Anionic polymerization initiated by the lamellar compounds of Lic$_{12}$:
2. Thermodynamics and the propagation mechanisms in 1,4 *Cis* and 1.4 *Trans* of isoprene, –H–n.m.r. study

E. Loria, J. Gole and J. P. Pascault
Laboratoire des Matériaux Macromoléculaires, Era 745–403/*Insa*–69621, *Villeurbanne, France*

and Q. T. Pham
Laboratoire des Matériaux Organiques, CNRS, BP 24–69300 *Vernaison, France*

and I. B. Rashkov
Central Laboratory for Polymers, Bulgarian Academy of Sciences, Sofia, 1113, *Bulgaria*
(*Received* 28 *April* 1980)

The polymerization of isoprene initiated by LiC$_{12}$ in cyclohexane yields polymers whose microstructures are quite different from those obtained in homogeneous media. These microstructures change during the reaction. For the low yields, the polymer may contain up to 96% 1,4 *cis*. The evolution of the microstructure with the mass of the polymer formed per g of initiator is also temperature dependent. With certain types of 'ternary' lamellar compounds it is possible to obtain (at high yields) polymers with a high content of 1,4 *cis*. A mechanism of polymerization is proposed that takes into account the influence of one (or more) graphite layer over the interactions between the lithium cation of the growing living end and the monomer.

INTRODUCTION

The microstructures of polyisoprenes and polybutadienes initiated in cyclohexane by the lamellar compounds of the alkali metals and the graphite, are different from those obtained in an anionic polymerization in homogeneous media. Evidence for this arose from earlier work[1,2] concerning the polymerization initiated by LiC$_{12}$, NaC$_{52}$ and KC$_{24}$ (*Table 1*). It seems that the best initiators for the polymerization are the second stage compounds. In compounds with the higher concentration of metal inside the graphite layers (first stage compounds) like LiC$_6$, KC$_8$ and BaC$_6$, no polymer is formed after several days of reaction. However, the compounds with the lower concentration of metal inside the graphite layers, react at a slow rate compared with that of the second stage compounds, but the microstructure is no longer modified whatever the stage of the compound (KC$_{24}$ or KC$_{36}$ for instance).

As reported earlier[1,2], the interlayer distance in the binary lamellar compounds has an influence over the microstructure of the obtained polymer. We tried, in the

Table 1 Results for the polymerization of isoprene initiated by different insertion compounds in cyclohexane (T = 15°C)

<table>
<tr><th rowspan="2">Initiator weight (g)</th><th rowspan="2">Time (<i>h</i>)</th><th rowspan="2">Yield (%)</th><th rowspan="2">$\bar{M}_n.10^{-3}$</th><th colspan="4">Microstructure</th></tr>
<tr><th>1,4 <i>cis</i></th><th>1,4 <i>trans</i></th><th>1,2</th><th>3,4</th></tr>
<tr><td>Li$^+$</td><td colspan="3">Homogeneous (solvent CH)</td><td>73</td><td>22</td><td>0</td><td>5</td></tr>
<tr><td>LiC$_{12}$ Ceylan, 0.136</td><td>21</td><td>13</td><td>343</td><td>84</td><td>12</td><td>0</td><td>4</td></tr>
<tr><td>LiC$_{12}$ Madagascar, 0.149</td><td>24</td><td>82</td><td>230</td><td>37</td><td>37</td><td>0</td><td>26</td></tr>
<tr><td>Na$^+$</td><td colspan="3">Homogeneous (solvent CH)</td><td colspan="2">44</td><td>6</td><td>50</td></tr>
<tr><td>NaC$_{52}$ Ceylan, 0.042</td><td>163</td><td>11</td><td>98</td><td colspan="2">27</td><td>0</td><td>73</td></tr>
<tr><td>K$^+$</td><td colspan="3">Homogeneous (solvent CH)</td><td>22</td><td>37</td><td>5</td><td>36</td></tr>
<tr><td>KC$_8$ Madagascar</td><td>–</td><td>0</td><td>–</td><td>–</td><td>–</td><td>–</td><td>–</td></tr>
<tr><td>KC$_{24}$ Madagascar, 0.135</td><td>24</td><td>100</td><td>310</td><td colspan="2">38</td><td>5</td><td>57</td></tr>
<tr><td>KC$_{36}$ Madagascar, 0.198</td><td>120</td><td>76</td><td>244</td><td colspan="2">44</td><td>6</td><td>50</td></tr>
</table>

