The Rate of Ethylene Polymerization Initiated by Various Chelating Tertiary Diamine : n-Butyllithium Complexes

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SYNOPSIS

The initial rates of ethylene polymerization initiated by 13 chelating tertiary diamine:n-butyllithium complexes were determined under a standard set of conditions. Complexes of the cyclic diamines 1,2-dipyrrolidinoethane, sparteine, and 1,2-dipiperidinoethane resulted in higher polymerization rates and larger ultimate polymer yields than did complexes of acyclic diamines such as N,N,N',N'-tetramethylethylenediamine. The rates of polymerization and also the polymer yields were also strongly affected by the length of the chain segment connecting the two amino groups in the diamine. Two carbon segments were superior to three carbon segments which were better than one or four carbon segments. The decomposition rate of n-butyllithium was also strongly accelerated by the presence of many of these diamines.

INTRODUCTION

The anionic polymerization of ethylene via alkyllithiums complexed by chelating tertiary diamines has been known since the early sixties.[1-5] A wide variety of chelating tertiary diamines have been used, but direct comparison between them is difficult since different reports seldom used identical conditions. In this work thirteen different tertiary diamines were examined as chelants under identical conditions for the n-butyllithium initiated polymerization of ethylene. The conditions chosen were ones which promoted the formation of long chain alkyllithiums.[3] Since the anionic polymerization of ethylene is a "living" polymerization, the polymerization could be stopped, a sample taken for analysis then restarted. The initial rates of ethylene polymerization were determined by gas chromatographic (GC) analysis of the volatile n-alkanes produced by hydrolysis of the initially formed oligomeric alkyllithiums. Later polymerization rates were determined by size exclusion chromatographic (SEC)

analyses of the higher molecular weight polyethylenes produced.

EXPERIMENTAL

Materials

Ethylene was supplied by Scott Gases and scrubbed with Dow Q catalyst and 3A and 4A molecular sieve beds. Toluene, cyclohexane and ether were supplied by Burdick and Jackson. The cyclohexane was purified by passage through an activated alumina column and was purged with nitrogen. The amines N,N,N',N'-tetramethylmethylenediamine (TMMDA), N,N,N',N'-tetramethylethylenediamine (TMEDA), N,N,N',N'-tetraethylethylenediamine (TEEDA), N,N,N',N'-tetramethyl-1,3-propanediamine (TMPDA), N,N,N',N'-tetramethyl-1,4-butanediamine (TMBDA), dipiperidinomethane (DIPIM), 1,2-dipiperidinoethane (DIPIE), and 1,8-bis(dimethylamino)naphthalene (BDMAN) were obtained from Aldrich. The amine, N, N, N', N' - tetramethyl - o - phenylenediamine (TMOPDA) was obtained from Kodak. TMEDA was distilled prior to use. BDMAN was used as received. The rest of the amines were stored over a mixture of 3A and 4A molecular sieves and passed

down an activated alumina column under nitrogen prior to use. The amines 1,2-dipyrrolidinoethane (DIPYE), 1,3-dipiperidinopropane (DIPIP), and 1, 2 - bis (2, 6 - dimethylpiperidino) cyclohexane (BDMPC) were synthesized from starting materials obtained from Aldrich (*vide infra*). Sparteine sulfate was obtained from K & K and converted to sparteine (*vide infra*). Solutions of n-butyllithium in cyclohexane were obtained from Foote Chemical Company.

1,2-Dipyrrolidinoethane (DIPYE)[6,7]

A solution of 67.2 g (0.95 mol) of pyrrolidine and 44.4 g (0.24 mol) of 1,2-dibromoethane in a mixture of 200 mL of toluene and 75 mL of 2-propanol was refluxed under nitrogen for 120 h. The reaction mass was washed with water and the two phases separated. The aqueous phase was made basic with NaOH and extracted with ether. The ether extracts were combined with the organic portion of the initial reaction mass. This solution was dried (MgSO$_4$), concentrated *in vacuo*, and distilled to produce 22.7 g (57%) of 1,2-dipyrrolidinoethane (DIPYE): bp 136–137°C (40 mm).

1,3-Dipiperidinopropane (DIPIP)

This diamine (94%, bp 115°C at 2.8 mm Hg) was prepared from piperidine and 1,3-dibromopropane using the procedure described above.

1,2-Bis(2,6-dimethylpiperidino)cyclohexane (BDMPC)

This diamine (61%) was prepared from 2,6-dimethylpiperidine and 1,2-dibromocyclohexane using the procedure described above. The crude product was 97% pure (GC analysis) and was not distilled.

Sparteine

An aqueous solution of sparteine sulfate was treated with two equivalents of NaOH and extracted with ether three times. The combined extracts were dried (MgSO$_4$) and concentrated *in vacuo* leaving sparteine (90%). Gas chromatography indicated a purity of 99+%.

