Reactions of living polytetrahydrofuran with amines: 2. Other tertiary amines

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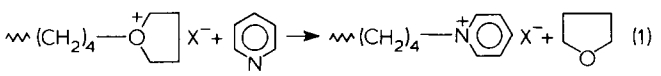
The reactions of living cationic polyTHF with tertiary amines have been examined. In all cases reaction results in the formation of quaternary salts which do not exchange with oxonium ions. The rates of reaction reflect the basicities of the amines; for heterocycles the order is 4-ethyl pyridine > pyridine > isoquinoline > quinoline > acridine, and for aliphatic tertiary amines triethylamine > tributylamine > diethylaniline. Triphenylamine does not react in a timescale of several hours but the more basic amines react quantitatively under equimolar conditions at −10°C within minutes. Di-tertiary amines have been studied as linking agents and tetramethylethylenediamine (TMEDA) has been shown to be virtually quantitative. 4,4′-bipyridyl appears not to be so efficient, and pyrazine reacts only monofunctionally.

INTRODUCTION

In Part 1 of this series[1] it was shown that pyridine reacts rapidly and quantitatively with the oxonium ions of 'living' polytetrahydrofuran (polyTHF) under equimolar conditions to form the pyridinium salt (equation 1). This species is stable and was shown not to exchange with any excess oxonium ions present in solution.



(1)

In the present paper the reactions of living polyTHF with other tertiary amines have been examined to establish whether equation (1) is of general applicability. The amines chosen included other heterocyclics, such as quinoline, isoquinoline and acridine — extending the reaction to molecules of lower basicity — and a series of aliphatic amines. Three di-tertiary amines have also been studied as a means of linking polyTHF chains to create polymers possessing ionic groups at predetermined positions along the polymer backbone.

Gel permeation chromatography (g.p.c.) was used extensively to study the polyTHF–pyridine reaction, and it was observed that the product possessed a retention time significantly longer than its methoxy-terminated equivalent polymer because of specific interactions with the Styragel columns. Further, this interaction caused the polymer to elute with a skew distribution, the actual retention time observed increasing with decreasing concentration injected. The ability to distinguish pyridinated material in the presence of a methanol-killed fraction of identical degree of polymerization, both by its u.v. absorption and its different retention time allowed the time for completion of the polyTHF–pyridine reaction to be estimated by periodic sampling of the reaction mixture into methanol. This same procedure has been employed in this work to correlate the rate of reaction with the basicity of the tertiary amine used.

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EXPERIMENTAL

Materials

Tetrahydrofuran, silver hexafluorophosphate, *p*-methylbenzyl bromide, and *p*-xylylene dibromide were used as described previously[1]. Quinoline (BDH), isoquinoline (BDH, 99+%), 4-ethylpyridine, triethylamine (Fisons, 98%), tri-n-butylamine, *N*,*N*′-diethylaniline, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (BDH) were distilled from calcium hydride, mostly under reduced pressure, taking a middle fraction for use.

Acridine (Aldrich) was recrystallized three times from toluene/petroleum ether. Pyrazine (Aldrich 99+%) was recrystallized twice from toluene. 4,4′-bipyridyl (BDH, 98%) was recrystallized from toluene. Triphenylamine (BDH, 98%) was recrystallized from toluene.

Methods

Preparation of living polyTHF and its reaction with tertiary amine. Living monofunctional polyTHF free from silver bromide was prepared under nitrogen by reacting *p*-methylbenzyl bromide with $AgPF_6$ in THF. The technique has been described in Part 1[1]. Living difunctional polyTHF was prepared in like manner by replacing *p*-methylbenzyl bromide with *p*-xylylene dibromide[2].

Again, the procedures for reacting living polyTHF with the various tertiary amines were minor variations of those described in Part 1 for pyridine[1].

Coupling reactions between living polyTHF and ditertiary amines (DTA). Single stage reaction. Living polyTHF (20 ml, 0.2 mmol mol. wt ~3000) was injected at −20°C on to a solution of DTA (0.1 mmol) in 2 ml THF, the reaction being carried out under nitrogen in a 50 ml sealed flask. A further sample of polyTHF was simultaneously terminated with methanol to act as a standard. The flask was maintained at about −10°C for 3.5 h,

during which time samples were removed and terminated with methanol, and the solvent removed.

Two stage reaction. Living polyTHF (140 ml, 2.8 mmol mol. wt ~2400) was filtered from AgBr at −25°C directly on to excess DTA (up to 30 mmol) with rapid stirring. The solution was allowed to warm to −10°C and, after 30 min, methanol was added and the solvent stripped off. When tetramethylethylene diamine (TMEDA) was used, excess reagent was removed by prolonged pumping. Excess bipyridyl was removed by fractional precipitation of the polymer by water from methanol solution until the u.v. intensity of bipyridyl in the g.p.c. trace of the product was below 1% of that of the polymer.

The purified product (1 g, 0.4 mmol) was weighed into a 50 ml flask and pumped for 12 days under high vacuum, then sealed under nitrogen with a rubber septum. Sufficient THF was added to give a 2×10^{-2} M solution and a sample was removed to confirm the absence of degradation by this drying treatment. The solution was then reacted at −20°C with an equivalent amount of living polyTHF (mol. wt ~4500). Samples were withdrawn after 10 min and compared with the product obtained after 5 h at −10°C.

In both the coupling reactions described above the molecular weights of the polyTHF components were determined from the g.p.c. retention times of methanol terminated samples obtained during filtration[3].

