10 min, according to the $(RLi)_0$, as can be observed from the disappearance of the red colour of the initiator. This gives rise to a slight initial curvature in the plot of log a vs. t, where $a = (h_0 - h_\infty)/(h_t - h_\infty)$, and $(RLi)_0$ values are close to 10^{-2} M. (h_0, h_t and h_∞ are the heights of the meniscus in the dilatometer at times zero, t and final.) In these cases, the reaction was followed up to several times the half-life; no deviations from linearity were observed, showing that the initiation was complete. Once the initiator was used up, the solution became entirely colourless in *n*-hexane, but a slightly yellow colour remained in benzene throughout. (This faint colour was also observed in experiments using *sec*-butyl-lithium in benzene, but not in *n*-hexane.)

Figure 1 shows experimental data on the rate of propagation. Straight lines are obtained when plotting log a vs. t, meaning that the rate of polymerization is given by

$$-\frac{d(M)}{dt} = k_0(M)$$

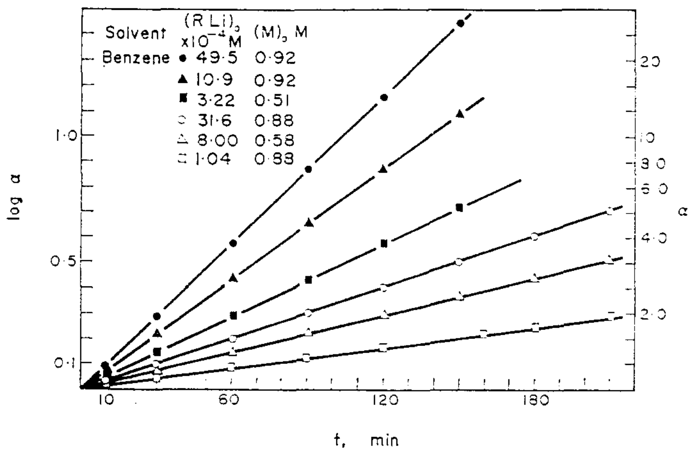

FIG. 1. First order linear plots for the propagation of polyisoprenyl-lithium at 30°.

k_0 being the observed rate constant. This constant depends on $(RLi)_0$. Assuming a relationship of the type

$$k_0 = k_a(RLi)_0^r$$

the exponent r can be evaluated. Figure 2 shows the plot of log k_0 vs. log $(RLi)_0$, for both solvents. Results from other sources are also included (in benzene, from Cramond *et al.*,(6) and from Margerison *et al.* activation energies and k_0 values.(7) Results in other solvents have been collected by Bywater.(1)

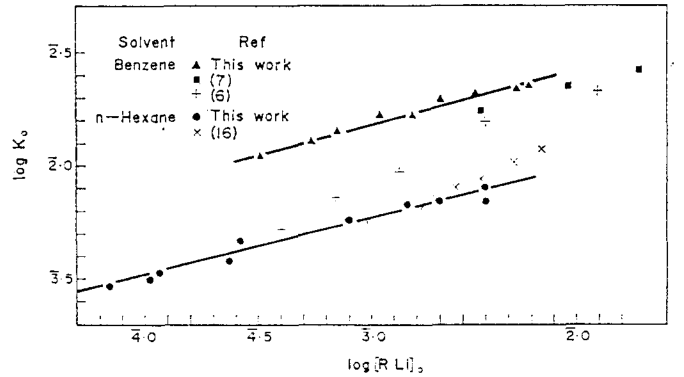

FIG. 2. Rate of propagation as a function of the total concentration of polyisoprenyl-lithium at 30°.

It can be observed that our results give a straight line plot (cf. Fig. 2) over the range of $(\mathrm{RLi})_0$ employed, both in benzene and *n*-hexane. The best fitting to the line $\log k_0 = \log k_a + r \log (\mathrm{RLi})_0$ in both solvents was obtained by least squares. The correlation coefficient c for the straight lines was evaluated, as well as the confidence limits at 95 per cent level for $1/r$, considering eight (*n*-hexane) and seven (benzene) degrees of freedom. Results from other sources are also reported in Table 1.

