Anionic polymerization initiated by lamellar compounds of LiC_{12}: 1. Kinetics of the polymerization of styrene and isoprene — initiator efficiency

E. Loria, G. Merle and J. P. Pascault
Laboratoire des Matériaux Macromoléculaires, ERA 745, 403/*INSA*, 69621 *Villeurbanne, France*
and I. B. Rashkov
Central Laboratory for Polymers, Bulgarian Academy of Sciences, Sofia 1113, *Bulgaria*
(*Received* 3 *December* 1979; *revised* 31 *March* 1980)

The polymerizations of styrene and isoprene initiated by LiC_{12} in cyclohexane are far slower than those observed in homogeneous media. The initiator's efficiency is estimated from a determination of the polymer molecular weight at differents reaction steps. Keeping in mind the monomer diffusion inside the graphite layers and in allowing some assumptions, some of the propagation rate constants were estimated. These values are much lower than those found in homogeneous polymerization. Temperature speeds up the reaction. The initiator's efficiency depends on the rate at which the graphite separates under the conjugated action of temperature and polymer growth.

INTRODUCTION

Graphite lamellar compounds of potassium have long been used as initiators of anionic polymerizations[1]. Recently the particular nature of that kind of initiator has been shown if potassium is replaced by lithium[2,3]. All the monomers commonly used in anionic polymerization can be initiated by LiC_{12} but, some interest has also been shown in diene polymerization. Here, the polymerization rates are far slower than those observed in homogeneous media, regardless of the solvent or the monomer. Bulk polymerization of isoprene or butadiene gives microstructures quite different from those observed in homogeneous media. This is also the case if polymerization takes place in cyclohexane. In aromatic solvents the isoprene–styrene copolymers are statistical and the mean length of styrene blocks is less than 5. An earlier work[2] concluded that in non polar solvents the monomer interaction with the intercalation compound and the growing chain geometry between the carbon layers, or on the surface of one carbon layer, are the factors controlling either the stereospecificity of the polymerization or the selectivity of the copolymerization. In these solvents the polymerization reaction proceeds without any homogeneous contribution, a very slow rate reaction is observed together with quite a different polymer microstructure. Nevertheless, the results are no different from those when polymerization takes place in polar solvents.

The aim of the present work is to investigate further the mechanism of the anionic polymerizations initiated by LiC_{12}. During the first part of this paper, the kinetics of the polymerization reaction of styrene and isoprene in cyclohexane will be examined first at 15°C and then at different temperatures. An attempt will be made to specify the influence of the diffusion phenomenon at the different stages of the reaction.

EXPERIMENTAL

The monomers and the solvents are purified using the classical methods normally employed in anionic polymerization. The lamellar compound of lithium LiC_{12}, second stage, was synthesized by D. Guerard as he has previously described[4] with a Ceylan or Madagascar graphite. In the former case the granularity is 100–125 μm, in the latter the flakes must be grinded and sifted in order to have the same granularity (100–125 μm). The catalyst samples are weighed and stored under vacuum.

The polymerizations are accomplished in 80 ml of solvent (cyclohexane or methyl-cyclohexane) with 0.135 g of LiC_{12} and 6×10^{-2} mole of monomer. After a reaction time t some drops of methanol are added to the mixture. The solvent is then evaporated and the polymer formed is dryed and weighed.

The molecular weight measurements are made by gel permeation chromatography (g.p.c.) in tetrahydrofuran and with a set of seven columns packed with 'styragel' (the porosity being: 60, 100, 500, 10^3, 10^4, 10^5 and 3×10^5 Å). The calibration is obtained by the means of polystyrene and polyisoprene samples (PI samples with a high content of 1.4).

DISCUSSION

Kinetic curves at 15°C

The percentage of polymer formed *versus* time was plotted (*Figure* 1) for styrene and isoprene polymerized in cyclohexane at 15°C. The reaction rates are very much slower than in homogeneous media, the half-reaction time is 17 h for styrene and 61 h for isoprene, the initiator being LiC_{12} Ceylan. For the styrene a relatively short induction time can be observed, while for