Initiator Decomposition Rates

The decomposition rates of n-butyllithium and n-butyllithium in the presence of equimolar amounts of DIPYE, DIPIE, DIPIP, and TMEDA, respectively, were determined under nitrogen in octane at 115°C. Initial concentrations of n-butyllithium were 0.029 M. At timed intervals an aliquot was with-

drawn and reacted with an excess of trimethylsilyl chloride in octane. When no chelating diamine was added, dimethylphenylsilyl chloride was used. The samples were analyzed via GC to determine the amount of n-butyllithium left by determining the amount of butyltrimethylsilane or of butyldimethylphenylsilane present. The GC analysis also indicated whether the diamine itself was decomposing or being metalated. This procedure was repeated with n-butyllithium and DIPYE at 60 and 80°C.

Ethylene Polymerizations

The polymerizations were carried out in a 1-L Parr autoclave equipped with stirrer, shot tank, sampling valve, bottom dump valve, heater, and hardwired controller. The autoclave was rinsed prior to each use with 800 mL of 0.045 M n-butyllithium in cyclohexane under nitrogen. The autoclave was charged with 350 mL of dry cyclohexane via cannula under nitrogen pressure then heated to 60°C. Ten millimoles of the desired chelating tertiary diamine was introduced via syringe through the sampling valve which was equipped with a rubber septum. Then 10 mmol of n-butyllithium solution was added via syringe through the sampling valve. Ethylene, 100 psig, was introduced. When a sample was desired, the autoclave was vented and the sample taken by syringe through the sampling valve. Then the autoclave was repressurized to 100 psig with ethylene. The sample (∼ 7 mL) was added to about 7 mL of 50/50 cyclohexane/2-propanol. Such samples were used for GC analyses if no precipitated polymer was evident. If precipitated polymer was evident, the polyethylene was isolated and analyzed by SEC. At the end of each experiment, the autoclave was vented and an excess of 2-propanol added. The autoclave was disassembled, its contents were placed in a baking pan. The pan was put in a forced air oven for 8 h at 90°C. The dried polyethylene was removed and the yield determined.

Gas Chromatographic Analyses

The gas chromatographic analyses were performed using a Hewlett-Packard 5840A gas chromatograph equipped with two 6 ft × 1/8 in. columns packed with OV-1 on Chromosorb WHP (80–100 mesh). For the GC analyses of the ethylene polymerizations early in the reaction the GC was temperature programmed to increase from 80 to 300°C at a rate of 20°C/min and then remain at 300°C for 10 min. The flow rate used was 45 mL/min. Standards used were decane, dodecane, tetradecane, hexadecane, and docosane. Lithium efficiencies were determined

by using an internal standard such as tridecane or by finding the sensitivity ratios between the tertiary diamine used and the alkanes. Reproducibility of the two methods was good giving values within 2% of each other.

Size Exclusion Chromatographic Analyses

Samples which contained precipitated polymer were analyzed by SEC using a Waters 150C size exclusion chromatograph using 1,2,4-trichlorobenzene solvent at 135°C. Molecular weights reported are relative to polystyrene standards.

RESULTS AND DISCUSSION

Our goal was the preparation of living polymeric 'lkyllithiums of uniform molecular weight by ini-

tiating the polymerization of ethylene with tertiary diamine:n-butyllithium complexes. To do this conditions were sought that minimized chain transfer and termination reactions reported to occur during these polymerizations.[4,8] The stability of the initiator complexes were studied at several temperatures and using a variety of chelating tertiary diamines. The results were assumed to be indicative of the stabilities of the corresponding oligomeric and polymeric n-alkyllithium:chelating tertiary diamine complexes produced during the polymerizations.

