Oligomerization of ethylene by several normal butyllithium-amine complexes: 8. Kinetic study

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A detailed study of the effect of new amines: dimethyl-diethylethylene diamine (DMDEEDA) and pentamethyldiethylenetriamine (PMDT), on the addition of ethylene to n-butyllithium has been made in order to determine the mechanism of the growth step. The results obtained indicate the absence of aggregated species and the following equation has been established for both amines:

$$V_p = k_p[\text{n-BuLi:Amine}][\text{Et}]$$

Keywords Anionic oligomerization; ethylene; kinetics; amines; growth step

INTRODUCTION

The low reactivity of ethylene in anionic polymerization and the difficulty of obtaining high molecular weight polymers delayed this field of research for some considerable time.

However, the special feature of many homogeneous anionic systems is to make precisely tailored polymers. The first difficulty encountered was ascertaining those conditions that favour the growth reactions for ethylene while avoiding the chain transfer reaction.

Hanford and coworkers[1] prepared polyethylenes of molecular weight 1400 using phenyllithium in ether solvent at high temperatures and pressures of ethylene. The propagation reaction was found to be in competition with the termination of the active lithium ends. Eberhardt and coworkers[2,3] found that lithium alkyls are active toward the telomerization of ethylene and benzene when a tert-amine or chelating diamine, such as sparteine or N,N,N',N' tetramethylethylene diamine (TMEDA), is used. Langer[4] observed that the addition of TMEDA to alkyllithium compounds in paraffinic solvents activated the initiation and propagation of ethylene to give a polyethylene of high molecular weight without chain transfer to the monomer. This work was later confirmed by Kamienski[5] and Smith[6]. Bunting and Langer[7] proposed that the activation of the alkyllithium is due to the solvation of the lithium by the two nitrogen atoms of the diamine. A five-membered cyclic structure (I) was proposed as the solvated structure present in the paraffinic solvent.

(I)
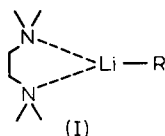
Langer claimed that structure (I) is monomeric at a concentration of less than 0.1 M.

A kinetic study of the oligomerization of ethylene using alkyllithium-TMEDA complexes was carried out by Hay and coworkers[8,9]. These workers reported that the rate of ethylene consumption was first order at ethylene pressure and n-BuLi concentration. Even though TMEDA is essential for the polymerization of ethylene, the rate of ethylene usage was found to be independent of TMEDA concentration. However, the explanation offered by Hay et al.[8,9] appears to be in direct conflict with Langer's suggestion that the five-membered cyclic structure (I) is responsible for the enhanced activities of the complexed n-BuLi-TMEDA initiator system.

The oligomerization of ethylene using complexed alkyllithium compounds has been further studied by Schué et al.[10-19].

A kinetic study of ethylene oligomerization in hexane, in the presence of n-BuLi-TMEDA complexes, allowed these workers to suggest a new mechanism for the anionic ethylene oligomerization. n-BuLi and n-Bu(CH$_2$CH$_2$)$_n$Li species have the same reactivity. The RLi-TMEDA complex, in a 1 to 1 stoichiometry, is the active species. The following equation has been established:

$$V_p = k_p K_D^{1/2}[(\text{n-BuLi-TMEDA})_2]^{1/2}[\text{Et}]$$

This equation reflects the intervention of the associated species (n-BuLi-TMEDA)$_2$ as well as the influence of the concentration of the complexing agent on the kinetics of the oligomerization.

A kinetic study, as a function of temperature, of ethylene oligomerization using the n-BuLi-TMEDA complex allowed them to evaluate the thermodynamic parameters ($\Delta S^* < -23.7$ e.u.) and thus to support a transition state where the ethylene is coordinated to the lithium atom.
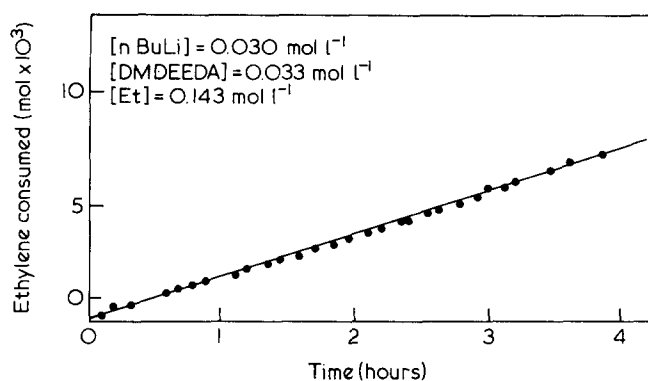
Figure 1 Consumption of ethylene as a function of time

Table 1 Variation of V_p with r = [DMDEEDA]/[n-BuLi] *

r	Amine ($\times 10^2$ mol l^{-1})	V_p ($\times 10^6$ mol l^{-1} s^{-1})
0.24	0.72	4.72
0.35	1.07	5.00
0.48	1.48	5.27
0.60	1.80	5.50
0.84	2.50	5.70
1.2	3.60	5.83
1.5	4.50	5.83
2.0	6.00	5.69