0032-3861/81/010095-06$02.00

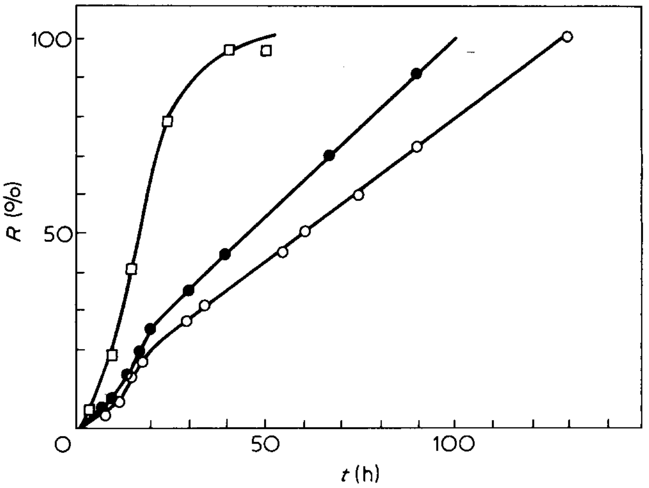

Figure 1 Polymerization of isoprene and styrene, initiated by LiC_{12} in cyclohexane at 15°C. ○ – isoprene, LiC_{12} Ceylan; ● – isoprene, LiC_{12} Madagascar; □ – styrene, LiC_{12} Ceylan

isoprene the induction time is 12 h. This is in complete agreement with the previous results of Rashkov *et al.*[5] who showed that the diffusion rate of styrene into the graphite layers is faster than that of isoprene due to the strong π–π interactions between aromatic rings and graphite layers.

It can also be noticed (*Figure* 1) that the polymerization rate of isoprene is different according to the origin (Ceylan or Madagascar) of the graphite used to synthesize the catalyst LiC_{12}. The induction times are similar and the conversion rate of isoprene is practically the same up to 18% yield, but beyond this the reaction is faster with Madagascar, the half-reaction time being 46 h instead of 61 h with Ceylan.

In *Figure* 2 the evolution of the initiator's efficiency (f) is plotted as a function of the reaction. f Is defined as the ratio (as a percentage) of the consummated active centres over the total number of centres. In calculating these the molecular weight ($\overline{Mn}$) of the polymer formed and the bifunctional initial step were taken into account. For styrene initiated by LiC_{12} Ceylan, f quickly reaches a limiting value (about 2%). For isoprene, initiated by LiC_{12} Ceylan, f increases up to the end of the polymerization and reaches 22%. If isoprene is initiated by LiC_{12} Madagascar, f increases more rapidly but never exceeds 5%.

Expression of the polymerization rate and estimation of the constant rates at 15°C

If it is inferred that there is neither transfer nor termination reaction, (this has been proved for the bulk polymerization of isoprene initiated by LiC_{40} THF_2 [3c]), the monomer rate of diffusion V_D, the initiation rate V_a and the propagation rate V_p are in constant competition during the polymerization. The concentration in active centres changes during the reaction (at least during a long period) and it is not possible to write the steady state approximation.

(a) Supposing that similar behaviour exists between the graphite–lithium LiC_{12} and the radical-ion naphthalene–lithium, the different mechanisms (initiation step, coupling of the radical-ions formed and propagation of the di-anion) well known in anionic polymerization may then be used. The following simplifying assumptions may also be made – that the coupling reaction is very fast, the initiation and the propagation reaction are first-order with respect to the monomer and the catalyst (this assumption has been proved for the bulk polymerization of styrene initiated by KC_{24} THF_2 [3a], *Figure* 3); and finally that the reactivity of the active centres is identical whatever the chain-length: the initiation and the polymerization rates can then be expressed as follows:

$$V_a = \frac{d\{M\}}{dt} = k_a\{M_i\}\{A\} \tag{1}$$

and

$$V_p = -\frac{d\{M_i\}}{dt} = k_p^*\{^-MM^-\}\{M_i\} \tag{2}$$

where $\{M_i\}$ is the monomer concentration inside the graphite layers.

(b) An equation taking into account the monomer diffusion can evaluate $\{M_i\}$. This diffusion includes several phenomenons — monomer sorption, interaction with the graphite layers, penetration, complexation, alteration of the crystalline lattice — and depends on several parameters, some of which change during the polymerization. In the absence of the monomer, the distance h between the graphite layers separated by Li is very small, about 0.35 Å (*Figure* 4*a*). Nevertheless, the monomer will penetrate and polymerize (the insertion compound is then completely broken by the reaction). Consequently it must be assumed that the interlayer space h reaches a value