Comment. Experiments which involve sampling from the reaction vessel prior to addition of amine are subject to systematic error. The amount of amine to be added was calculated on the volume of polyTHF solution estimated to remain after sampling had occurred. However, no allowance was made for contraction of the solution through polymerization so that an overestimate of 4–5% was generally made of the amount of amine required for molar equivalence.

G.p.c. and n.m.r. measurements

The equipment and analytical procedures used for both these techniques have been described previously[1].

RESULTS AND DISCUSSION

The approach chosen to study the interaction between living polyTHF and the tertiary amines was similar to that used in examining the equivalent reaction with pyridine. The growing living polyTHF was maintained at a low temperature — usually −10°C — until the desired molecular weight had been attained, and then divided into three portions, two small and one large. One of the small portions was terminated with excess methanol to act as a low molecular weight standard. Simultaneously the large portion was reacted with the tertiary amine and maintained at the polymerization temperature whilst samples were removed at intervals and immediately terminated with excess methanol. The third portion was allowed to polymerize undisturbed until sampling was complete, when it was terminated with excess methanol and used as the high molecular weight standard. All samples were then subjected to g.p.c. analysis, and some were worked up for ^{1}H n.m.r. analysis to confirm that a quaternization process had taken place and to assess its efficiency (Appendix).

HETEROCYCLES

Quinoline

G.p.c. traces obtained from reactions of living polyTHF with equimolar quinoline are presented in *Figure* 1. After 5 min two distinct peaks are observed, that at longer retention time being asymmetric and possessing significant u.v. absorption whilst the other is symmetrical, exhibits only weak u.v. absorption and has a peak position coincident with the low molecular weight standard. In successive time intervals the latter peak moves to shorter retention times and diminishes in size relative to the almost stationary u.v. absorbing fraction so that the ratio of the total areas of the u.v. and differential refractometer signals (u.v./RI) increases with reaction time. Finally, after 150 min reaction the second peak has disappeared and the polymer sample is almost entirely included in the high u.v. absorbing peak which is at a significantly longer retention time than the high molecular weight standard. This peak maximum has moved fractionally but significantly to shorter retention times over the reaction period and although in its final form it exhibits the long trailing edge observed with pyridinated polymer[1], its leading edge is more rounded.

The two peaks at 5 min reaction clearly correspond to the polyTHF–quinoline adduct and the methoxy-terminated material, the former appearing at longer retention time because of interaction with the matrix of the g.p.c. columns. The diminution in the signal from the living u.v. transparent material is due to its continuing reaction with quinoline and is confirmed by the increase in u.v./RI with time. After 150 min the reaction is seen to be complete, and is therefore much slower than the equivalent pyridine reaction. Nevertheless, there is no evidence that the process is reversible since reacted and unreacted polymer chains exist independently of each other.

Because the rates of propagation and adduct formation are comparable, the average degree of polymerization of the adduct increases with time, so that the distribution of chain lengths becomes distorted from the initial Poisson distribution by an increasing proportion of higher molecular weight product. Thus the sharp leading edges obtained with the products arising from the much faster reacting pyridine systems[1] are not observed and the traces exhibit more rounded shapes on the high molecular weight side of the peaks whilst retaining the characteristic elongated tails. The gradual incorporation of higher molecular weight product partly accounts for the slow movement of the peak toward shorter retention time. A further contribution to this movement is caused by the increasing proportion of adduct in the sample since there is an inverse relationship observed between the retention times of polymers possessing terminal quaternary ammonium salts and their concentrations (see later and ref 1).

The rate of reaction between amine and polymer increases with reagent concentration; experiments using 50% molar excess quinoline exhibited a trend similar to, but faster than that observed in *Figure* 1. Traces showed that the bulk of the reaction had taken place in 8 min, and complete reaction was indicated by a single asymmetric peak, the leading edge of which was distinctly sharper than that obtained in *Figure* 1 because of the faster rate of reaction.

^{1}H n.m.r. measurements confirmed the formation of the quinolinium salt (see Appendix), and the inverse de-