0032–3861/81/101419–06$02.00

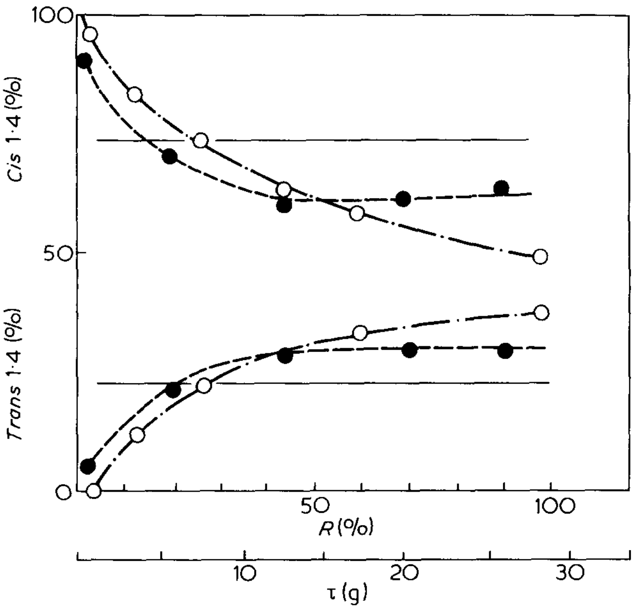

Figure 1 Variation of polyisoprene microstructures as a function of the yield initiated by LiC_{12} in cyclohexane at 15°C: (●), LiC_{12} Madagascar; (○), LiC_{12} Ceylan; (——), results in homogeneous ionic polymerization

present work, to go into further detail concerning the influence of the degree of advancement of the reaction, the temperature, and the complexation of the cation inside the graphite layers over the microstructure of polyisoprenes initiated in cyclohexane (or in methyl-cyclohexane) by LiC_{12}.

EXPERIMENTAL

The preparation of the initiator, the purification of the monomer and the solvents then the recuperation of the polymer formed were described precisely in a previous paper[3] as well as the molecular weight measurements. The ^1H-n.m.r. spectra of the polyisoprenes were realized with a Varian XL 100 equipped with an accumulation system by Fourier transform. The total percentage of 1,4 units is calculated from the resonance of olefinic protons; the 1,4 *cis*, *trans* proportions from the resonance of aliphatic protons.

Preparation of the ternary lamellar compounds $LiC_{12}D_X$ also used as initiators.

The ternary graphites were prepared according to the reaction $LiC_{12} + nD \rightarrow LiC_{12}D_X + n'D$, putting into contact the binary graphite LiC_{12} with the complexing agent D pure or dissolved in cyclohexane or benzene, at room temperature. The graphite is then washed in order to eliminate the excess of D. The penetration of the complexing molecule is demonstrated by X-ray diffraction[4]. From these results two different cases may be distinguished: (1) The X-ray diagram shows a total modification of the crystalline lattice, this is the case for dimethoxyethane (DME) and tetramethylene diamine (TMEDA). We observed the complete disappearance of the rays corresponding to the original binary compound. Instead new rays appear corresponding to a well defined ternary compound. (2) The X-ray diagram shows a slight modification of the original lamellar compound. We observed mainly the rays corresponding to the original binary compound LiC_{12} but also a few weak rays of an eventual ternary compound. This is the case for four other complexing agents: the tetraoxaperhydroquaterene (QAT), a polyethylene oxide (PEO) of $\overline{M}_n = 80\,000$, the dioxanne (DOX) and the triethylamine (TEA).

RESULTS AND DISCUSSION

Influence of the yield over the microstructure of polyisoprenes

The microstructure of the polymers obtained by the reaction with LiC_{12} Ceylan or Madagascar in cyclohexane never contains 1,2 units but only the 1,4 and the 3,4 forms. In *Figure 1* we have plotted the percentage of 1,4 units as a function of the yield *R* in polymer formed in 80 ml of cyclohexane and with 6.10^{-2} mol^{-1} of isoprene and 0.135 g of LiC_{12}. We have also plotted the percent of 1,4 not as a function of *R* but as a function of τ expressing the mass of polymer formed from 1 g of LiC_{12}. *Figure 1* shows that the percentage of 1,4 *cis* and 1,4 *trans* changes during the reaction, the percentage of 1,4 *cis* decreases and the percentage of 1,4 *trans* increases when *R* or τ grows. We did not plot in *Figure 1* the percentage of 3,4 that, as for the 1,4 *trans*, increases slightly. When the initiator is LiC_{12} Ceylan for $R = 3.5\%$ the polymer has 96% 1,4 *cis* units, no 1,4 *trans* and 4% of 3,4; when *R* reaches 100% the microstructure is then 49% 1,4 *cis*, 37% 1,4 *trans* and 14% 3,4. The obtained microstructures are, in any case, not similar to those obtained in an homogeneous polymerization[5] where there is no variation of microstructure as a function of yield (at least for polymers with a degree of polymerization beyond 20).