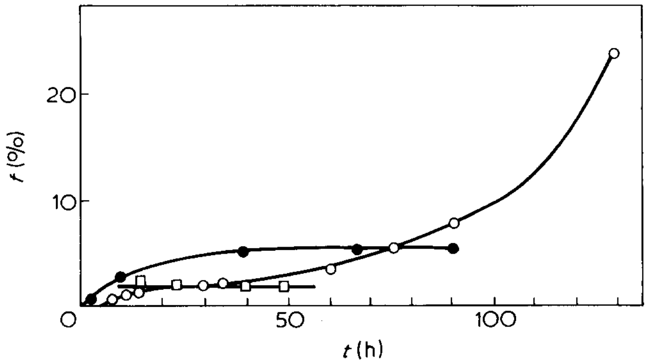

Figure 2 Variation of the initiator efficiency f as a function of the polymerization time. ○ – isoprene, LiC_{12} Ceylan; ● – isoprene, LiC_{12} Madagascar; □ – styrene, LiC_{12} Ceylan

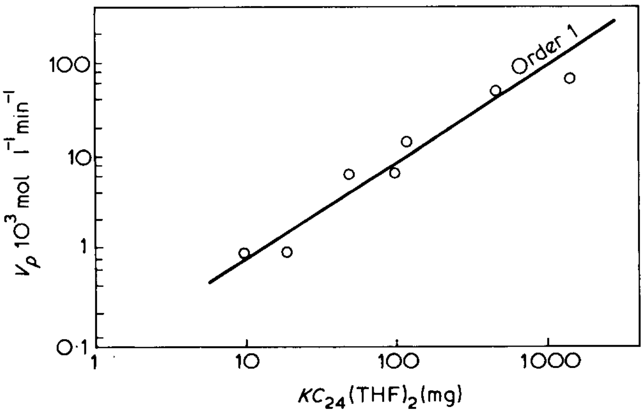

Figure 3 Influence of the initiator weight on the polymerization rate in bulk, of styrene (reference 3a)

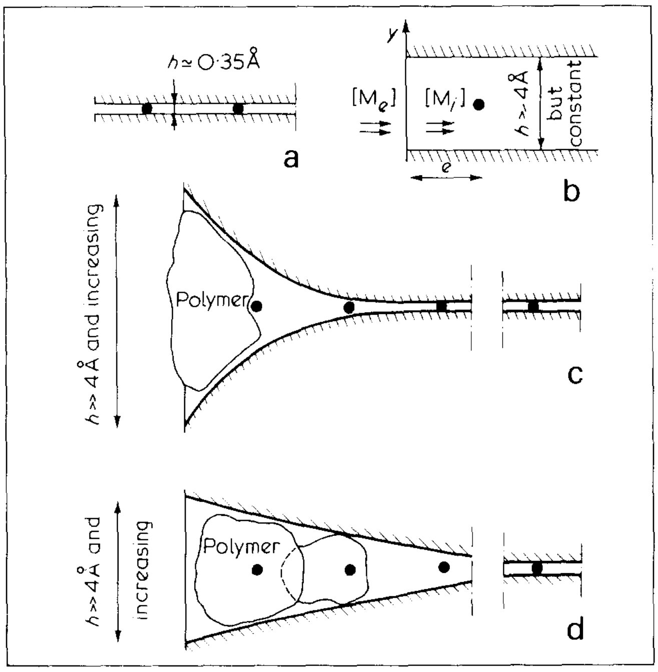

Figure 4 Diffusion of the monomer inside the graphite layers. a — initial LiC_{12} compound, ●, Li cation or atom; b — simplified model of the diffusion of a monomer inside the LiC_{12}; c — styrene as monomer; d — isoprene as monomer

exceeding 4 Å, this value being the smallest dimension of a flat monomer molecule. To support this hypothesis two experimental facts can be mentioned. When a molecule like benzene reacts with an insertion compound[6], only a penetration reaction takes place, but the crystalline lattice is broken at the start, after which time a new crystalline lattice is formed since there is no polymerization. In the case of vapour polymerization Rashkov *et al.*[5] measured important inflating values of the insertion compounds and variable spacing rates of the graphite layers according to the nature of the monomer. The energy needed to pass from the model (*Figure* 4*a*) to the model (*Figure* 4*b*) results from the complexation interactions or π–π and from the electron transfer.

The model in *Figure* 4*b* is greatly simplified. It is assumed that the diffusion only exists in one direction; h is constant. This model corresponds to the diffusion through an interlayer space with an average depth $\bar{l}$. The monomer concentrations, $\{M_e\}$ and $\{M_i\}$ respectively, at the surfaces $x=0$ and $x=l$, with respect to a x-y axis, are constants.