TABLE 1. STATISTICAL ANALYSIS OF THE PROPAGATION REACTION OF POLYISOPRENYL-LITHIUM IN HYDROCARBONS

Solvent	$\log k_a$	r	c	Confid. limits 95% for $1/r$ upper	lower	Reference
n-Hexane	$\bar{2}$·504	0·246	0·948	5·24	3·32	This work
Benzene	$\bar{2}$·963	0·260	0·979	4·24	3·52	This work
Benzene	—	0·306	—	4·7	1·8	(7)

The high values of c point to the fact that a high linear correlation exists between the variables plotted in Fig. 2; this means that the following equation is satisfied

$$k_0 = k_a(\mathrm{RLi})_0^{1/4}. \tag{1}$$

$r = 1/4$ is the closest fractional value to 0·246 and 0·260. We can write then for propagation:

$$-\frac{\mathrm{d}(M)}{\mathrm{d}t} = k_a(\mathrm{RLi})_0^{1/4}(M). \tag{2}$$

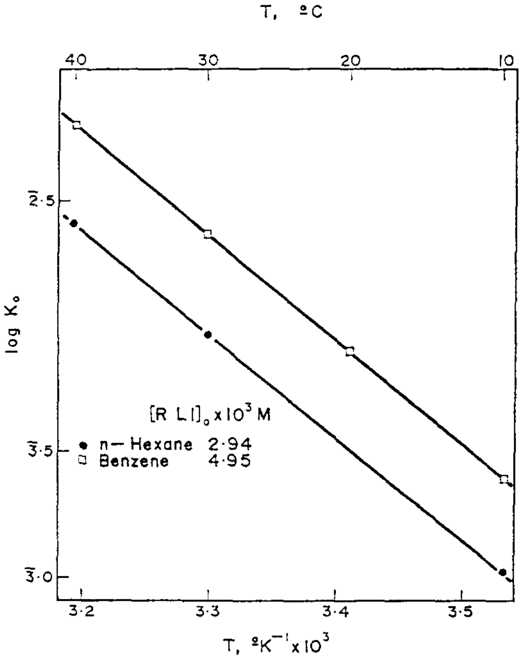

FIG. 3. Rate of propagation as a function of the temperature at $(\mathrm{RLi})_0$ constant.

The influence of temperature was studied between 10 and 40°, keeping constant $(\mathrm{RLi})_0$ and $(M)_0$ in each solvent. Figure 3 shows the plot of log k_0 vs. $1/T$, both in n-hexane $[(\mathrm{RLi})_0 = 2{\cdot}92 \times 10^{-3};\ (M)_0 = 0{\cdot}94)]$ and benzene $[(\mathrm{RLi})_0 = 4{\cdot}95 \times 10^{-3};\ (M)_0 = 0{\cdot}92]$. For each solvent we can write therefore,

$$k_0 = A_0 \exp(-E_0/RT).$$

A similar expression could be written for k_a. Considering Eqn. (1), it follows that

$$A_a = A_0(\mathrm{RLi})_0^{1/4} \tag{3a}$$

$$E_a = E_0. \tag{3b}$$

Table 2 collects several data from this and other sources. Our A_a values have been calculated from Eqn. (3a).

TABLE 2. EFFECT OF TEMPERATURE ON THE PROPAGATION RATE IN HYDROCARBONS

Solvent	A_a	E_a (kcal/mol)	Reference
n-Hexane	$8{\cdot}9 \times 10^{11}$	18·6	This work
Benzene	$3{\cdot}0 \times 10^{12}$	18·9	This work
	$1{\cdot}8 \times 10^{12}$	18·5	(7)
	$1{\cdot}0 \times 10^{9}$	13·3	(6)

The microstructure of the polyisoprene was determined by the method of Chen.(22) The influence of $(\mathrm{RLi})_0$ at constant $(M)_0$ and temperature, as well as that of temperature, was studied. Fig. 4(a) and (b) show the per cent configuration (*cis*- and *trans*-1,4) vs. log $(\mathrm{RLi})_0$, for both solvents. Figure 5 shows the influence of temperature on the microstructure.