This variation in the stereospecificity of the reaction with the weight of the polymer formed must be emphasized by the fact that the values plotted in *Figure 1* are cumulative values. During our kinetic study of the polymerization[3] we assumed that the graphite layers interfere with the ionic interactions and with the possible complexations between the growing ion pairs and the monomer. The distance *h* separating two graphite layers plays a large part in the complexation phenomena. It is possible to call upon the same hypothesis in order to explain the variations in microstructures with *R* or τ. When small quantities of polymer are formed, the space between the graphite layers is not so important, in arriving near the cation the monomer is placed in such a manner that the interactions between the π orbitals of isoprene and the π orbitals of the graphite layers are at its maximum (the five carbon atoms of isoprene being located in a plane parallel to that of the graphite layers). This could promote exclusively a propagation in 1,4 *cis* because of the possibilities of *cis-trans* isomerization of the growing living end could be light, *Figure 2a*. As the reaction goes on the distance between the graphite layers increases and then it is possible for the living end to isomerize. Consequently the percentage of 1,4 *trans* and 3,4 increases. However, at high yields the percent of 1,4 *trans* and 3,4 units is so high (compared with that observed in homogeneous polymerization) that it must be admitted that the presence of a single graphite layer near the ion-pair polyisoprenyl–lithium protects the latter from perturbations. That means that the living end can take the more stable *syn* (*trans*) configuration easier than in homogeneous media (*Figure 2b*).

Influence of the origin of graphite

It can be seen in *Figure 1* that the results are different if the initiator is LiCl$_{12}$ Ceylan instead of Madagascar. The latter is less stereospecific, for $R = 1.5\%$ the microstructure is as follows: 91% 1,4 cis; 3% 1,4 *trans* and 6% 3,4 and for $R = 91\%$: 63% 1,4 *cis*, 28% 1,4 *trans* and 9% 3,4. Kinetics differences were already observed between the two kinds of initiator, isoprene polymerizes faster with LiC$_{12}$ Madagascar. The Madagascar graphite is by far better orientated and organized over longer distances than the Ceylan one. During the polymerization the perturbations caused by the penetration of the monomer and by the polymer growth will be transmitted further on the inside of the graphite layers (this is the case for the Madagascar) instead of being limited for few crystallites (as for the Ceylan)[6]. (This phenomenon is similar to the propagation of a craze in a rigid material). This hypothesis seems to be corroborated by the fact that the initiator LiC$_{12}$ synthesized from an artificial graphite (in powder) allows us to obtain the same microstructures as with LiC$_{12}$ Ceylan.