After some time, the steady state in monomer concentration $\{M\}$ is reached and $\{M\}$ is constant in every point of the plan. Supposing that the diffusion coefficient D is constant, $\mathrm{d}^2\{M\}/\mathrm{d}x^2=0$. From this and after integration and application of the limit conditions, it is possible to obtain the monomer concentration gradient inside the graphite layers:

$$\frac{\{M\}-\{M_e\}}{\{M_i\}-\{M_e\}}=\frac{x}{\bar{l}} \tag{3}$$

$\{M\}$ is the monomer concentration inside the graphite layers at the distance x; $\{M_e\}$ is the monomer concentration outside the graphite layers ($x=0$); and $\{M_i\}$ the concentration inside the graphite layers in the vicinity of the cation ($x=\bar{l}$).

The monomer transfer rate F per unity section of the plan area is proportional to the concentration gradient. This rate is the same at every point of the plan and can be expressed as:

$$F=-D\frac{\mathrm{d}\{M\}}{\mathrm{d}x}=\frac{D}{\bar{l}}(\{M_e\}-\{M_i\}) \tag{4}$$

In equation (4) F is constant. From this and from equation (2) that gives V_p, the following equation (5) can be obtained:

$$-\frac{\mathrm{d}\{M_e\}}{\mathrm{d}t}=k_p\{M^{2-}\}\left(\{M_e\}-\frac{F\bar{l}}{D}\right) \tag{5}$$

The concentration in living ends is also assumed constant.

Integration of (5) gives:

$$\frac{\{M_e\}-\dfrac{F\bar{l}}{D}}{\{M_0\}-\dfrac{F\bar{l}}{D}}=\exp\{-k_p\{M^{2-}\}t\} \tag{6}$$

Equation (6) takes into account the diffusion and the propagation processes.

Styrene's case

For this monomer the curve f *versus* time (*Figure* 2) can be divided into two domains. At the beginning for $t<15$ h (or $R<40\%$) the propagation rate V_{pr} is slower than the diffusion rate V_D, because of the small number of active centres and the diffusing monomer will be able to create new active centres. Hence, in this interval $0<t<15$ h the efficiency f of the initiator increases. Afterwards, for $t>15$ h (or $R>40\%$) there is no more initiator step and f becomes constant — all the monomer diffusing inside the graphite layers is consumed by the growing chains. Consequently for $t>15$ h, taking into account that there is no more creation of active centres, it is possible to apply equation (6). In *Figure* 5 the relation $\ln\{M_0\}/\{M_e\}$ *versus* time (t) is a straight line when $t>15$ h. This means that equation (6) can be simplified and the term $F\bar{l}/D$, expressing the diffusion phenomenon, can be neglected in front of $\{M_0\}$ and $\{M_e\}$. In other words, beyond 15 h, the polymerization of styrene would be controlled by the

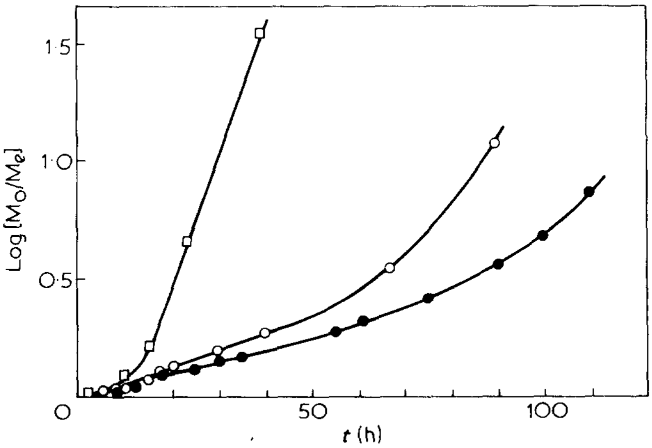

Figure 5 Estimation of k_{pr}. ○ — isoprene, LiC_{12} Ceylan; ● — isoprene, LiC_{12} Madagascar; □ — styrene, LiC_{12} Ceylan

Table 1 Experimental results

Monomer	Homogeneous	LiC_{12} Ceylan
Styrene	$k_{pr} \simeq 10$ l.mol^{-1} s^{-1} (C_6H_6)[7] $k_{pr} \simeq 10$ l.mol^{-1} s^{-1} (THP)[8] $k_{pr} \simeq 0.9$ l.mol^{-1} s^{-1} (DOX)[9]	$k_{pr} = 0.36$ l. mol^{-1} s^{-1} for $t > 15$ h
Isoprene	$k_{pr} \simeq 20$ l.mol^{-1} s^{-1}	$k_{pr} = 0.033$ l.mol^{-1} s^{-1} for 15 h $< t <$ 60 h
	$E_a \simeq 16.5$–19 kcal.mol^{-1} (C_6H_6 and cyclohexane)[7]	$E_{a_1}^* = 14 \pm 0.4$ kcal. mol^{-1} for $R \leqslant 5\%$ $E_{a_2}^* = 18 \pm 0.5$ kcal. mol^{-1} for $20\% < R < 100\%$