The decomposition rates of n-butyllithium alone and in the presence of an equimolar amount of DIPYE, DIPIE, DIPIP, and TMEDA were measured in octane at 115°C. These results are presented in Figure 1. In the absence of a chelating tertiary diamine the concentration of n-butyllithium decreased very slowly. However, all the diamines dramatically accelerated its decomposition rate. The
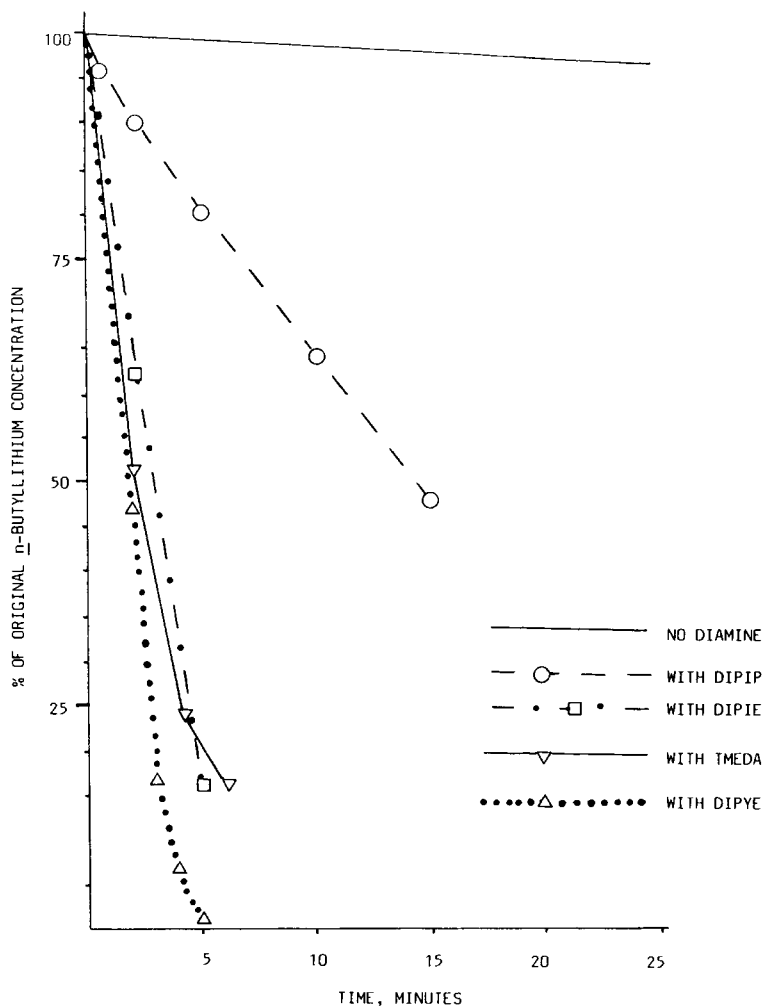

Figure 1 The decomposition rates of n-butyllithium in the presence of equimolar diamine at 115°C in octane. Initial concentration was 0.029 M.

most effective diamine was DIPYE. It was followed in turn by DIPIE, TMEDA, and DIPIP. In the presence of an equimolar amount of DIPYE the half-lives of n-butyllithium at 60, 80, and 115°C were 185, 23.1, and 0.8 min, respectively.

The concentrations of the diamines were also monitored by gas chromatography. The concentrations of DIPYE and DIPIE remained unchanged indicating that these diamines were not readily attacked by n-butyllithium. DPIP, however, slowly disappeared and TMEDA was rapidly metalated (see Fig. 2). These results suggested that diamines that bore methyl groups on nitrogen were readily attacked by n-butyllithium and their complexes were not likely to yield clean polymerizations. However, chelating diamines containing only methylene units adjacent to nitrogen were much more stable and were more likely to yield clean ethylene polymerizations.

A temperature of 60°C was chosen as the polymerization temperature. At this temperature the polymerization was still reasonably rapid, decomposition of the chelated alkyllithiums were reasonably slow and oligomeric alkyllithium complexes up to C_{40} were soluble. The polymerizations were carried out under 100 psig of ethylene using 10 mmol of n-butyllithium and 10 mmol of diamine in 350 mL of cyclohexane.