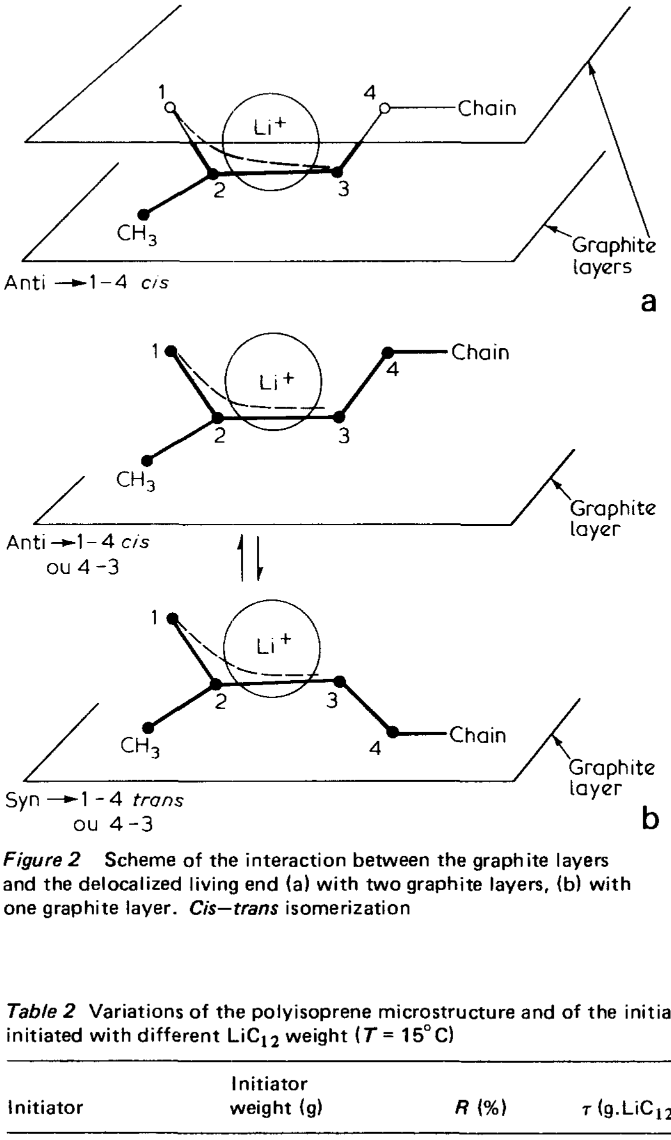

Figure 2 Scheme of the interaction between the graphite layers and the delocalized living end (a) with two graphite layers, (b) with one graphite layer. *Cis–trans* isomerization

Influence of the quantity of initiator

Keeping the quantity of monomer constant (6.10^{-2} mol.l^{-1}) we changed the quantity of initiator LiC$_{12}$. The results are in *Table 2*. In this case it is advisable to compare the microstructures obtained for the same τ of polymer and not for the same yield. Even in these conditions an increase of 1,4 *cis* can be observed when the quantity of LiC$_{12}$ increases.

The initiator efficiency f is never constant, and the number of active centres increases with the weight of LiC$_{12}$. So, taking into account all these experimental data, it can be inferred that the distance h between two graphite layers will be less modified (or more slowly modified, the pressure of the grown polymer being better distributed), the influence of two graphite layers will be felt over a longer period of time and so the polymer will be richer in 1,4 *cis*. To the contrary, the microstructure obtained with little (0.032 g) LiC$_{12}$ Madagascar, was rich in 1,4 *trans*, the lamellar compound being destroyed rapidly by the polymer formed.

Influence of τ (mass of polymer formed per g of LiC$_{12}$) and of the temperature over the variations of microstructures

In *Figure 3* the evolution of percentages in 1,4 *cis* and 1,4 *trans* as a function of R at 0°C, 15°C, 40°C, 50°C and 60°C for polyisoprenes initiated by LiC$_{12}$ Ceylan in cyclohexane (or methylcyclohexane at 0°C) were plotted.

In all the cases variations in *cis* and *trans* percentages can be observed. It discloses a fundamental difference of the polymerization in homogeneous media, the percent in 1,4 *cis* increases as the conversion rate increases: (a) For a constant value of R (or τ) the percent of 1,4 *cis* decreases as the temperature increases. With $R = 5\%$ we obtain 92% and 58% of 1,4 *cis* at 15°C and 60°C respectively. Beyond $R = 90\%$ the differences are negligible and the percentage of 1,4 *cis* nearly reaches 50%.

(b) for $R = 20\%$ and in comparison with the polymerization in homogeneous media at 15°C, the polymers here are richer in 1,4 *cis* than when the temperature is equal or less than 15°C.

For a certain value of R (or τ) the percentage Y of 1,4 *cis* measured by ^{1}H-n.m.r. represents the cumulated variations since the formation of the first unity. We made a derivation of $Y(R)$ with respect to R that allows us to estimate the instantaneous value and the percent of 1,4 *cis* addition and gives us a better explanation of the phenomenon (*Figure 4*). It can be seen that the propagation is

Table 2 Variations of the polyisoprene microstructure and of the initiator's efficiency as a function of polymer yield, when monomer is initiated with different LiC$_{12}$ weight (T = 15°C)

Initiator	Initiator weight (g)	R (%)	τ (g.LiC$_{12}$)	f (%)	1,4 *cis*	1,4 *trans*	3,4
LiC$_{12}$ Ceylan	0.135	60	17.5	5.1	58	33	9
	0.135	37	10.7	2.1	64	27	9
	0.223	60	10.7	12.8	70	25	5
LiC$_{12}$ Madagascar	0.032	70	87.5	0.7	44	35	21
	0.135	70	20.4	5.1	61	29	10
	0.135	27	8.0	4.6	67	25	8
	0.352	70	8.0	8.7	70	26	4