Experimental results concerning the homogeneous anionic polymerization and the polymerization initiated by LiC_{12} Ceylan (k_{pr} is the propagation rate constant and E_a the activation energy of the polymerization)

propagation rate. This can be explained if we consider that when the diffusion of styrene at the beginning of the reaction is very fast and exothermic[5] the layers spread out (h is very large hence D is also very large). Nevertheless, with f remaining constant and equal to 2, the graphite layers must open locally to give access to some active centres, but this does not permit the styrene to diffuse towards other cations (*Figure* 4*c*). To reach the first Li cation the diffusion rate $(V_D)_1$ is fast whereas the diffusion rate $(V_D)_2$ to attain the second Li cation is slow and it can be supposed that $(V_D)_2 < V_{pr}(V_D)_1$).

Consequently, for $t > 15$ h, the reaction is first-order with respect to the monomer, and it is possible to determine a propagation rate constant for styrene $(k_{pr})_s$ taking the slope of the linear part of the curve in *Figure* 5: $(k_{pr})_s = 0.36$ l mol^{-1} s^{-1}.

Comparison of this value of (k_{pr}) with those found by other authors for the propagation of styrene in homogeneous media is difficult, because in the latter case the active centres are associated as a dimer[7]. Nevertheless Szwarc[8] estimates (k_{pr}) for polystyryl–lithium in benzene at 25°C ($k_{pr} > 10$ l mol^{-1} s^{-1}). A similar value has been estimated in tetrahydrofuran[9] whereas in dioxane $k_{pr} = 0.9$ l mol^{-1} s^{-1} at 25°C[10]. These differences in homogeneous media are explained by the fact that the living end is complexed by dioxane and the approach of the monomer then becomes difficult. The value of k_{pr} that we have found is 25 times smaller than the one obtained homogeneously in benzene (estimated by Szwarc) and 2.5 times smaller than the one found in similar conditions in dioxane. This small value may be explained by the presence of the graphite layers which makes the complexation of the monomer molecule with the living-end more difficult.

Isoprene's case

Figure 2 shows for isoprene equation (6) cannot be applied because initiation and propagation occurs during all the reaction. Nevertheless, when the reaction is initiated by LiC_{12} Ceylan and in the interval between 15 h $< t <$ 60 h, there is only a slight variation in f and it is possible to consider that f is constant and equal to 2. On the other hand, the plot of ln $\{M_0\}/\{M_e\}$ *versus* t in the same interval is practically a straight line (*Figure* 5). As in the preceding case it is possible to simplify equation (6) and to neglect the diffusion process. Then, the importance of the propagation rate constant of isoprene $(k_{pr})_I$ inside the graphite layers can be calculated: $(k_{pr})_I = 3.3 \times 10^{-2}$ l mol^{-1} s^{-1}. (It is not possible to use the same approximation when the reaction is initiated by LiC_{12} Madagascar because if f is constant, the variation ln$\{M_0\}/\{M_e\}$ is not linear and the term $F\bar{l}/D$ from equation (6), i.e. cannot be neglected in other words, we cannot neglect the diffusion phenomena.

As for styrene, comparison of this value with the results obtained in homogeneous media is difficult, because in hydrocarbon media polyisoprenyl–lithium only exists in associated form. Nevertheless our value is 600 times smaller than the one found by Bywater[11] in cyclohexane at 20°C.

As can be seen in *Table* 1, the differences between the propagation rates V_{pr} in our system and the homogeneous media are more important for isoprene than for styrene. The mechanisms for the monomer diffusion are, however, not the same. This affects the initiator efficiency f and the evolution of f during the polymerization (*Figures* 4*c* and 4*d*).

Temperature dependence of the polymerization rate of isoprene initiated by LiC_{12} *Ceylan in cyclohexane*

Figure 6 shows the curves of yield (R) as a function of the polymerization time (t) at different temperatures, from −20° to +60°C. As in any endothermic reaction, R is favoured by an increase in temperature. 100 h are required for $R = 1.5\%$ at −20°C; the half reaction time is 173 h at 0°C and 0.9 h at 60°C. *Figure* 7 shows that over the temperature range studied, the efficiency f varies constantly during the reaction. Unlike the case of styrene at 15°C, the three phenomenons — diffusion, initiation and propagation — coexist until the end of the reaction and consequently equation (6) cannot be applied. In order to better illustrate the influence of the temperature and to specify which of the three phenomenon prevails at each stage of the reaction, the evolution of f as a function of R is plotted (*Figure* 8). For lower yields, $R < 12\%$, f varies in the same way for the entire range of temperature analyzed. For $R > 12\%$, f increases very rapidly for the polymerization carried out at 0°C and more slower for those carried out at higher temperatures. At 50°C yield for instance, $f = 22\%$ at 0°C and 4% at the other temperatures.