The following reactions are possible under these conditions using chelating tertiary diamines:
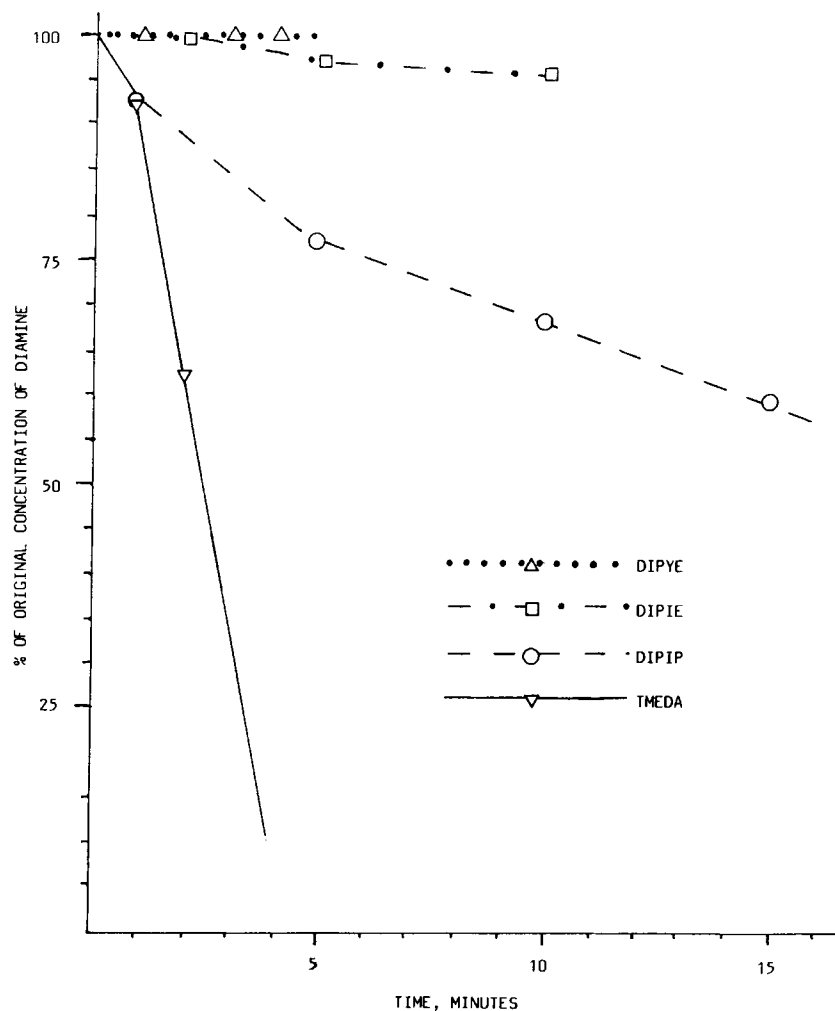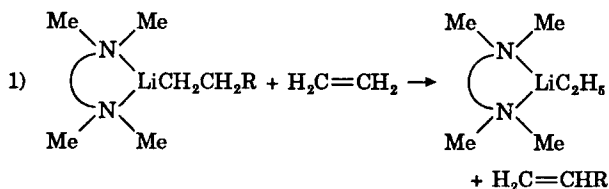
1)
$$\underset{\text{Me}}{\overset{\text{Me}}{\diagdown}}\underset{\text{N}}{\diagup} \text{LiCH}_2\text{CH}_2\text{R} + \text{H}_2\text{C}=\text{CH}_2 \longrightarrow \underset{\text{Me}}{\overset{\text{Me}}{\diagdown}}\underset{\text{N}}{\diagup}\text{LiC}_2\text{H}_5 + \text{H}_2\text{C}=\text{CHR}$$
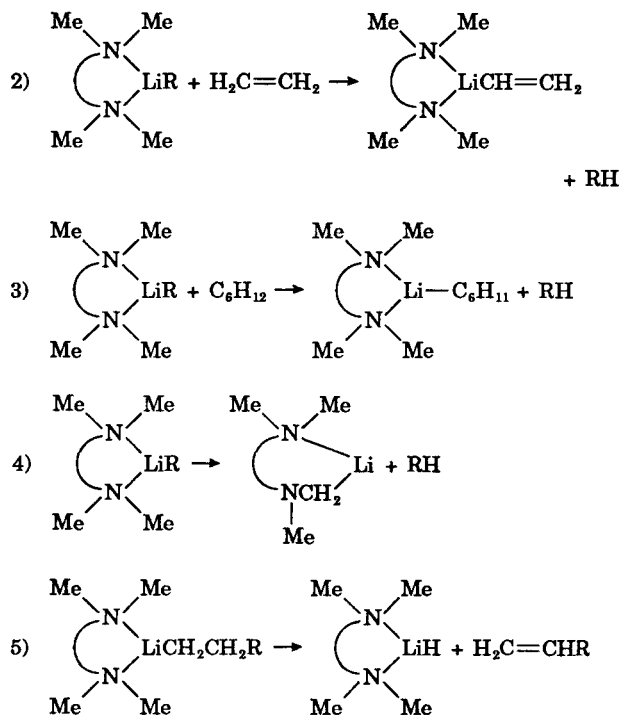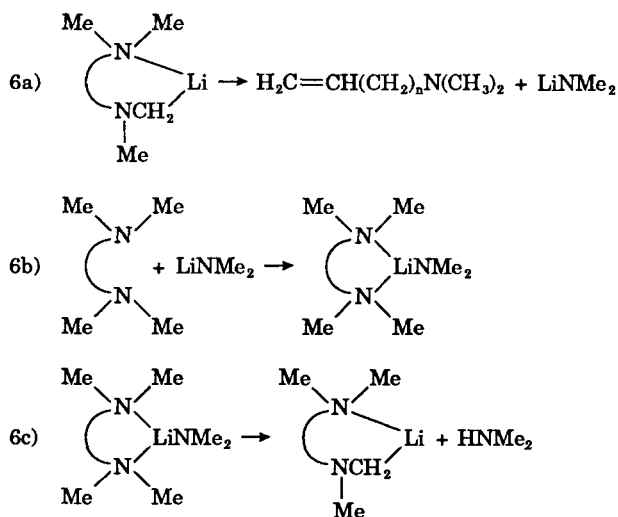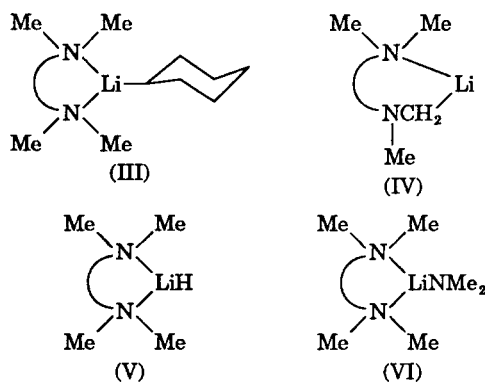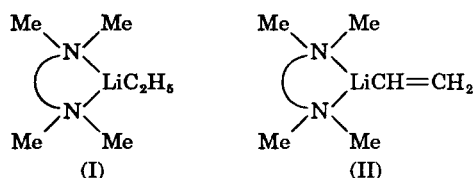

Figure 2 Decomposition rates of various diamines at 115°C in octane in the presence of n-butyllithium. Initial concentration of diamine was 0.029 M.