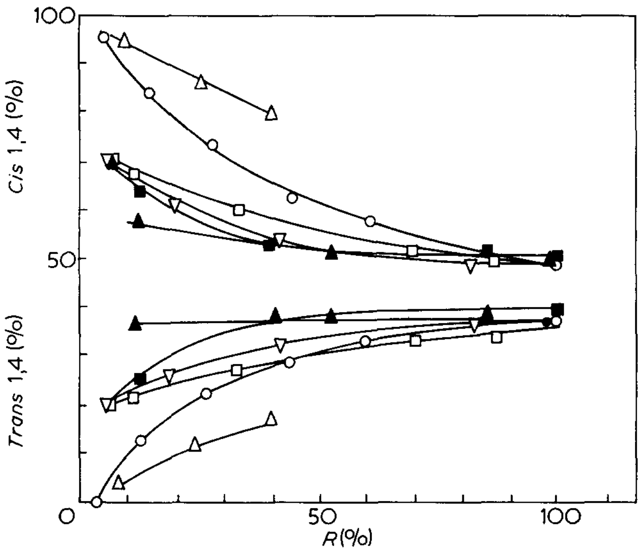

Figure 3 Variation of the polyisoprene microstructures initiated by LiC_{12} Ceylan in cyclohexane (or methyl cyclohexane) at different temperatures: (△), 0°C; (○), 15°C; (□), 30°C; (▽), 40°C; (■), 50°C; (▲), 60°C

purely 1,4 *cis* in the first instance of the polymerization but this stereospecificity rapidly lessens as the polymerization progresses. Finally, for $R \geqslant 30\%$ this variation diminishes as the temperature increases and for $T = 60°C$ the microstructure does not change.

When the polymerization takes place in a homogeneous media and in a hydrocarbon solvent, the 1,4 *trans* and the 3,4 forms are favoured when the temperature is raised because of the thermic agitation that destroys the *cis* coordination of the monomer molecule with the growing living end[7]. This mechanism, valid in a homogeneous media, is going to be highly disturbed by the presence of the graphite layers, the interactions between the growing ions pair and the monomer are no longer the same. As stated above, the presence of two graphite layers in the vicinity of the growing ions pair favours the propagation in 1,4 *cis* whereas the spacing of layers promotes the 1,4 *trans* and 3,4 units.

The distance h between two graphite layers is modified by the addition of the monomer and the formation of the first macromolecules[3]. The space between the layers will be more important if the temperature is raised because of the thermic agitation of the diffusing monomer molecules and of the forming macromolecules. The *cis–trans* isomerization of the delocalized living end becomes more likely. Nevertheless, at high yields the influence of one single layer (over which the growing living end is adsorbed) persists. This is corroborated by the high values of 1,4 *trans* and 3,4 that are superior to those obtained in homogeneous media (comparison for $T = 15°C$, *Figure 2*). The living end coordinated by one graphite layer could propagate easier in *trans* than in homogeneous media (in an inert solvent). We tried to sum up this propagation mechanism with the help of the diagram in *Figures 2a* and *b*.

Thermodynamics of the stereospecific polymerization in 1,4 cis *and 1,4* trans

Applying the 'activated complex theory' and the Arrhenius law it is possible to determine the thermodynamic values

$$\mathrm{Ln}\frac{k_{cis}}{k_{trans}} = \frac{\Delta S^{*cis}_{trans}}{R} - \frac{\Delta H^{*cis}_{trans}}{RT}$$

k_{cis} and k_{trans} are the constant rates for the propagation in 1,4 *cis* and 1,4 *trans* proportional to the percent of 1,4 *cis* and 1,4 *trans* + 4,3 (Essel *et al.*[7] showed that the formation of the 3,4 is closely related to the appearance of the 1,4 *trans* configuration). However, $\Delta S^{*cis}_{trans} = \Delta S^{*}_{cis} - \Delta S^{*}_{trans}$ is the difference between the variations of activation entropies and $\Delta H^{*cis}_{trans} = \Delta H^{*}_{cis} - \Delta H^{*}_{trans}$ is the difference between the variations of the activation enthalpies.

These parameters may be easily determined in plotting

$$\mathrm{Ln}\frac{\%\ 1{,}4\ cis}{\%(1{,}4\ trans + 4{,}3)}$$

as a function of $1/T$ using the instant values of the percentage in 1,4 *cis* and 1,4 *trans* given by *Figure 4*. A careful examination of the curves in *Figure 5* shows that: (i) at high yields ($R = 100\%$) the polymerization follows one single mechanism; (ii) at low yields ($R = 5$ and 50%) two mechanisms exist.

We only examined the influence of the temperature at the beginning of the reaction ($R < 5\%$) and at the end of the reaction ($R = 100\%$). The estimated values of the differences of the activation enthalpies and entropies are summarized in *Tables 3* and *4*.

The specific propagation in 1,4 *cis* is really favoured by $\Delta H^{*cis}_{trans} = 15$ kcal.mol^{-1} only at very low conversion rates ($R = 5\%$). But there is a compensation effect ($\Delta S^{*cis}_{trans} = 50$ kcal.mol^{-1}.K^{-1}). Early formation of the polymer between the graphite layers changes the stereospecificity. This phenomenon is emphasized when the temperature is raised.