The number of active centres involved during one polymerization depends on the competition between

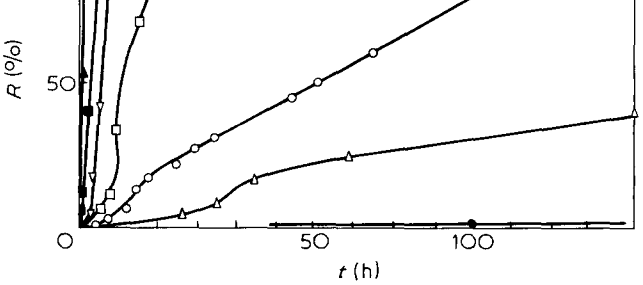

Figure 6 Polymerization of isoprene initiated by LiC_{12} Ceylan in cyclohexane or methylcyclohexane, at different temperatures. ●, 20°C (MeCH); △, 0°C (MeCH); ○, 15°C (CH); □, 30°C (CH); △, 40°C (CH); ■, 50°C (CH); ▲, 60°C (CH)

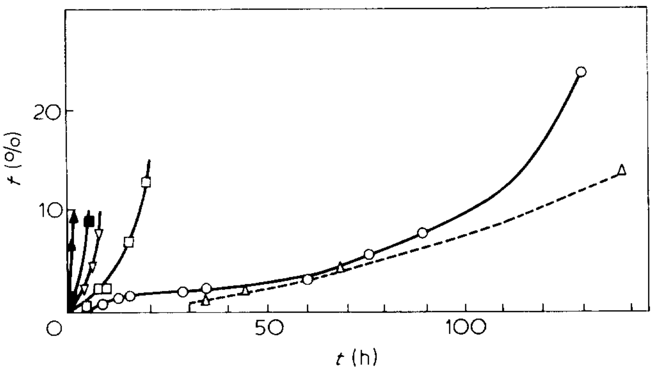

Figure 7 Variation of the initiator efficiency *f* as a function of the polymerization time at different temperatures. △, 0°C (MeCH); ○, 15°C (CH); □, 30°C (CH); △, 40°C (CH); ■, 50°C (CH); ▲, 60°C (CH)

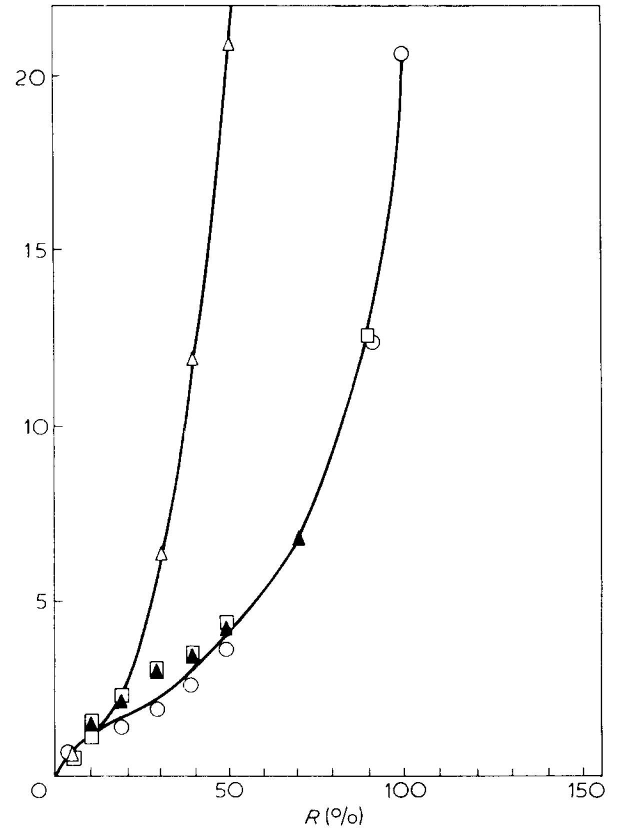

Figure 8 Variation of the initiator efficiency *f* as a function of yield at different temperatures. △, 0°C (MeCH); ○, 15°C (CH); □, 30°C (CH); ▲, 40°C, 50°C and 60°C (CH)