* [n-BuLi] = 0.03 mol l^{-1}, [Et] = 0.143 mol l^{-1}, P_{Et} = 68.4 mmHg, T = 0°C, V = 100 ml of hexane

Also the oligomerization of ethylene in hexane, initiated by n-BuLi complexed with tetraethylethylene diamine (TEEDA), was studied. Steric hindrance due to the ethyl groups of TEEDA seems to forbid easy access of the nitrogen atoms to the lithium counterion. These results agree well with the kinetic studies which indicate the absence of aggregated species. The following equation has been established:

$$V_p = k_p[\text{n-BuLi-TEEDA}][\text{Et}]$$

In the present work a detailed study of the effect of new amines dimethyl diethylethylenediamine (DMDEEDA) and pentamethyldiethylenetriamine (PMDT), on the addition of ethylene to n-butyllithium has been made in order to determine the mechanism of the growth step.

EXPERIMENTAL

The purification of the reagents as well as the kinetic studies have been described elsewhere[13].

The degree of association was found by measuring the apparent molecular weight by freezing point depression in cyclohexane and has been described elsewhere[20].

RESULTS AND DISCUSSION

Oligomerization of ethylene by n-BuLi-DMDEEDA

The rate of consumption of ethylene has been measured and related to the mole ratio r = [amine]/[n-BuLi] and the n-BuLi concentration.

The rate of consumption of ethylene is reported in *Figure 1*. Initially a constant rate of consumption, V_p, is observed and is used to characterize the addition reaction.

This result is indicative of equal reactivities of the initiator and the propagating species as well as for their stabilities. By varying the molar ratio r from 0.24 to 2, the rate of consumption increases up to the ratio r = 1, at which point the rate becomes independent of r (*Table 1*). In agreement with Langer[7], we considered the reactive species to be a 1:1 complex.

For $r \geqslant 1$, a nearly first order dependence on n-BuLi concentration was observed (*Table 2*). The general rate expression appeared to fit equation (1). In other words:

$$V_p = k_1[\text{n-BuLi}]^\alpha \qquad (1)$$

The slope of the straight line is equal to 0.90 which is reasonably close to 1. Under these conditions we can assume that α = 1. The intercept of the line with log n-BuLi = 0, allows us to determine k_1, which in these conditions is equal to:

$$\log k_1 = -3.83$$

$$k_1 = 1.48 \times 10^{-4} \text{ s}^{-1}$$

With a first order dependance on ethylene concentration being observed, the following equation has been established:

Table 2 Variation of V_p with n-BuLi (the experimental conditions are the same as in *Table 1*)

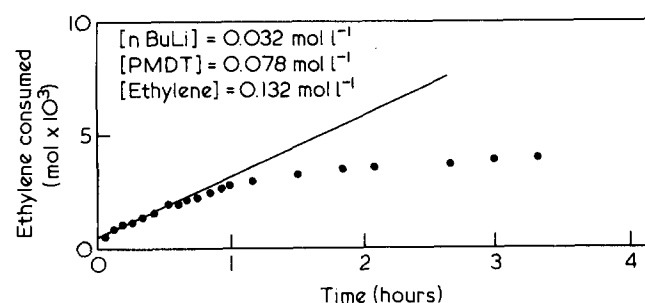| r	n-BuLi ($\times 10^2$ mol^{-1})	V_p ($\times 10^6$ mol l^{-1} s^{-1})
1.11	0.45	1.38
1.25	1.20	3.33
1.20	1.50	3.88
1.02	1.95	5.52
1.20	3.00	5.83

Figure 2 Consumption of ethylene as a function of time

Table 3 Variation of V_p with r = [PMDT]/[n-BuLi] *

r	Amine ($\times 10^2$ mol l^{-1})	V_p ($\times 10^6$ mol l^{-1} s^{-1})
0.25	0.85	2.50
0.49	1.65	5.00
0.67	2.50	6.60
0.90	3.00	7.00
1.25	4.15	7.70
1.62	5.30	7.50
2.21	7.18	7.80

* [n-BuLi] = 0.03 mol l^{-1}, [Et] = 0.143 mol l^{-1}, P_{Et} = 68.4 mmHg, T = 0°C, V = 100 ml of hexane

Table 4 Variation of V_p with n-BuLi (the experimental conditions are the same as in *Table 3*)

r	n-BuLi ($\times 10^2$ mol l^{-1})	V_p ($\times 10^6$ mol l^{-1} s^{-1})
1.46	0.65	1.48
1.45	0.90	2.50
1.46	1.70	4.17
1.49	2.65	6.94
1.50	3.00	7.50
1.50	3.90	8.88

Table 5 Degree of association of n-butyllithium in cyclohexane

	Concentration (mol l^{-1})	Degree of association n
n-BuLi	0.150	6.1
n-BuLi : TMEDA	0.140	2.1
n-BuLi : TEEDA	0.150	1.1
n-BuLi : DMDEEDA	0.136	1.1

with
$$V_p = k_p[\text{n-BuLi:DMDEEDA}][\text{Et}]$$

$$k_p = \frac{k_1}{[\text{Et}]} = 1.03 \times 10^{-3} \text{l.mol}^{-1}.\text{s}^{-1}$$

Oligomerization of ethylene by n-BuLi–PMDT

The rate of consumption of ethylene has been measured and related to the mole ratio $r = [\text{amine}]/[\text{n-BuLi}]$ and the n-BuLi concentration.