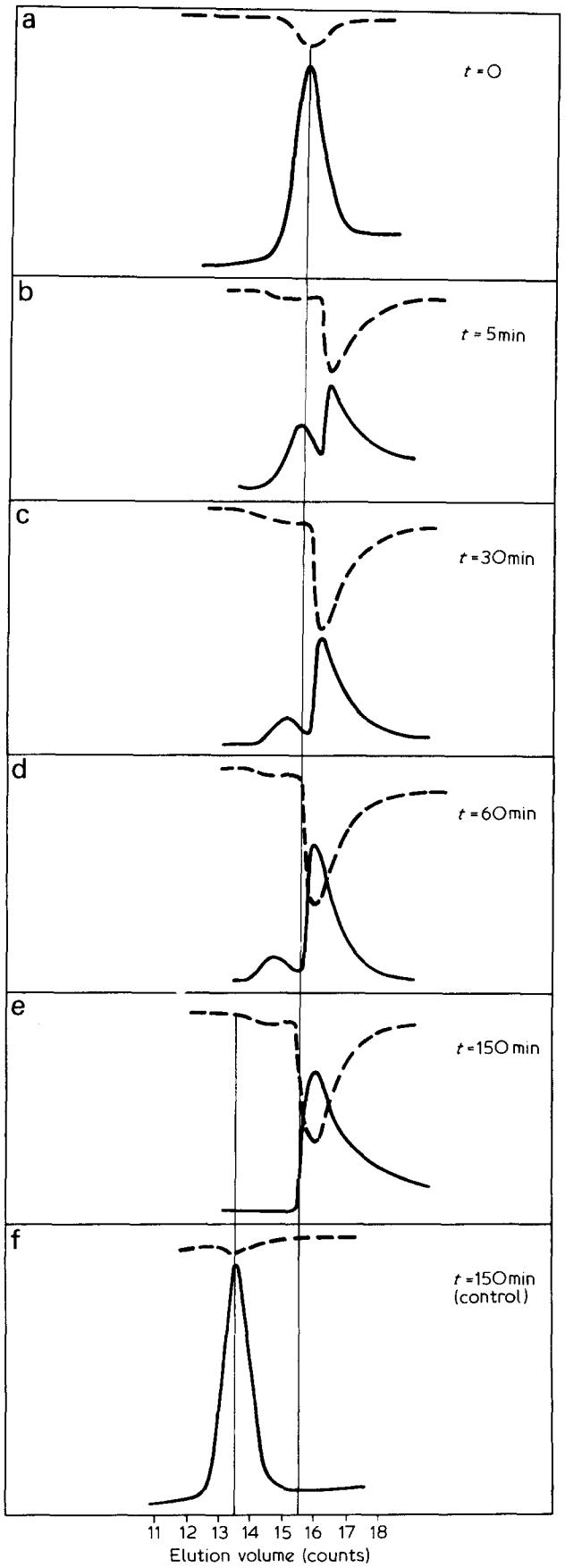


Figure 1 Reaction of living polyTHF with quinoline (1:1). Mixture sampled into methanol at the times indicated. G.p.c. sample concentration 0.2% w/v: – – – –, u.v., 32x; ——, RI, 4x

pendency between the retention time and sample concentration observed with polymers possessing terminal pyridinium salts[1] was tested with this system and found to hold.

Lastly, the consumption of quinoline was followed by subjecting samples taken at increasing reaction times from the equimolar reaction mixture to gas liquid chromatographic (g.l.c.) analysis. The results showed a fall off of residual quinoline with time at a rate which roughly paralleled the g.p.c. data.

Isoquinoline and 4-ethyl pyridine

When living polyTHF is reacted under equimolar conditions with isoquinoline or with 4-ethyl pyridine, small peaks representing unreacted polymer in the position of the low molecular weight standard were observable in the g.p.c. traces of the earliest samples taken at 1 min, but these had disappeared within 3 min reaction time. The products were again recognizable by their strong u.v. signals as fractions which eluted somewhat later in the traces with a skew distribution, but since reaction was close to completion in the earliest samples taken, the large displacement noted in the early stages of the reaction with quinoline was absent. Instead the two sequences closely resembled that described for pyridine (*Figure* 3, ref 1). Dilution of the solution of the product injected on to the g.p.c. columns again resulted in increased retention times whilst those of the methanol-killed fractions were unaffected.

Complete quantitative reaction of the living polyTHF with these two amines was also established by the absence of growth in equimolar systems run over several hours and the products were in both cases identified by ^{1}H n.m.r. as quaternary ammonium salts (Appendix). The times for complete reaction were estimated from g.p.c. to be about 1 min for 4-ethylpyridine and 2–3 min for isoquinoline (cf. pyridine 1–2 min).[1] G.l.c. traces of residual isoquinoline also confirmed its enhanced reactivity over quinoline.

Experiments in which sub-stoichiometric quantities of the amines were added showed that the residual oxonium ions grew at a rate unaffected by the presence of terminated material and that no exchange occurred between the two species.

Acridine

Figure 2 shows a typical series of g.p.c. traces resulting from the reaction of equimolar amounts of living polyTHF and acridine. Unlike those obtained with other heterocycles there is no observable splitting into two peaks — nevertheless there is evidence that a slow reaction takes place. Firstly, the u.v./RI area ratio of the growing peak increases from 0.19 after 15 min to 0.62 after 180 min, a trend which is the reverse of that expected if the u.v. absorbance were solely due to the initiator. Secondly, the RI peak develops a low molecular tail to which the u.v. signal appears to correspond and hence this probably represents terminated product.

These observations were supported by experiments involving two molar equivalents of acridine. Here the u.v./RI ratio increased to 1.1 in 80 min and the low molecular weight tail coincident with the u.v. peak, just observable in *Figure* 2, was readily apparent. Despite the slowness of the reaction, confirmed by g.l.c. measurement of acridine consumption, the adduct appears to be formed irreversibly.