At high temperatures (or higher conversion rates) $T > 30°–35°C$ for $R = 5\%$ or $T > 10°–15°C$ for $R = 50\%$) the simultaneous influence of two layers is abolished ($\Delta H^{*cis}_{trans} \simeq \Delta S^{*cis}_{trans} \simeq 0$). The same phenomenon is observed at high yields ($R = 100\%$).

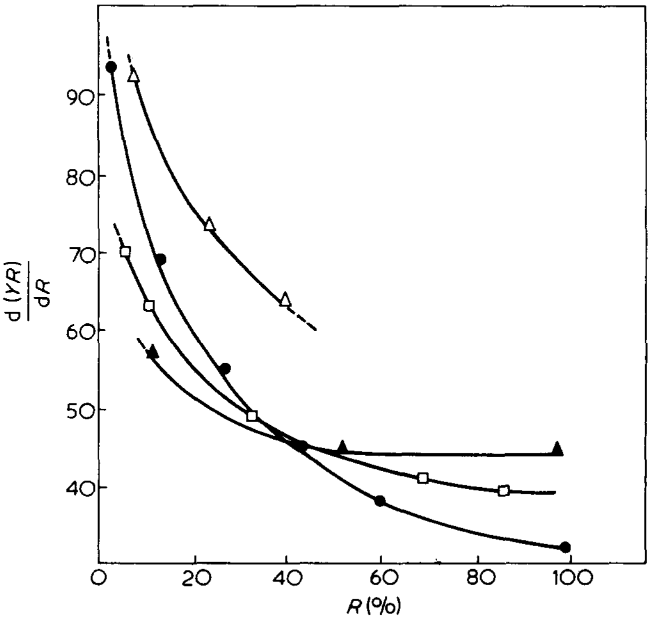

Figure 4 Variation of the instantaneous percentage of 1,4 *cis* units as a function of the yield, during the isoprene polymerization initiated by LiC_{12} Ceylan: (△), 0°C; (●), 15°C; (□), 30°C; (▲), 60°C

Nevertheless the present microstructure is markedly different from that observed in a homogeneous polymerization where the thermodynamic parameters are not zero (*Tables 3* and *4*). This seems to confirm that even at the end of the reaction the propagation takes place between the graphite layers. It can be seen that the effect of the thermic agitation of the living ends is noticeable only when the total volume occupied by the polymer is small (low R). When the conversion rate increases the breaking points in the Arrhenius curves correspond to greater low temperatures.

We think that these results confirm the double influence of the temperature and the conversion rate over the microstructure of the final polymer.

Polymerization initiated by 'ternary' lamellar compounds at 15°C in cyclohexane

In the section concerned with the experimental conditions we distinguished two types of complexing agents: those able to modify completely the binary compound LiC_{12} giving a purely ternary (DME or TMEDA) and those able to modify slightly the binary compound giving a badly defined mixture of binary and ternary structures (QAT, PEO, DOX, TEA).

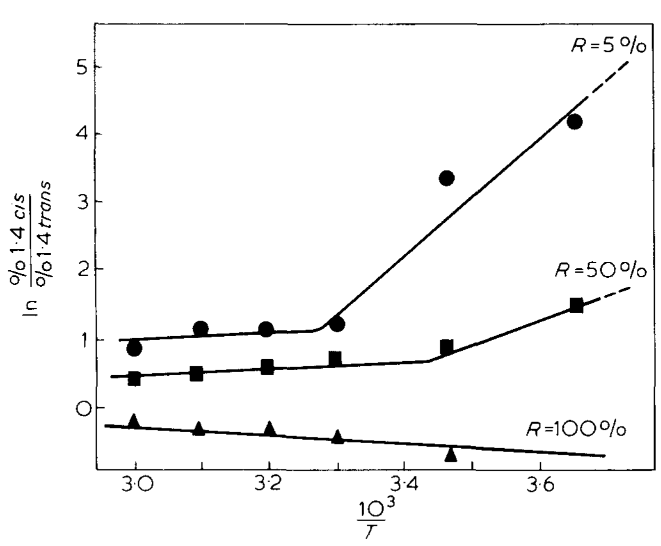

Figure 5 Variation of Ln 1,4 *cis*/1,4 *trans* + 4,3 as a function of $1/T$ for the isoprene polymerization initiated by LiC_{12} Ceylan: (●), R = 5%; (■), R = 50%; (▲), R = 100%

When the polymerization is initiated by the pure ternary compounds (see *Table 5*) the global polymerization rate is slightly higher (LiC_{12}, $TMEDA_X$) or practically the same (LiC_{12}, DME_X). The polymers have a high content of vinyl units. The percentages are close to those obtained in homogeneous polymerization in solvent mixtures, hexane + εDME or hexane + εTMEDA[8]: 19% of 1,4; 8% of 1,2 and 73% of 3,4 with LiC_{12}, DME_X; 36% of 1,4; 9% of 1,2 and 55% of 3,4 with LiC_{12}, $TMEDA_X$.