The rate of consumption of ethylene is reported in *Figure 2*. At the beginning, we observe a constant rate of consumption which we consider to be V_p and this is used to chacterize the addition reaction. After this initial period, we observe a slowing down of the consumption due probably to some side reaction of the carbanion with PMDT, the resulting products being unable to reinitiate the oligomerization of ethylene.

By varying the molar ratio r from 0.25 to 2.21, the rate of consumption increases up to the ratio $r = 1$, at which point the rate becomes independent of r (*Table 3*).

In agreement with Langer[7], we have considered the reaction species to be a 1:1 complex.

For $r \geqslant 1$, a first order dependence on n-BuLi concentration was observed (*Table 4*).

The general rate expression appeared to fit equation (2). In other words:

$$V_p = k_1'[\text{n-BuLi}]^\alpha \tag{2}$$

The slope of the straight line is equal to one ($\alpha = 1$). The intercept of the line with log n-BuLi = 0, allows the determination of k_1', which is equal to:

$$\log k_1' = -3.58$$

$$k_1' = 2.63 \times 10^{-4} \text{s}^{-1}$$

A first order dependence being observed on ethylene concentration, the following equation has been established

$$V_p = k_p'[\text{n-BuLi:PMDT}][\text{Et}]$$
with

$$k_p' = \frac{k_1'}{[\text{Et}]} = 1.83 \times 10^{-3} \text{l.mol}^{-1} \text{s}^{-1}$$

Degrees of association of n-BuLi in a 1:1 complex with several tertiary diamines

The results of the association studies are in *Table 5* and show a degree of association for n-butyllithium of 6 (within experimental error). When n-butyllithium is complexed with tertiary diamines in a 1:1 ratio the degree of association drops to 2 with TMEDA and 1 with TEEDA and DMDEEDA.

The results agree with the kinetic studies which indicate the intervention of an associated species (n-BuLi–TMEDA)[13] and their absence in the case of TEEDA[16] and DMDEEDA.

No experiments have been performed with PMDT, due to the instability of the n-BuLi PMDT complex.

REFERENCES

1 Hanford, W. E., Poland, J. R. and Young, H. S. US Patent 2377779 (1975)
2 Eberhardt, G. G. and Butte, W. A. *J. Org. Chem.* 1964, **29**, 2928
3 Eberhardt, G. G. and Davis, W. R. *J. Polym. Sci., A* 1965, **3**, 3753
4 Langer, Jr., A. W. in 'Polyamine chelated alkali metal compounds (Ed. A. W. Langer, Jr.), Adv. Chem. Sci., Am. Chem. Soc., Washington, DC, 1974
5 Kamienski, C. W. ref. 4, ch. 7
6 Smith, Jr., W. N. US Patent 3579492 (1971)
7 Bunting, W. and Langer, Jr., A. W. ref. 4, ch. 10
8 Hay, J. N., McCabe, J. F. and Robb, J. C. *J. Chem. Soc. Faraday Trans.I* 1972, 1227
9 Hay, J. N., Harris, D. S. and Wiles, M. *Polymer* 1976, **17**, 613
10 Rodriguez, F., Abadie, M. and Schué, F. *Eur. Polym. J.* 1976, **12**, 17
11 Rodriguez, F., Abadie, M. and Schué, F. *Eur. Polym. J.* 1976, **12**, 23
12 Rodriguez, F., Abadie, M. and Schué, F. *J. Polym. Sci. Polym. Chem. Edn.* 1976, **14**, 773
13 Magnin, H., Rodriguez, F., Abadie, M. and Schué, F. *J. Polym. Sci. Polym. Chem. Edn.* 1977, **15**, 875
14 Magnin, H., Rodriguez, F., Abadie, M. and Schué, F. *J. Polym. Sci. Polym. Chem. Edn.* 1977, **15**, 897
15 Magnin, H., Rodriguez, F., Abadie, M. and Schué, F. *J. Polym. Sci. Polym. Chem. Edn.* 1977, **15**, 901
16 Crassous, G., Abadie, M. and Schué, F. *Eur. Polym. J.* 1979, **15**, 747
17 Crassous, G., Abadie, M. and Schué, F. *Eur. Polym. J.* 1979, **15**, 757
18 Aldissi, M., Schué, F., Geckeler, K. and Abadie, M. *Makromol. Chem.* 1980, **181**, 1413
19 Aldissi, M., Schué, F., Geckeler, K. and Abadie, M. *Makromol. Chem.* 1980, **181**, 1425
20 Bywater, S. and Worsfold, D. J. *J. Organometal Chem.* 1967, **10**, 1