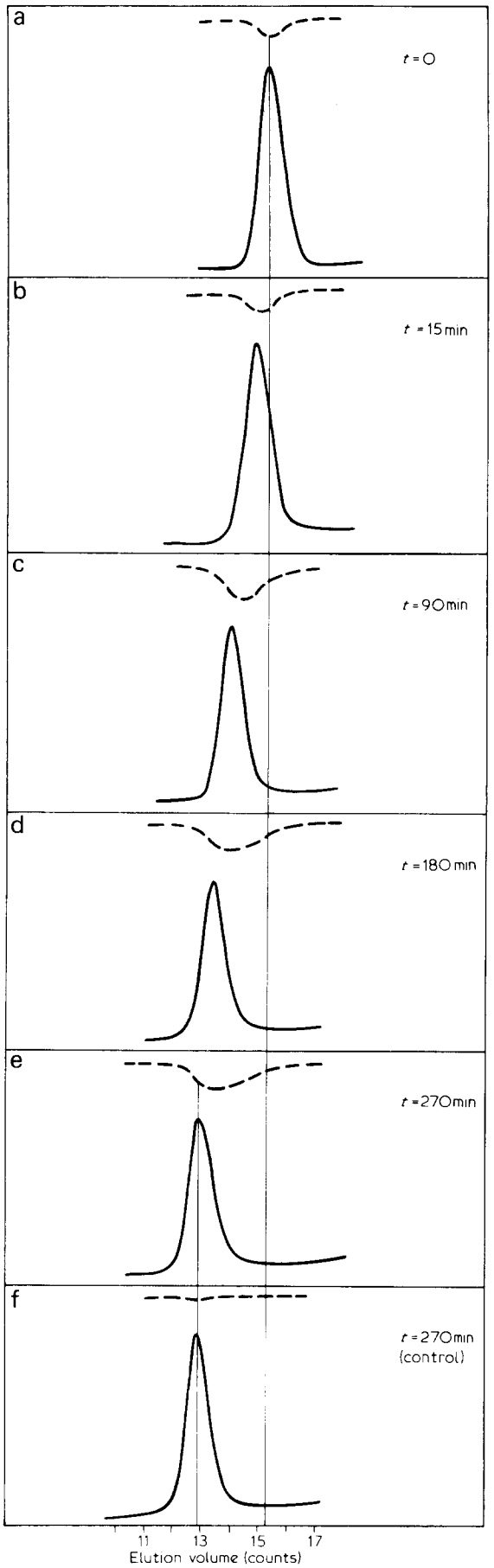


Figure 2 Reaction of living polyTHF with acridine (1:1). Mixture sampled into methanol at the times indicated. G.p.c. sample concentration 0.2% w/v: – – – –, u.v., 32x; ——, RI, 4x

Attempts were made to achieve quantitative addition by using a large excess of acridine. The addition of a 40-fold molar excess at a higher living polymer concentration (3×10^{-2} M) resulted in rapid termination; the retention time of the adduct after 270 min was identical with that of the low molecular weight blank and the peak shapes were similar. The material was shown to contain the acridinium salt (Appendix) but it was estimated that only about half the ends had been thus terminated. It is possible that the large excess of acridine used had allowed a more reactive impurity present in small concentration in the amine to terminate a significant number of ends.

The behaviour of this material on the g.p.c. columns was different from the salts of the other heterocycles in a number of ways. Firstly, the peak was symmetrical rather than skew; secondly its retention time was the same as, rather than longer than, the standard; and lastly the position of the peak was found to be independent of the quantity of polymer injected onto the column. The absence of the specific column interaction observed with the other quaternary ammonium salts suggested that in this case the quaternary nitrogen is inaccessible to the polar groups on the column matrix since it is flanked by two phenyl groups, and so the polymer behaves in a manner identical to its non-polar analogue.

The stability of the acridinium end group was tested by dissolving an isolated sample of the fully quaternized product in THF and allowing the solution to stand for several hours at -10°C. If the formation of the acridinium salt were governed by an equilibrium process then this would be indicated by spontaneous growth of the polymer via the dissociated form. However, no change in the polymer molecular weight was observed.

General

The reactivities of the heterocycles in the reaction with the oxonium ions of polyTHF can be placed in the following order: 4-ethyl pyridine > pyridine > isoquinoline > quinoline > acridine, and this order reflects the decreasing basicities of the reagents. In all cases, however, the reaction can be forced to completion in a reasonable time by using excess amine. The reactions are irreversible, even with bases as weak as acridine.

ALIPHATIC TERTIARY AMINES

Triethylamine and tributylamine

These two reagents are considered together since their behaviour in this reaction is similar. Both react rapidly with living polyTHF under equimolar conditions – reaction is complete within 5 min with triethylamine and within 20 min with tributylamine. G.p.c. traces of the products show the familiar asymmetric distribution at retention times longer than the methanol-terminated standards, and the retention times vary with sample concentration in the expected way. Again, studies with sub-stoichiometric quantities of amine demonstrate the lack of interchange between the quaternary ammonium salt and the propagating oxonium ion.

N,N'-*diethylaniline*

Tests under equimolar conditions showed that even after 180 min reaction time little adduct was formed (5–10%). Three-fold molar excess diethylaniline was there-