The results obtained with the other complexing agents are much more surprising (*Table 5*). Except with TEA, the total polymerization rate increases: for a similar reaction time the polymer yield is twice as high. With QAT, PEO and DOX, the polymerization remains stereospecific in 1,4 *cis* even at $R = 100\%$. *Figure 6* clearly shows that only the result obtained with LiC_{12}, TEA_X is on the curves of the binary LiC_{12} giving the percent of 1,4 as a function of R; the other three compounds behave as if no more variation of microstructure with yield occurs.

In the absence of adequate knowledge concerning the structure of the ternary initiator $LiC_{12}D_x$, these results are difficult to explain. When the modification of the crystalline lattice of LiC_{12} is total, it can be supposed that all the cations inside the graphite layers will be complexed by DME or TMEDA consequently, the influence of the graphite layers over the stereospecificity will disappear for the benefit of the entire influence of the complexing agent. However, in the case of a partial modification of the crystalline lattice of LiC_{12} by DOX, PEO or QAT the mechanisms go on as if the influence of the two graphite layers over the growing living end could be maintained during the entire reaction. If this is the case, what happens with the complexing agent? It can be considered that it could not penetrate inside the graphite layers but that it reacts just with the peripheric cations thus playing the

Table 3 Values at ΔH^{*cis}_{trans} at different temperatures and for different yields

R (%)	0°C–30°C	30°C–60°C
5%	−15.3 ± 1.5	−0.6 ± 0.5
50%	−5.4 ± 0.6	−0.6 ± 0.5
100%	+0.8 ± 0.5	
Homogeneous	−2.0[7]	

Table 4 Values at ΔH^{*cis}_{trans} at different temperatures and for different yields

R (%)	0°C–30°C	30°C–60°C
5%	−50 ± 5	−4 ± 1
50%	−15 ± 1.5	−3 ± 1
100%	+4.5 ± 1	
Homogeneous	−0.4[7]	

Table 5 Isoprene polymerization initiated by ternary lamellar compounds LiC_{12}, D_X Madagascar in cyclohexane (T = 15°C)

Complexant D	Reaction time (*h*)	R (%)	f (%)	1,4 *cis*	1,4 *trans*	1,2	3,4
QAT	43	100	13	83	13	0	4
POE	30	100	12	89	7	0	4
DOX	38	90	22	87	10	0	3
TEA	67	70	4.2	56	36	2	6
TMEDA	65	90	11	36		9	55
DME	65	63	0.4	19		8	73

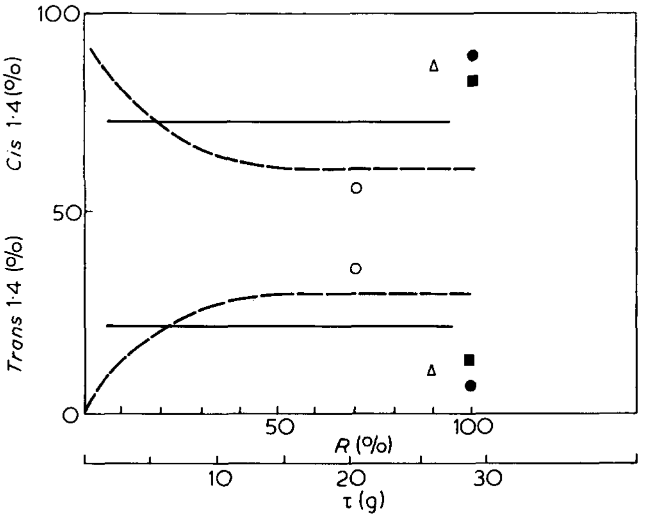

Figure 6 Microstructures of polyisoprene initiated by LiC_{12}, D_X in cyclohexane at 15°C: (○), TEA; (△), DOX; (●), POE; (■), QAT; (– – – –), polyisoprene initiated by LiC_{12}; (——), homogeneous anionic polyisoprene

part of a chock that facilitates the penetration of the monomer inside the graphite layers. This hypothesis is reinforced by the fact that the reaction is accelerated and that the initiator's efficiency increases (it can be also considered that the number of active centres participating in the polymerization being greater, the pressure of the grown polymer is better shared and consequently the graphite layers are less well spread so its influence leads to preserve for a longer time the stereospecificity 1,4 *cis*).