2) (Me₂N—CH₂CH₂—NMe₂)LiR + H₂C=CH₂ → (Me₂N—CH₂CH₂—NMe₂)LiCH=CH₂ + RH

3) (Me₂N—CH₂CH₂—NMe₂)LiR + C₆H₁₂ → (Me₂N—CH₂CH₂—NMe₂)Li—C₆H₁₁ + RH

4) (Me₂N—CH₂CH₂—NMe₂)LiR → (Me₂N—CH₂CH₂—N(Me)CH₂)Li + RH

5) (Me₂N—CH₂CH₂—NMe₂)LiCH₂CH₂R → (Me₂N—CH₂CH₂—NMe₂)LiH + H₂C=CHR

Additionally the decomposition of the metalated diamine is possible:[8]

6a) (Me₂N—CH₂CH₂—N(Me)CH₂)Li → H₂C=CH(CH₂)ₙN(CH₃)₂ + LiNMe₂

6b) (Me₂N—CH₂CH₂—NMe₂) + LiNMe₂ → (Me₂N—CH₂CH₂—NMe₂)LiNMe₂

6c) (Me₂N—CH₂CH₂—NMe₂)LiNMe₂ → (Me₂N—CH₂CH₂—N(Me)CH₂)Li + HNMe₂

Thus, in addition to chelated n-butyllithium, the potential initiators for ethylene polymerization in solution are

(I) (Me₂N—CH₂CH₂—NMe₂)LiC₂H₅

(II) (Me₂N—CH₂CH₂—NMe₂)LiCH=CH₂

(III) (Me₂N—CH₂CH₂—NMe₂)Li—C₆H₁₁

(IV) (Me₂N—CH₂CH₂—N(Me)CH₂)Li

(V) (Me₂N—CH₂CH₂—NMe₂)LiH

(VI) (Me₂N—CH₂CH₂—NMe₂)LiNMe₂

Species I would be expected to act very similarly to tertiary diamine chelated n-butyllithium. Species III, if it occurs, would probably add ethylene as fast or faster than chelated n-butyllithium and then react similarly. The species II, IV, V, and VI, in which the diamine was TMEDA, were investigated as possible initiators for the anionic polymerization of ethylene. Their reactivities were compared to n-butyllithium under the standard conditions used. Species II and IV initiated the polymerization of ethylene slowly. Species V and VI did not initiate the polymerization of ethylene under the chosen conditions. These results indicate that reactions 1–4 are chain transfer reactions and reactions 5 and 6a are termination reactions under the chosen conditions.