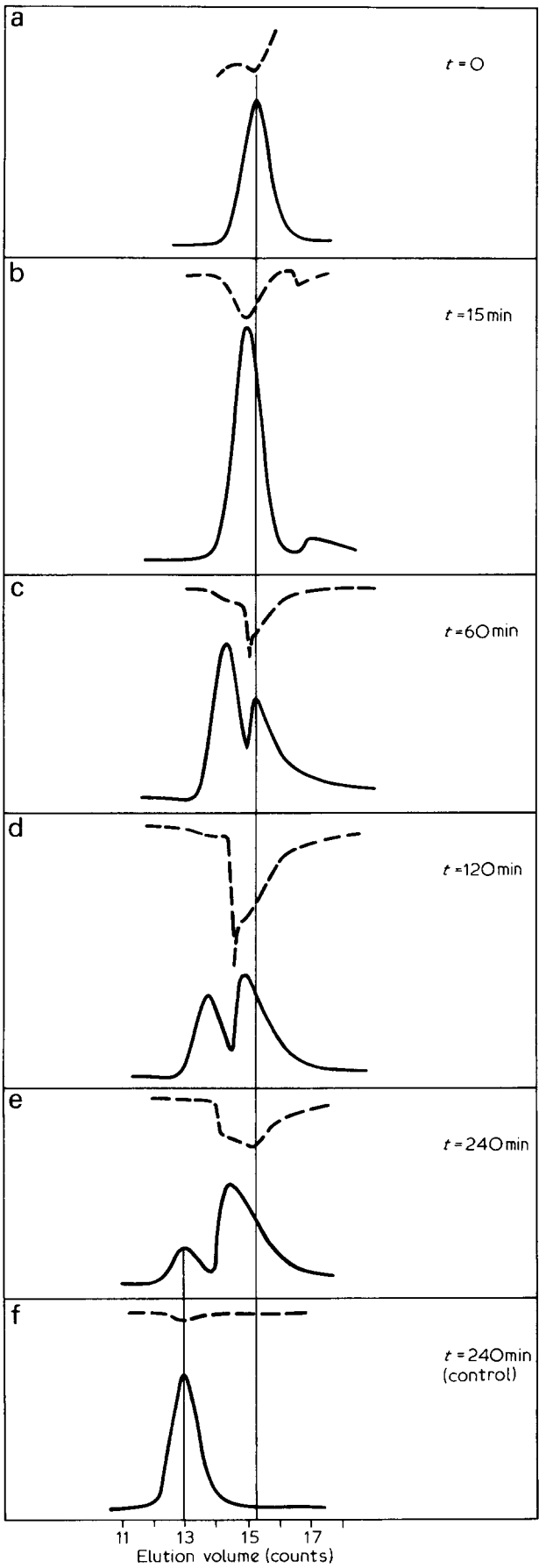


Figure 3 Reaction of living polyTHF with *N,N'*-diethylaniline (1:3). Solution sampled into methanol at the times indicated. G.p.c. sample concentration 0.2% w/v: — — — —, u.v., 32x; ——, RI, 8x (curves a and f, 16x)

fore introduced and the traces obtained with time under these conditions are shown in *Figure* 3 (some spiking of the u.v. traces is observed which is regarded as being a malfunction of the detector rather than reflecting a property of the polymer, since a similar effect is not observed in the RI trace). Clear evidence of slow addition is obtained; a small peak due to the adduct appears at high retention time after 15 min reaction, and this grows at the expense of the propagating peak until by 120 min it becomes the major component. In 240 min at least 75% of the chains have been terminated with diethylaniline.

The position of the adduct peak moves to shorter retention times as the reaction proceeds both because of its increasing concentration and continual inclusion of higher molecular weight material, and the changing distribution which also results in a leading edge more rounded than observed with the faster reacting amines (cf. quinoline).

Triphenylamine

Experiments in which living polyTHF was reacted with triphenylamine in three fold excess for 225 min gave no evidence of adduct formation; the product peaks had retention times and shapes identical to those of the standards, and they exhibited no enhanced u.v. absorbance. It is therefore concluded that the basicity of triphenylamine is too low to replace the THF molecule solvated on to the end of the propagating chains within the normal timescale, at least at this concentration.

General

The reactivities of the aliphatic tertiary amines are directly related to their basicities, being in the following order: triethylamine > tributylamine ≫ diethylaniline and no observed reaction with triphenylamine.

DITERTIARY AMINES

The rapid and apparently quantitative reactions observed between living polyTHF and the more reactive tertiary amines suggest that diamines of equivalent structure could be used as effective chain coupling agents. The coupling reaction may be approached in one of two ways: living polyTHF and diamine can be reacted in 2:1 molar stoichiometry to produce directly a polymer in which the quaternary nitrogens are centrally placed along the polymer chain. Alternatively, the polyTHF may be reacted with excess diamine to yield predominantly a polymer with a terminal tertiary amine grouping which may be isolated and subsequently reacted with further living polyTHF. This latter process, although multistage, has the advantage that the positions of the quaternary nitrogens along the chain may be predetermined by appropriate selection of the molecular weights of the two polyTHF polymers employed. Both techniques have been used in this investigation.

Tetramethylethylene diamine (TMEDA)

When living polyTHF was added to one molar equivalent of TMEDA a mixture of products in which one and both nitrogens were quaternized was obtained, showing that the second nitrogen was not significantly deactivated by reaction of the first.

By adding the living polymer solution slowly to a well-stirred ten-fold excess of the diamine a product with only