three rates: the diffusion V_D, the initiation V_a and the propagation V_{pr}. At low temperature the complexation phenomena between the growing living ends, the graphite layers and the monomer are favoured. In these conditions it can be supposed that at 0°C, V_D will be more important than V_a and V_{pr} (the more complexation phenomena will slow down these two values). Thus at 0°C more monomer penetrates inside the graphite layers that can be consumed by the growing chains and the excess monomer molecules will be able to be initiate other lithium atoms. In *Figure* 4*d* the diffusion rate (V_{D2} necessary to attain a second lithium is comparable with the one necessary to reach the first lithium. It is thought that at this polymerization stage the space between the graphite layers is not large, this is not the case with styrene (*Figure* 4*c*). Consequently *f* increases regularly with *R*.

Between 15°C and 60°C the phenomena is difficult to explain. Probably V_a and V_{pr} will increase with the rise in temperature while V_D should normally decrease because the diffusion phenomenon is accompanied by an exothermic sorption of the monomer[5,6]. The fact that *f* varies as a function of *R* in the same way regardless of temperature shows that the equilibrium between V_D, V_a and V_{pr} is independent of the temperature, and compels V_D to increase with temperature. To reconcile these inconsistent assertions, V_D can be written as $V_D = \alpha(1/T) + \beta(T, R)$. The first term $\alpha(1/T)$ is the intrinsic parameter of any sorption phenomena; this term explains the fact that V_D decreases when *T* increases. But the system used is not as simple as the one described in *Figure* 4*b*, the distance *h* is not constant, the graphite layers part progressively as the reaction advances and the polymer is formed inside (*Figure* 4*d*). This will make the diffusion of the monomer easier. The spacing between the graphite layers will be accelerated by an increase of temperature. This is what the second term $\beta(T, R)$ tries to explain, and then, in these conditions it is possible that $V_D = \alpha(1/T) + \beta(T, R)$ may increase with temperature.

Activation energy

From the curves of *Figure* 6 it is possible to calculate the polymerization rate V_p at any instant of the reaction. However we merely measured the slope of the tangents to the curves at two different points: the slope at the origin gives an apparent rate constant k^*_{p1}, the slope of the linear part of the curve gives k^*_{p2}. *Figure* 9 shows that the variation of k^*_{p1} and k^*_{p2} as a function of temperature follows the Arrhenius law. Thus two activation energies can be calculated $E^*_{a_1} = 14 \pm 0.4$ kcal mol^{-1} for $R < 5\%$ and $E^*_{a_2} = 18 \pm 0.5$ kcal mol^{-1} for $20\% < R < 100\%$.

Similarly, apparent activation energies take into account the three phenomena — diffusion, initiation and propagation. As before they can be expressed using two terms: a negative term for the sorption phenomena and a positive term representing the thermic activation of initiation and propagation and the fact that the graphite layers separate during polymerization, this separation being favoured by an increase in temperature.

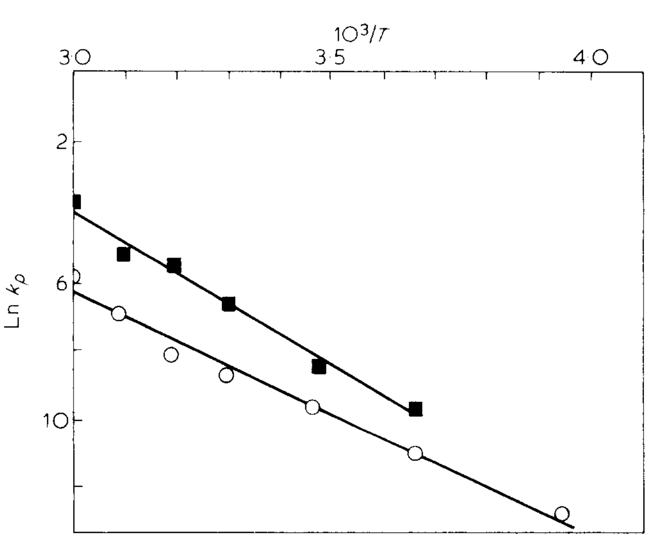

Figure 9 Variation of the apparent polymerization rate constant $k_p{}^*$ as a function of the temperature: ○, $k^*_{p_2}$ when $R < 5\%$ and ■, $k^*_{p_2}$ for $20\% < R < 100\%$

Regardless of the reaction temperature, when $R < 5\%$ it can be assumed that the spacing of the graphite layers remains unmodified. On the other hand when $70\% < R < 100\%$ the distance h increases and at a much faster rate when the temperature is higher. The augmentation of the activation energy due to the spread of the graphite layers can explain the difference $E^*_{a_2} - E^*_{a_1} = 4$ kcal mol^{-1}.