Analyses of samples taken in during ethylene polymerizations prior to the precipitation of polyethylene were used to determine initial rates. Figure 3 shows some representative GC traces from this type of analysis. Table I presents the initial rate data in ethylene insertions per minute (per active lithium). The chelating tertiary diamines which gave the fastest initial rates were DIPYE, sparteine, and DIPIE. It is interesting to note that in these chelating diamines there are no methyl groups. The initial rate for polymerizations initiated by n-butyllithium complexes of TMEDA, TMPDA, and TEEDA followed in that order. It is also apparent from the data in Table I that the polymerization rates depended strongly on the length of the hydrocarbon bridge separating the two nitrogens of the diamine. Polymerizations were fastest when the diamine contained a two carbon bridge, slower for those containing a three carbon bridge and slowest for those containing one or four carbon bridges. This is demonstrated clearly in Figure 4 for the series (CH₃)₂N(CH₂)ₙN(CH₃)₂ and (C₅H₈N)(CH₂)ₙ-(NC₅H₈). It was also possible to determine the fraction of initially charged n-butyllithium that was actively polymerizing ethylene. This could be done
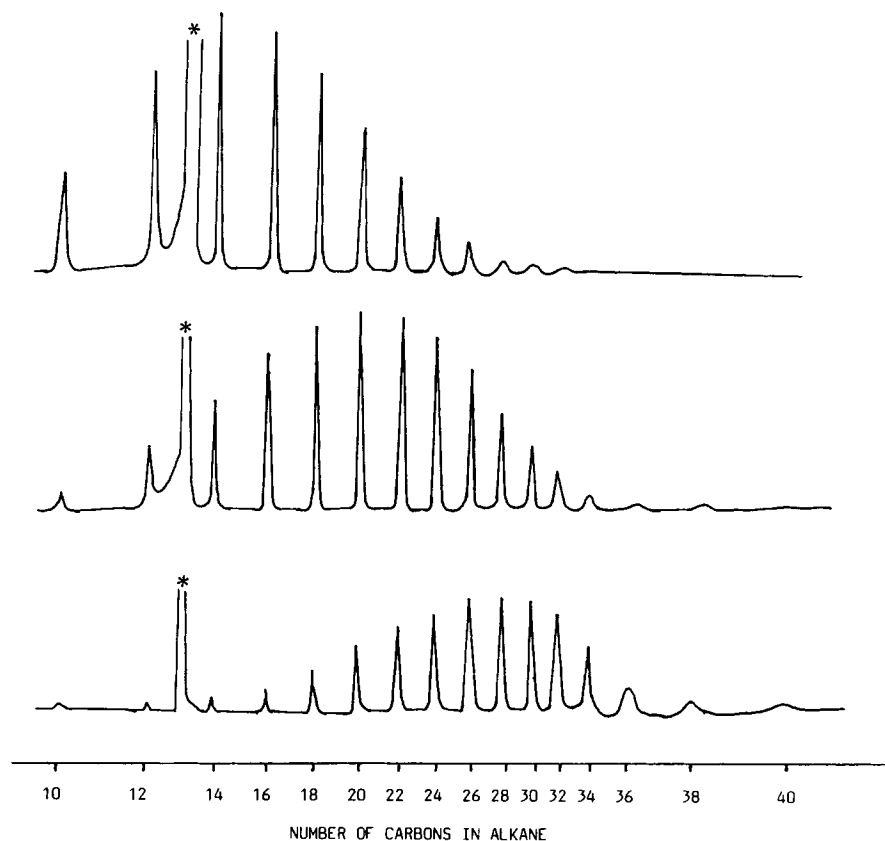
Figure 3   Representative GC traces from ethylene polymerization by tertiary chelating diamines and n-butyllithium: (a) after 120 min with DIPIM : n-butyllithium; (b) after 180 min with DIPIM : n-butyllithium; (c) after 1 min with DIPYE : n-butyllithium. Peaks marked with an asterisk are due to the chelating diamine.

early in the polymerization when the oligomeric alkyllithiums were still soluble in the reaction solvent so that withdrawn samples were representative of the entire reaction mass and when the hydrocarbons produced by hydrolysis of these samples were still volatile enough to be quantitatively analyzed by GC. These lithium efficiencies were determined by dividing the total moles of hydrocarbon detected by the moles of initially charged n-butyllithium. The calculation assumed that little or no chain transfer had occurred early in the polymerizations. This belief was supported by the fact that no significant amount of lower alkanes were detected in hydrolyzed samples taken later in the polymerization. Thus, the lower alkanes produced on hydrolysis of early samples must have been present in the reaction mass as oligomeric alkyllithiums which continued to add ethylene. These lithium efficiencies are reported in Table II as percentages. It is once again significant to note that all the chelating diamines, except DIPIM, which do not have methyl groups attached to the nitrogen gave lithium efficiencies above 90%.

TMMDA, DIPIM, and TMEDA gave lithium efficiencies of around 80%. The lithium efficiency of TMOPDA : n-butyllithium complex is low, perhaps due to lithiation of the dimethylamino groups. If teleomerization was to occur it would show falsely high lithium efficiencies, which does occur. The TMPDA : n-butyllithium complex also had a low lithium efficiency, even though its initial rate was the fifth fastest indicating that the majority of the n-butyllithium was not contributing to polymerization.

Under the conditions used the reaction mass was homogeneous early in the polymerization when the initial rates were determined and became heterogeneous as the number of carbon atoms in the polymeric alkyllithiums exceeded about forty. At that point the polymer began to precipitate and a slurry was formed. The growth of the polyethylene in this portion of the reaction was monitored by taking samples of the precipitated polyethylene and using SEC analysis to provide M_n, M_w, peak molecular weight and the polydisperity, M_w/M_n. Tables III–
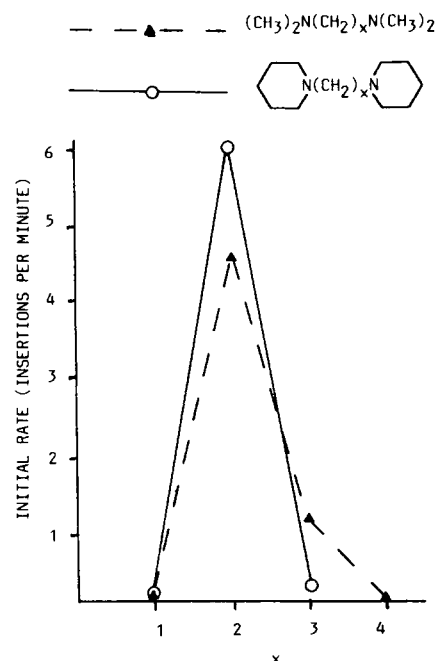
Table I Initial Rates of Ethylene Polymerization by n-Butyllithium Chelated by Various Tertiary Diamines