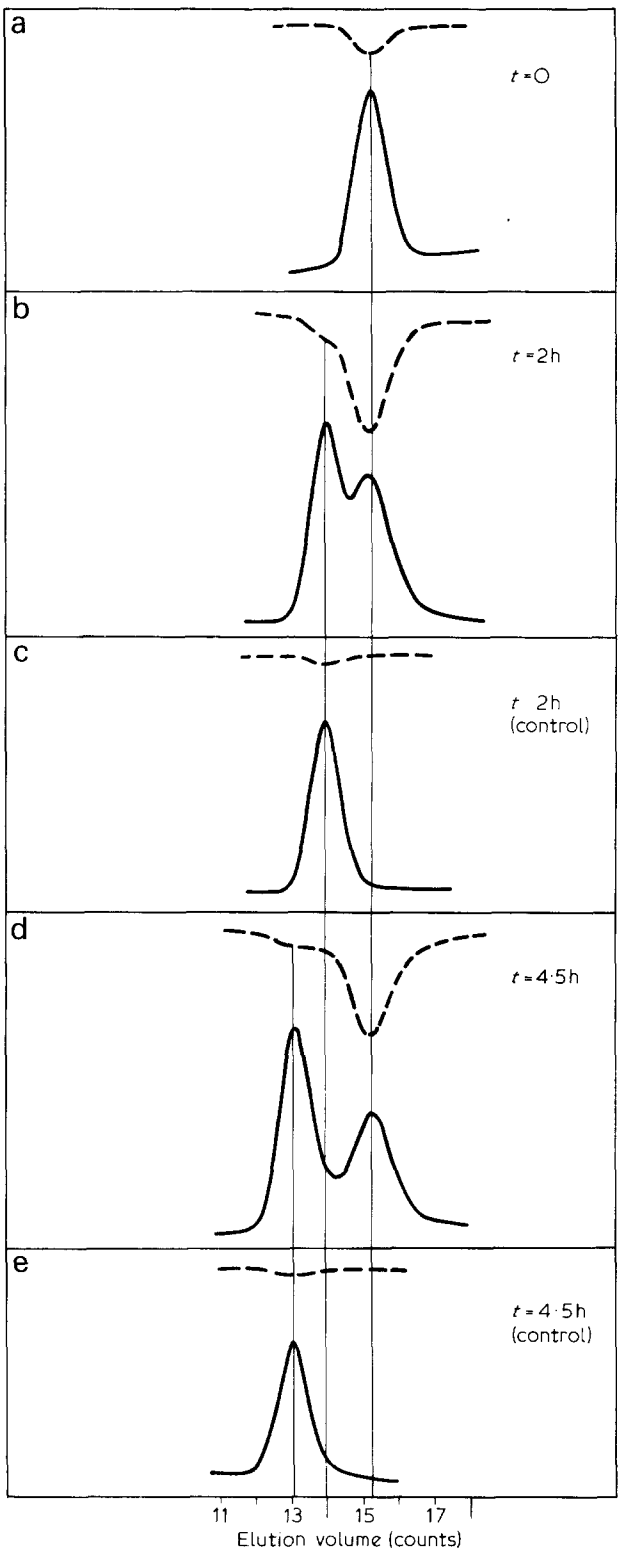


Figure 4 Reaction of living polyTHF with pyrazine (1:0.7). Samples taken into methanol at the times indicated. G.p.c. injection concentration 0.1 to 0.2% w/v: – – – –, u.v. 32x; ——, RI, 4x (a, c and e, 8x)

one quaternized nitrogen was obtained, whereas reaction under similar conditions with 2:1 stoichiometry yielded uniquely the doubly-linked product. G.p.c. traces of materials displayed the usual skew distribution and concentration effects expected, and were identified as the mono- and di-adducts by calibration of the retention times observed at high concentration where the effects of column adsorption are minimal. No evidence of a second component was found in either by varying the concentration, and these facts taken in conjunction with the methods of preparation imply that each can be prepared largely free from the other. ^{1}H n.m.r. confirmed the product in each case to be the expected mono- or di-quaternary ammonium salt.

A product possessing only one quaternized nitrogen was isolated and reacted with living polyTHF of different chain length in a second separate step. The product trace obtained after 15 min was identical with those obtained after longer reaction times showing that reaction is complete in that period. Again, by eliminating the effect of concentration on retention time through using fairly high injector concentrations, the product was shown to have the expected molecular weight.

Thus TMEDA may be used to link monofunctional living polyTHF in a single or two stage process.

4,4′-Bipyridyl

4,4′-Bipyridyl was found to react in a manner similar to TMEDA. Perhaps surprisingly in view of conjugation effects the diadduct is readily formed and careful addition of the living polyTHF to an excess of the diamine is required to prepare the single adduct quantitatively. The latter material was also successfully coupled with living polyTHF of different molecular weight in a separate stage.

Difunctional living polyTHF

The use of difunctional living polyTHF with diamines might in principle lead to high molecular weight materials with pairs of ionic groups spaced regularly along the chains. Using *p*-xylylene dibromide to initiate the difunctional polyTHF, the product with TMEDA was a tough rubbery material, quite different from the normal waxy polyTHF. Despite its superior physical properties it remained soluble in THF and methanol, and it appears to be another example of polymer in which the creation of ionic groupings and their association leads to substantially different bulk properties[4].

Confirmation that this material was the high molecular weight coupled product expected could not, however, be obtained by g.p.c. The traces were irregular and broadly spread at high retention times, and were also characterized by failure of much of the injected polymer to elute. This behaviour does not seem inconsistent with a multiply-charged high molecular weight polymer interacting more strongly with the column than the products of TMEDA with monofunctional THF. Indeed these effects may be strong evidence for such a product.

Attempts to couple bipyridyl with difunctionally initiated polyTHF to high molecular weights were not successful. Despite an apparent increase in viscosity after addition of the amine, g.p.c. traces showed that, although bipyridyl had been incorporated as evidenced by enhanced u.v. absorption, molecular growth took place at the rate characteristic of unterminated polymer. This is surprising in view of the apparent ease of coupling both functionalities to monofunctional polyTHF, but further investigatory work was not carried out.