CONCLUSION

After a thorough examination of the microstructures of polyisoprenes synthesized with the help of the lamellar compound LiC_{12} we have come to the conclusion that the reaction is an heterogeneous one taking place inside the graphite layer.

(1) The percentage of 1,4 *cis* and 1,4 *trans* changes continuously during the reaction. This is a basic difference in front of polymerization in homogeneous media. At the beginning when the yield R is still low ($R = 5\%$) and when the geometry of the graphite layers is not yet seriously modified by the hindrance produced in the presence of the grown polymer, the percentage of 1,4 *cis* is 96%. As the reaction progresses the percent of 1,4 *trans* and 3,4 increases.

The high content of 1,4 *cis* units at the beginning of the reaction (the 'nascent polymer') can be explained in supposing that the entering isoprene coordinates with the inserted Li with its two double bonds, so the *cis–trans* isomerization of the delocalized living end cannot take place because of the presence of the graphite layers.

The distance between the graphite layers grows because of the formation of the polymer and the *cis–trans* isomerization of the growing living ends becomes possible from that time and an increase in the 1,4 *trans* percentage is observed. Nevertheless the observed value of 1,4 *trans* is higher compared with that normally obtained when the polymerization takes place in an homogeneous media. Thus beside the simultaneous influence of two graphite layers from the beginning of the polymerization the influence of one single graphite layer can be observed over the propagation of polyisoprenyl lithium till the end of the reaction.

(2) The temperature T also has an influence over the stereospecificity of the propagation, a rise in T has a strong effect upon the specific propagation in 1,4 *cis*. At 60°C and for $R = 5\%$ the percentage of 1,4 *cis* is only 58%. The thermodynamic parameters ΔH^{*cis}_{trans} and ΔS^{*cis}_{trans} which control the propagation mechanisms are quite different compared with those found in the homogeneous media.

(3) Differences in the behaviour of the initiator according to the origin of the graphite (Ceylon or Madagascar) were already reported as far as the kinetics of polymerization is concerned[3]. These differences exist also with regard to the microstructures of the synthesized polymers. It is possible that the structure of the better oriented graphite (the Madagascar) could be destroyed more easily, the pressure of the polymer formed is distributed over a wider surface of the graphite layers. Consequently there is a faster deterioration of the specific propagation in 1,4 *cis*.

We observed some surprising behaviour from several ternary initiators with the general formula $LiC_{12}D_X$. When D = DOX, QAT or PEO, the specificity of the 1,4 *cis* propagation remains even at high yields. As yet we are not able to give a more precise hypothesis.

These results are in good agreement with those obtained during a previous kinetic study[3] and explain how the graphite layers play a big part when the lamellar compound LiC_{12} is used to polymerize in cyclohexane. The part of the graphite layers changes during the reaction, the distance between them being modified by the polymer formed.

REFERENCES

1 Merle, G., Pascault, J. P., Pham, Q. T., Pillot, C., Salle, R., Gole, J., Rashkov, I., Panayotov, I., Herold, A. and Guerard, D. *J. Polym. Sci. Chem.* 1977, **15**, 2067

2a Loria, E., Pascault, J. P., Merle, G., Gole, J., Rashkov, I. B., Panayotov, I. and Pham, Q. T. Meeting Varna (Bulgaria), Preprint p 329, October 1977

2b Loria, E., Pascault, J. P., Merle, G., Salle, R., Gole, J., Pham, Q. T., Panayotov, I. and Rashkov, I. Meeting 'Ionic polymerization', Strasbourg, Preprint p 146, February 1978

3 Loria, E., Gole, J., Pascault, J. P. and Rashkov, I. B., in press

4 Merle, G. and Rashkov, I. B. (résultats non publiés)

5 Essel, A., Salle, R., Gole, J. and Pham, Q. T. *J. Polym. Sci. Chem.* 1975, **13**, 1847

6 'Les Carbones' by GFEC, Part 'Graphites polycristallins', Ed. Masson (Paris) p 410, 1965

7 Essel, A., Salle, R. and Pham, Q. T. *J. Polym. Sci. Chem.* 1975, **13**, 1869

8 Salle, R., Essel, A., Gole, J. and Pham, Q. T. *J. Polym. Sci. Chem.* 1975, **13**, 1855