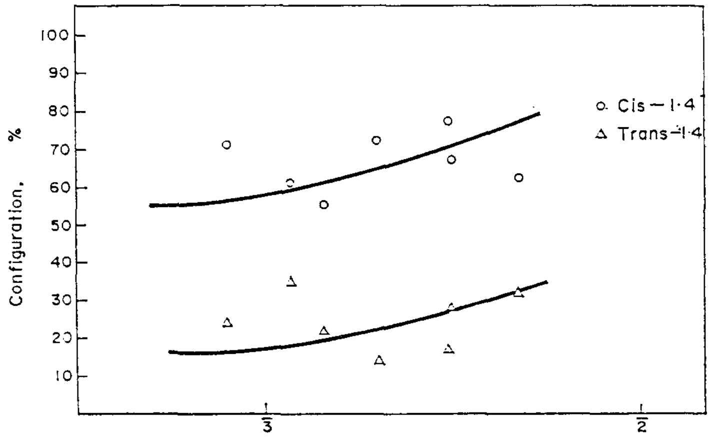

Fig 4A

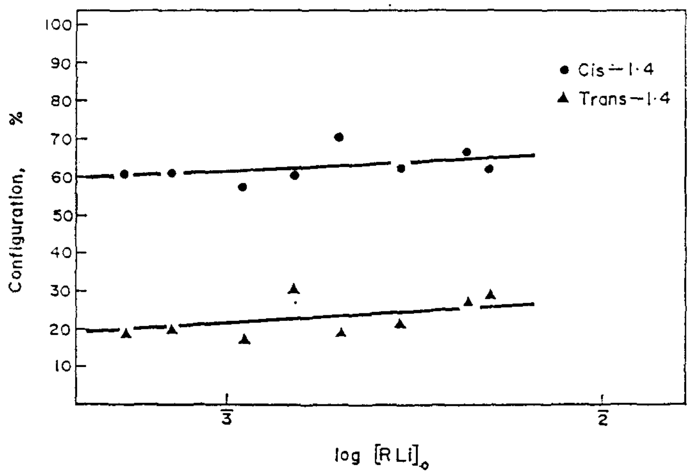

Fig. 4B

FIG. 4. Microstructure of the polyisoprene prepared in: (a) *n*-hexane, (b) benzene, at 30°.

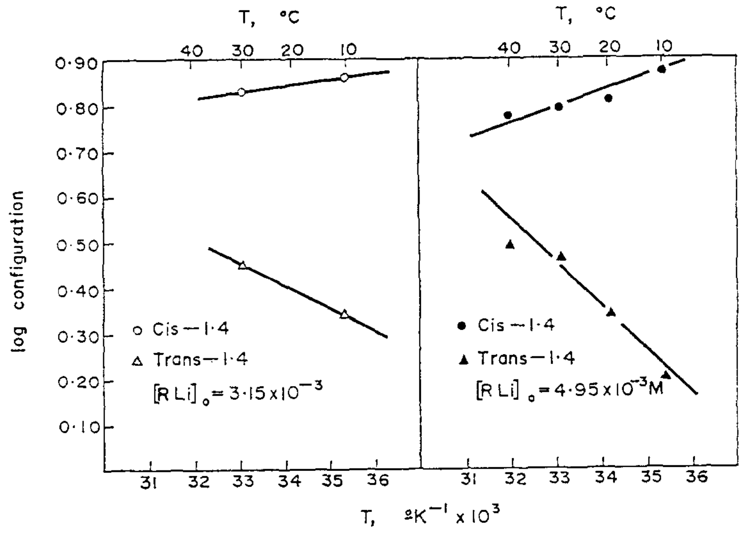

FIG. 5. Microstructure of polyisoprene prepared in: (a) *n*-hexane, (b) benzene, as a function of the temperature.

DISCUSSION

The initiation reaction in both solvents is slower than in other systems of anionic polymerization but it is fast enough to yield a fairly large ratio of rate of initiation to rate of propagation, so as to reach a stationary concentration of active ends in a comparatively short time.

The observation of a non-instantaneous initiation points to the existence of DPHLi aggregates in both solvents. This association seems to be weaker than that of polyisoprenyl-lithium (PILi), meaning that the equilibrium

$$(\mathrm{DPHLi})_n \rightleftarrows n(\mathrm{DPHLi})$$

is displaced to the right to a greater extent than that of the polymeric chains. Assuming that the active species for initiation are monomeric, the next step would be

$$\mathrm{DPHLi} + M \rightarrow \mathrm{DPH}(M)\mathrm{Li}$$

and this would give rise to a rate of initiator consumption

$$-\frac{\mathrm{d}(\mathrm{DPHLi})}{\mathrm{d}t} = k_i(\mathrm{DPHLi})_0{}^{1/n}(M)$$

$(\mathrm{DPHLi})_0$ being the total concentration of the initiator originally present.

The results of Bywater and Worsfold$^{(12)}$ on the initiation of the polymerization of isoprene and styrene by *sec*-butyl-lithium show that the mechanisms are different in cyclohexane and in benzene. Using DPHLi as initiator, we have not found significant differences between *n*-hexane and benzene. Particularly, we have not found induction periods in *n*-hexane, as shown by the sudden change in the colour intensity of the red solution of DPHLi when added to the isoprene. There is little doubt that a great difference in structure between *sec*-butyl-lithium and DPHLi seems to be responsible for the observation. Thus, the presence of two phenyl groups at the C atom close to the Li counter-ion may be the reason for the increase in the ionic character of the C—Li bond, and as a consequence the association of the ion-pair $\mathrm{R{-}C^-, Li^+}$ is probably of little importance in hydrocarbon solvents.