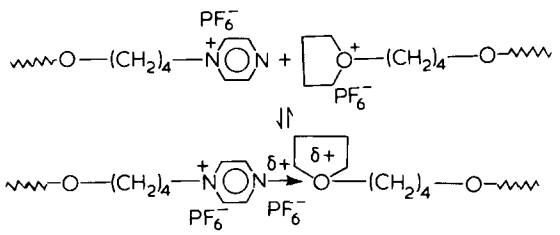
Pyrazine

Living polyTHF was found to react completely with slight ($\sim 10\%$) excess pyrazine within 15 min to form the mono adduct exclusively. The g.p.c. peak of the product was symmetrical, was at the same retention time as the

low molecular weight standard and its position was insensitive to injected sample concentration. This indicates the absence of specific interaction on the column with the inference that the positive nitrogen is shielded.

Attempts to use the amine as a coupling agent failed. For example, with 0.7 molar equivalents of pyrazine (*Figure* 4), after 2 and 4.5 h reaction time the g.p.c. traces exhibit two peaks. The stationary component at longer retention time is strongly u.v. absorbing and corresponds to the equivalent methanol-terminated sample, whilst the second peak moves to higher molecular weight and remains transparent.

Perhaps more significantly the rate of movement of the uncoupled peak appears to be marginally less than that of the reference solutions, suggesting that the rate of propagation is reduced by the presence of the pyrazine adduct. If real, this may be caused by interaction between the two species to form a complex as shown in equation (2):



(2)

Solvation of the oxonium ion by the pyrazine-terminated polymer should confer stabilization with a consequent reduction or even cessation of propagation which would therefore proceed principally via its dissociated form. Since two peaks exist on the trace, one moving and u.v. transparent and the other static and u.v. absorbing, it is evident that the equilibrium cannot be extended to allow exchange of the pyrazine ligand between chains. Presumably the quaternary nitrogen bond is not easily ruptured and the basicity of the second nitrogen is reduced by its formation to a degree where its interaction with the oxonium ion of the second polymer molecule is limited to solvation rather than bond formation by nucleophilic replacement of the THF molecule.

General

The coupling efficiency of the diamines is in the order TMEDA > 4,4′-bipyridyl ≫ pyrazine. This is understandable in terms of conjugation effects associated with the quaternization of the first nitrogen.

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APPENDIX

Identification of reaction products by ^1H n.m.r.

N.m.r. data for the polyTHF–tertiary amine adducts are presented in the *Table*. All the polyTHF samples show peaks at 7.2 δ (4H) and at 4.5 δ (2H) characteristic of the aromatic protons and benzylic methylene protons respectively of the *p*-methylbenzyl bromide initiator. The relative areas of the hydrogen signals of the quaternary ammonium end groups and of these initiator protons can be used to give estimates of the efficiency of quaterni-

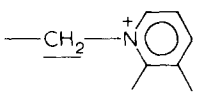
Table 1 Chemical shifts of ^1H n.m.r. spectra of polyTHF–Tertiary amine adducts

Tertiary Amine	Chemical shifts (ppm relative to TMS)	$\frac{Q^*}{I}$
Quinoline	9.4 (doublet, 1H); 9.1 (doublet, 1H); 8.0–8.4 (multiplet, 5H); 7.2 (multiplet, 4H, Initiator); 5.1 (triplet, 2H), 4.5 (singlet, 2H, Initiator)	1.0
Isoquinoline	9.9 (singlet, 1H); 8.0–8.4 (multiplet, 6H); 7.2 (multiplet, 4H, Initiator); 4.9 (triplet, 2H); 4.5 (singlet, 2H, Initiator)	1.0
4-Ethylpyridine	8.7 (doublet, 2H); 7.8 (doublet, 2H) 7.2 (multiplet, 4H, Initiator); 4.6 (triplet, 2H); 4.5 (singlet, 2H, Initiator); 3.0 (quartet, 2H); 1.4 (triplet, 3H)	1.0
Acridine	9.8 (singlet, 1H); 7.8–8.5 (multiplet, 8H); 7.2 (multiplet, 8H, Initiator); 4.5 (singlet, 4H, Initiator)	0.5
Triethylamine	7.2 (multiplet, 4H, Initiator); 4.5 (singlet, 2H, Initiator); 3.3 (quartet, shoulder on poly THF peak); 1.3 (triplet, 9H)	1.0
Tri(n-butyl) amine	7.2 (multiplet, 4H, Initiator); 4.5 (singlet, 2H, Initiator); 1.0 (triplet, 9H)	1.0
Diethylaniline	7.5 (multiplet, 3.6H); 7.2 (multiplet, 4H, Initiator) 6.6 (multiplet, 2.4H); 4.4 (singlet, 2H, Initiator) 1.1 (multiplet, methyl peaks)	0.4
Triphenylamine	7.2 (multiplet, Initiator); 4.5 (singlet, Initiator)	0
4,4′-Bipyridyl 0.5 mole ratio	9.0 (broad singlet, 4H); 8.3 (broad singlet, 4H); 7.2 (multiplet, 2H, Initiator); 4.7 (broad singlet, 4H); 4.5 (broad singlet, 4H, Initiator)	0.5
4,4′-Bipyridyl equimolar	8.9 (doublet, 2H); 8.8 (doublet, 2H); 8.2 (doublet, 2H); 7.6 (doublet, 2H); 7.2 (multiplet, 4H Initiator) 4.7 (triplet, 2H); 4.5 (singlet, 2H, Initiator)	1.0
Pyrazine equimolar	9.4 (doublet, 2H); 8.8 (doublet, 2H); 7.2 (multiplet, 4H, Initiator); 4.6 (triplet, 2H); 4.4 (singlet, 2H, Initiator)	1.0
TMEDA equimolar	7.2 (multiplet, 4H, Initiator); 4.5 (singlet, 2H, Initiator); 3.1 (singlet, 6H); 2.36 (singlet, 3H, Initiator); 2.32 (singlet, 6H)	1.0

* Q = quaternary salt; I = initiator

zation, although the accuracy of such figures are only about ± 20%. These estimates are given in the last column of the *Table*.