CONCLUSION

The kinetic study of the anionic polymerization of styrene and isoprene initiated by LiC_{12} in cyclohexane showed:

(a) The reaction rate is much slower than in homogeneous media. For isoprene there is an important induction period.

(b) The efficiency of the initiator LiC_{12} is weak and becomes stable at 2% with styrene and increases up to 22% with isoprene at 15°C. This difference can be explained by a different diffusion rate for each monomer inside the graphite layers.

(c) There are differences in reactivity between the two varieties of graphite Ceylan and Madagascar.

(d) A simplified model of the diffusion of the monomer inside the graphite layers allowed the actual concentration of monomer $\{M_i\}$ in the vicinity of the active centres to be estimated and led to equation (6), giving the disparition of monomer as a function of the reaction time. With several hypothesis the rate propagation constants of styrene and isoprene at 15°C were calculated. The one corresponding to styrene is 25 times smaller than the one found in homogeneous media in benzene and 2.5 times smaller than the one found in dioxane. The value k_{pr} estimated for isoprene is 600 times smaller than the one found in homogeneous media in cyclohexane. These differences can be explained by the presence of the graphite layers that prevents the access of the molecule to the living end.

(e) A rise in temperature accelerates the reaction rate. At -20°C the polymerization of isoprene initiated by LiC_{12} Ceylan is very slow, it is necessary to wait several days to get a yield of about 2%. On the other hand $R = 100\%$ in one hour at 60°C.

The catalyst efficiency is very high for temperatures below room temperature, when the monomer has time for diffusing inside the graphite layers before polymerization. The efficiency is no longer temperature dependent since $T > 15$°C. To explain this result it is necessary to suppose that the diffusion model changes during the reaction because of the spacing of the graphite layers. The polymer formed pushes the graphite layers and this can continue until the exfoliation of the graphite. The delaminating of the graphite layers is accelerated by rising temperature.

The same reasoning allows the differences in apparent activation energy for two stages in the reaction to be explained, when $R < 5\%$ and when $20\% < R < 100\%$. During the polymerizations initiated by the lamellar compound LiC_{12}, the role of the graphite layers is very important. Before the initiation step takes place, the monomer must diffuse inside the graphite layers. Afterwards the reaction probably continues to take place inside the graphite layers, or on the surface of one graphite layer, slowing down the propagation and explaining the differences in kinetic behaviour observed in comparison with the polymerization in homogeneous media. However, the spacing between the graphite layers is not constant, it depends on the temperature of the reaction and on the course, and it is necessary to make a distinction between several stages in the reaction. The mechanisms at the initiated stage and at the final stage of the reaction could therefore be expressed as a function of the temperature.

REFERENCES

1 Podall, H., Forster, W. E. and Giraitis, A. P. *J. Org. Chem.* 1958, **23**, 82

2 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.* (*Polym. Chem. Edn*) 1977, **15**, 2067

3a Loris, E., Pascault, J. P., Merle, G., Gole, J., Rashkov, I., Panayotov, I. and Pham, Q. T. *Meeting in Varna* (Bulgaria), Preprint Oct. 1977, 329

3b Loria, E., Pascault, J. P., Merle, G., Salle, R., Gole, J., Pham, Q. T., Stein, C. and Gole, J. *Bull. Soc. Chim.* 1966. **10**, 3175

3c Rashkov, I. and Panayotov, I. *Meeting 'Ionic polymerization' Strasbourg*, Preprint Feb. 1978, 146

4 Guerard, D. and Herold, A. *C.R. Acad. Sci. Paris* 1972, **275C**, 571

5 Rashkov, I. B., Panayotov, I. M. and Shishkova, V. C. *Carbon* in press

6 Merle, G., Mai, C., Gole, J. and Rashkov, I. B. *Carbon* 1977, **15**, 243

7 Johnson, A. F. and Worsfold, D. J. *J. Polym. Sci.* (*Polym. Chem. Edn*) 1965, **3**, 449

8 Szwarc. M. 'Carbanion living polymers and electron transfer processes' Interscience publishers, 1968, 501

9 Parry, A., Roovers, J. E. L. and Bywater, S. *Macromolecules* 1970, **3**, 355

10 Bhattacharyya, D. N., Smid, J. and Szwarc. M. *J. Phys. Chem.* 1965, **69**, 624

11 Worsfold, D. J. and Bywater, S. *Can. J. Chem.* 1960, **38**, 1891