The straight line plots log α vs. t (cf. Fig. 1) show in effect that the initiation is complete in a very few minutes, that propagation is first order with regard to the monomer, and that there is negligible destruction of active species. From Figs. 1 and 2 equation (2) is obtained. This result together with the viscosity measurements reported elsewhere$^{(23)}$ prove that the propagation step can be formulated thus:

$$(\mathrm{RLi})_4 \rightleftarrows 4(\mathrm{RLi}); \quad K_D = \frac{(\mathrm{RLi})^4}{[(\mathrm{RLi})_4]} \tag{4a}$$

$$(\mathrm{RLi}) + M \rightarrow \mathrm{R}(M)\mathrm{Li}; \quad -\frac{\mathrm{d}(M)}{\mathrm{d}t} = k_p(\mathrm{RLi})(M) \tag{4b}$$

k_p being the true propagation constant, K_D is the dissociation constant for the equilibrium tetramers $\rightleftarrows$ monomers, and RLi represents an active growing chain. M is the isoprene unit.

The tetrameric species $(\mathrm{RLi})_4$ may be considered as "dormant" polymers, while the monomeric forms (RLi) are the active species or "living" polymers. Owing to the solvent nature, it can be expected that such active species are contact ion-pairs, which can be represented by .... $\mathrm{C^-, Li^+}$.

Comparing Eqns. (2), (4a) and (4b) with (5),

$$(\mathrm{RLi})_0 = 4(\mathrm{RLi})_4 + (\mathrm{RLi}) \tag{5}$$

one arrives at

$$(\mathrm{RLi})^4 + (1/4)\,K_D(\mathrm{RLi}) - (1/4)\,K_D(\mathrm{RLi})_0 = 0. \tag{6}$$

The concentration of active species could be found if K_D and $(\mathrm{RLi})_0$ were known. From Eqns. (2) and (4b), one gets:

$$k_0 = k_a(\mathrm{RLi})_0{}^{1/4} = k_p(\mathrm{RLi}). \tag{7}$$

Under condition $(\mathrm{RLi}) \leqslant (\mathrm{RLi})_0$, it can be simplified. From Eqn. (5):

$$(\mathrm{RLi})_0 \cong 4(\mathrm{RLi})_4$$

and from 4(a)

$$(\mathrm{RLi}) = K_D{}^{1/4}(\mathrm{RLi})_4{}^{1/4}.$$

Combining these last two equations, one obtains:

$$(\mathrm{RLi}) \cong \frac{\sqrt{2}}{2}\,K_D{}^{1/4}(\mathrm{RLi})_0{}^{1/4}.$$

and from this and Eqn. (7),

$$k_0 = k_p(\mathrm{RLi}) \cong \frac{\sqrt{2}}{2}\,k_p\,K_D{}^{1/4}(\mathrm{RLi})_0{}^{1/4}. \tag{8}$$

At a given temperature, therefore:

$$k_0 = \mathrm{const}\,(\mathrm{RLi})_0{}^{1/4}, \quad \text{for } (\mathrm{RLi}) \leqslant (\mathrm{RLi})_0.$$

From Fig. 2, it is shown that this is the situation in the case of *n*-hexane [$(\mathrm{RLi}) \leqslant (\mathrm{RLi})_0$] for the entire range of $(\mathrm{RLi})_0$ investigated, but in the case of benzene a slight curvature could also fit the experimental points. This could be explained if the tetrameric aggregates dissociate more in benzene, giving rise to a larger value of (RLi), than in *n*-hexane.

From Eqns. (7) and (8):

$$k_a = \frac{\sqrt{2}}{2}\,k_p\,K_D{}^{1/4}. \tag{9}$$

k_a values are reported in Table 1, at 30° and for each solvent. Therefore, from Eqn. (9):

$$k_p\,K_D{}^{1/4} = 13{\cdot}0 \times 10^{-2}\ \text{(benzene)}$$

$$k_p{}'\,K_D{}'^{1/4} = 4{\cdot}51 \times 10^{-2}\ (n\text{-hexane}).$$

Since no reliable values for the K_D's are known, it can be written:

$$\left(\frac{k_p}{k_p{}'}\right)\left(\frac{K_D}{K_D{}'}\right)^{1/4} \cong 3. \tag{10}$$

The greater rate observed in the case of benzene could originate in a larger dissociation of the aggregates ($K_D > K'_D$), in a higher rate ($k_p > k'_p$) or in both. In the limiting case, when $k_p = k'_p$, K_D/K'_D would be about 3^4, that is, the dissociation constant would be about one-hundred times higher in benzene than in *n*-hexane.