Chelating Diamine	Structure	Initial Rate (insertions/min)
DIPYE		9.00
Sparteine		9.00
DIPIE		6.00
TMEDA	Me$_2$NCH$_2$CH$_2$NMe$_2$	4.50
TMPDA	Me$_2$NCH$_2$CH$_2$CH$_2$NMe$_2$	1.10
TEEDA	Et$_2$NCH$_2$CH$_2$NEt$_2$	1.00
DIPIP		0.0750
TMOPDA		0.0571
DIPIM		0.0526
TMMDA	Me$_2$NCH$_2$NMe$_2$	0.0167
BDMPC		n.d.[a]
BDMAN		n.d.[a]
TMBDA	Me$_2$NCH$_2$CH$_2$CH$_2$CH$_2$NMe$_2$	n.d.[a]

[a] Initial rate not detectable over a 4-h period.

Figure 4 Initial rate as a function of the length of the methylene bridge between nitrogens of the chelating amines.

VIII present the SEC data for the polyethylene produced by the n-butyllithium complexes with DIPYE, DIPIE, sparteine, TMEDA, TMPDA, and TEEDA, respectively. Figure 5 presents M_w as a function of time for these chelating diamines. It is apparent that both DIPYE and DIPIE continue to polymerize ethylene at much greater rates after precipitation than the other chelating diamines. The increases in polydisperity noted as the polymerization time increased may be in part due to unequal access of growing chain ends to the monomer in the heterogeneous reaction mass. It is also likely that an accumulation of chain transfer and termination products resulting from reactions discussed earlier contributes significantly.

Table IX presents the yields of polyethylene obtained with the various chelating diamines. As would

be expected the chelant : n-butyllithium complexes with the highest initial and overall rates gave the highest yields. It is again apparent from this data that chelants with two methylenes between the nitrogens were preferable to those with three which were preferable to those with one or four. The trend in polymerization activity also paralleled the decrease in steric hindrance of the lithium site. The chelating diamines BDMPC and BDMAN were no more effective than unchelated n-butyllithium. In the case of BDMPC it is reasonable to speculate that this was due to extreme steric hindrance of the

Table II Lithium Efficiencies for Chelating Tertiary Diamines in the Anionic Polymerization of Ethylene by n-Butyllithium

Chelating Tertiary Diamine	Lithium Efficiency (%)
DIPYE	94
DIPIE	90
Sparteine	100
TMEDA	82
TMPDA	35
TEEDA	94
DIPIP	100
TMOPDA	36
DIPIM	83
TMMDA	85

Table III   SEC Data for Polyethylene Produced by DIPYE:n-Butyllithium

Time (min)	M_n	M_w	Peak MW	M_w/M_n
5	1380	2030	1780	1.47
15	1640	2280	1880	1.39
45	2220	3740	2940	1.69
60	2460	4220	3270	1.71
115	3290	6120	5150	1.86
240	4000	8190	6830	2.05

Table IV   SEC Data for Polyethylene Produced by DIPIE:n-Butyllithium

Time (min)	M_n	M_w	Peak MW	M_w/M_n
5	803	1200	1030	1.49
15	2200	3170	2940	1.44
25	2670	4210	4020	1.58
45	2740	4670	4230	1.70
60	2800	4660	4440	1.67
120	2900	4910	4670	1.69
150	2840	4970	4670	1.73

Table V   SEC Data for Polyethylene Produced by Sparteine:n-Butyllithium

Time (min)	M_n	M_w	Peak MW	M_w/M_n
5	840	1390	1160	1.48
15	1260	1750	1490	1.40
25	1650	2220	1880	1.34
45	1440	2100	1880	1.45
60	1420	2180	1880	1.54
120	1520	2440	1880	1.61
180	1680	2770	2110	1.65
240	1680	2790	2230	1.66

Table VI   SEC Data for Polyethylene Produced by TMEDA:n-Butyllithium

Time (min)	M_n	M_w	Peak MW	M_w/M_n
15	1010	1500	1320	1.49
25	1320	1860	1680	1.41
45	1690	2280	1880	1.35
60	1760	2430	2000	1.38
120	1960	2870	2500	1.46
180	2140	3190	2940	1.49
240	2320	3580	3270	1.55

lithium site. In the case of BDMAN low activity may have been due to the chelate having the wrong size "bite" or to lithiation of the aromatic hydrogens present to produce an aryllithium that did not ini-

Table VII   SEC Data for Polyethylene Produced by TMPDA:n-Butyllithium

Time (min)	M_n	M_w	Peak MW	M_w/M_n
25	705	1050	1030	1.48
45	1030	1470	1160	1.43
60	997	1470	1240	1.47
150	1670	2290	1880	1.37
210	1620	2310	1880	1.42