The temperature dependence of the reaction rate in both solvents has been studied at $(\text{RLi})_0 > 10^{-3}$ M; this is high enough to expect that $(\text{RLi}) \ll (\text{RLi})_0$, and in these conditions, from Eqn. (9):

$$E_a = E_p + \frac{\Delta H_D}{4}, \tag{11}$$

E_p being the true activation energy corresponding to Eqn. 4(b), and ΔH_D the heat of dissociation corresponding to the equilibrium (4a). The apparent activation energies in both solvents are very similar and agree fairly well with the data given by Margerison *et al.*(7) in benzene.

Over the range of $(\text{RLi})_0$ investigated, we have not observed any influence on the microstructure of the polyisoprene [cf. Fig. 4(a) and (b)]. As $(\text{M})_0$ was a constant in each solvent, it can be concluded that the configuration is independent of the molecular size, as expected. Also, the change from *n*-hexane to benzene does not influence the microstructure of the polymers.

On the other hand, low temperature favours the *cis*-1,4 configuration, at the expense of *trans*-1,4, that is, the activation energy of the combined processes leading to the *cis*-configuration is less than that corresponding to the *trans*-one.

It is worth mentioning that the *cis*-1,4 contents obtained in this work are generally lower than those reported by other authors for similar conditions.

Recently, Morton *et al.*(24) have measured by light scattering the molecular weight of "active" polyisoprenyl-lithium polymerized in *n*-hexane. Their data show that the ratio of $\bar{M}_w$ for the active and terminated polymers is equal to 2; it follows that the "active" polymeric species are associated in pairs. If this association number does not change in the presence of isoprene monomer (a point which has not been proved, but is likely to occur due to the relative slowness with which this monomer polymerizes), it is clear that the kinetic order and the degree of association are not directly related and, therefore, that the propagation would not follow the simple kinetic scheme given in (4a) and (4b).

In addition, simple rate measurements would not be sufficient to explain the mechanism which, on the other hand, should account for the drastic modification introduced in the microstructure of the polymer when the polarity of the solvent changes.

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Résumé—On a étudié les cinétiques de la polymérisation anionique de l'isoprène dans le *n*-hexane et le benzène amorcée par diphényl 1-1'-*n*-hexyllithium. On a montré que l'étape de propagation est du premier ordre par rapport au monomère et d'ordre 1/4 par rapport au polyisoprényl-lithium global. On a montré également qu'il existe un équilibre entre des espèces monomériques et associées du polyisoprényl-lithium.

L'énergie d'activation de la réaction de propagation est d'environ 19 kcal/mol. On a étudié par RMN les microstructures du polyisoprène formé. Ces polymères sont principalement des copolymères d'unités structurales *cis*-1,4 et *trans*-1,4 avec une prédominance des premières. La nature des polymères est semblable à celle du caoutchouc naturel.

Sommario—Siè stu diata la cinetica della polimerizzazione anionica di isoprene in *n*-esano e in benzene iniziata da 1,1'-difenil-*n*-esil-litio. Si mostra come la fase di propagazione sia di primo ordine rispetto al monomero e di ordine 1/4 rispetto il poliisoprenil-litio totale. Si è mostrato pure che esiste un equilibrio tra le specie e quelle associate di poliisoprenil-litio. L'energia di attivazione per la propagazione è di circa 19 kcal/mol. Si è studiata la microstruttura del risultante poliisoprene mediante NMR; tali polimeri sono basilarmente dei copolimeri di unità strutturale *cis*-1,4 e *trans*-1,4, con prevalenza del primo; la natura dei polimeri è simile a quella della gomma naturale.

Zusammenfassung—Die Kinetik der durch 1,1'-Diphenyl-*n*-hexyl-Lithium initiierte anionische Polymerisation von Isopren und *n*-Hexan und Benzol wurde untersucht. Der Wachstumsschritt ist, wie gezeigt wurde, 1. Ordnung in Bezug auf das Monomere und 1/4 Ordnung in Bezug auf das gesamte Polyisoprenyl-Lithium. Es wurde außerdem festgestellt, daß ein Gleichgewicht besteht zwischen der monomeren und der assoziierten Spezies von Polyisoprenyl-Lithium. Die Aktivierungsenergie für das Wachstum ist etwa 19 kcal/Mol. Die Mikrostruktur des entstehenden Polyisoprens wurde durch NMR untersucht; diese Polymeren sind im Grunde Copolymere aus *cis*-1,4 und *trans*-1,4 Struktureinheiten, über wiegend *cis*-1,4. Die Polymeren sind ihrer Art nach ähnlich mit natürlichem Kautschuk.