Table VIII   SEC Data for Polyethylene Produced by TEEDA:n-Butyllithium

Time (min)	M_n	M_w	Peak MW	M_w/M_n
25	616	916	791	1.49
45	825	1240	1030	1.50
60	863	1310	1030	1.51
120	1540	2060	1880	1.33
200	1640	2250	1880	1.37

Table IX   Yields of Polyethylene from the Anionic Polymerization of Ethylene by n-Butyllithium Chelated with Various Tertiary Diamines

Tertiary Diamine	Yield Polyethylene (g)[a]
DIPYE	58.25
DIPIE	24.00[b]
Sparteine	19.00
TMEDA	18.02
TMPDA	12.15
TEEDA	9.57
DIPIP	2.90
TMOPDA	1.84
DIPIM	1.70
TMMDA	0.53
TMBDA	0.32

[a] Yields are after 4 h at 60°C, 100 psig ethylene, with 10 mmol of n-butyllithium and 10 mmol of chelating diamine in 350 mL of cyclohexane.
[b] Yield after 3 h.

tiate further ethylene polymerization rapidly or to metallation of the dimethylamino groups.

The chelating diamines whose complexes with n-butyllithium were the most effective ethylene polymerization initiators were DIPYE, DIPIE, TMEDA, and sparteine. The reason for the improvement in the chelating properties of DIPYE over DIPIE is thought to be at least partially steric and probably partially electronic in nature. At this point it is still unknown whether tertiary chelating diamines containing even smaller nitrogen contain-
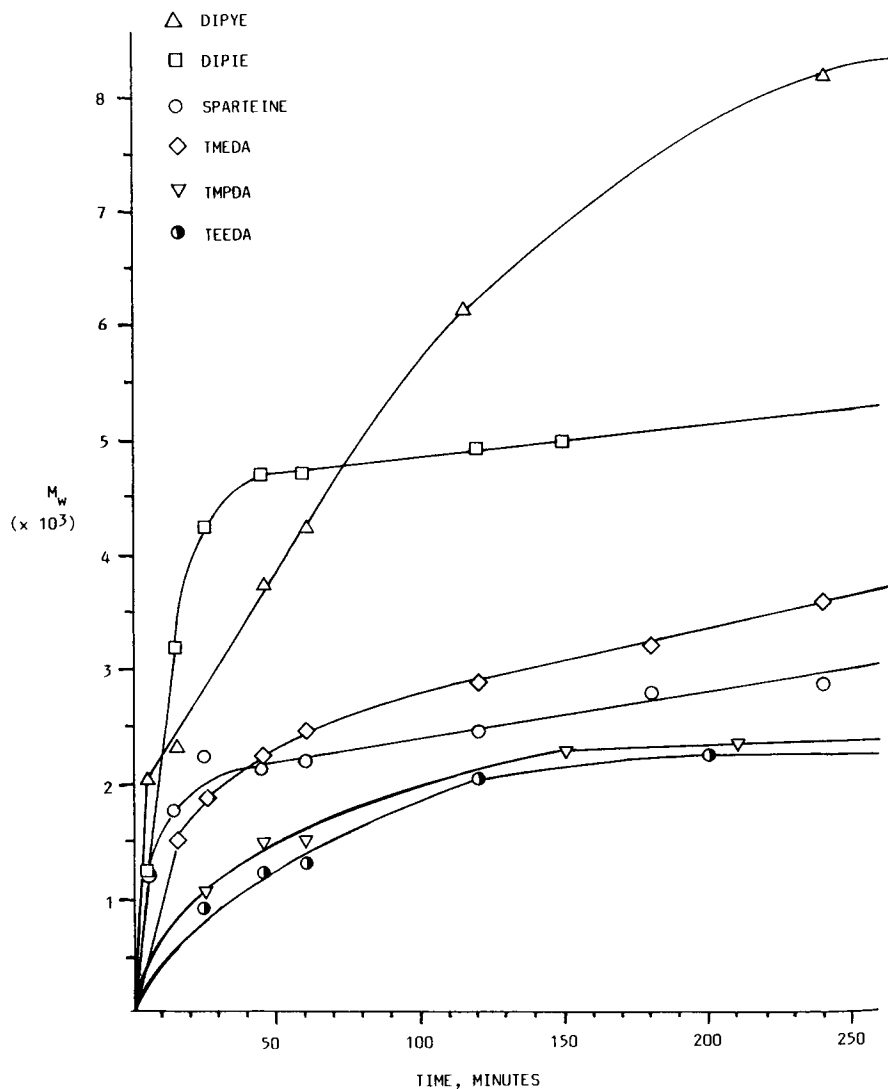
Figure 5 M_w as a function of time for various chelating diamine : n-butyllithium complexes for the polymerization of ethylene.

ing rings, such as 1,2-diazetidinoethane and 1,2-aziridinoethane might perform even better than 1,2-dipyrrolidinoethane.

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