The presence of the quinolinium groups on the polyTHF–quinoline adduct is indicated by the aromatic protons in the region 8.0 to 9.4 δ and in particular by the low field resonances at 9.1 δ and 9.4 δ. Further, the triplet at 5.1 δ demonstrates that this group is bound to polyTHF since it is characteristic of the terminal methylene unit bonded to the quaternary nitrogen as



Comparison of the strength of these signals with those of the initiator indicates quantitative conversion of the polymer into the quinolinium adduct.

A similar situation is found for isoquinoline. The quaternary species is indicated in particular by the low field proton at 9.9 δ and the terminal methylene group of the polyTHF chain adjacent to the isoquinolinium unit occurs as a triplet at 4.9 δ. Again, the relative areas of the isoquinolinium units and the initiator peaks indicate quantitative quaternization.

An equivalent analysis on the product of the reaction with ethyl pyridine also indicates that the quaternary ammonium salt is quantitatively formed.

With acridine systems the situation is less straightforward. Products from reaction with equimolar acridine showed no evidence of quaternization within the detection limit of the n.m.r. method. When a large excess of acridine was used it was necessary to remove unreacted acridine from the polymer by g.p.c. prior to analysis. This introduced impurities derived from the THF solvent, but it was possible to identify the acridinium species from, in particular, a singlet at 9.8 δ. However, within the limits of accuracy of the n.m.r. technique, the spectra indicated that only about 50% of the chains contained acridinium end-groups.

With the products of reaction with aliphatic amines, the analysis is less clear since the peaks of interest lie close to the much larger in-chain polyTHF peaks. Thus the peak due to the $-CH_2N^+R_1R_2R_3$ grouping should occur at about 3.3 δ when R_1R_2 and R_3 are all aliphatic, and this is close to the peak at 3.4 δ due to the $-CH_2O$ linkage in polyTHF. However, for both triethylamine and tributylamine there are strong indications that efficient quaternization has taken place.

The triethylamine derived sample shows the $-CH_2N^+$ linkage as a shoulder at 3.3 δ on the main peak due to polyTHF. In addition, the methyl peak is observable as a triplet at 1.3 δ, and its position indicates the quaternary ammonium salt rather than free amine. Moreover, there are suggestions of effects due to ^1H–^{14}N spin spin coupling which only occur in quaternary salts. If unreacted amine were present an absorption should have been observed at 2.5 δ due to the $-CH_2N$ grouping and this does not occur. Thus all the features of the spectrum indicate that the triethylamine derived species is the quaternary ammonium salt, and the relative areas of the methyl and initiator peaks are consistent with quantitative formation.

The spectrum of the product of the reaction with tributylamine is complicated by slight shifts in peak positions and the broader shape to be expected from the butyl $-CH_2N^+$ group, and it is much more difficult to distinguish this absorption from the in-chain polyTHF peak at 3.4 δ. However, the peak due to the methyl groups of the butyl ligands at 1.08 δ and the absence of a free amine peak at 2.5 δ again support a quaternary ammonium structure, and analysis by relative areas indicates a high efficiency.

The spectrum of the product obtained by using 50% molar excess of diethylaniline is more complicated than would be expected if quantitative addition had occurred, and showed that a substantial amount of the free amine had not been removed in the work-up procedure. The free amine should exhibit absorptions at about 3.3 δ due to the methylene component of the ethyl groups and these are therefore probably obscured by the polyTHF peaks, whereas quaternization would result in methylene absorption at about 3.8 δ (these peaks are, of course, moved downfield relative to those of purely aliphatic amines because of the effect of the phenyl group). There are indications of two types of methyl groups at 1.1 δ and 1.2 δ suggesting the presence of free amine and quaternary salt in the ratio of 2:1. Support for this interpretation is found in the aromatic region of the spectrum which shows multiplets at about 7.5 δ and 6.6 δ in the ratio of about 3:2. In the free amine, the two protons *meta* to the nitrogen would absorb at about 7.5 δ and the *ortho* and *para* protons at 6.6 δ. Thus the relative intensities would be 2:3 — the reverse of those observed. The effect of quaternization is to cancel the strong upfield shift due to the nitrogen so that all the aromatic protons resonate at about 7.5 δ, and this accounts for the extra intensity of the 7.5 δ peak in the observed spectrum. Thus this peak is due to the 5 protons of the quaternary species and the two *meta* protons of the free amine whereas the 6.6 δ peak is due to the 3 remaining protons of the free amine. Analysis based on the ratios of the sum of these peaks to those of the initiator moiety suggests about 40% quaternization.

Of the products derived from the difunctional amines those from 4,4'-bipyridyl are the clearest to analyse; the sharp peaks obtained are characteristic of this diamine and are well clear of all other bands in the spectra, enabling clean differentiation between free diamine, mono-addition and di-addition. Thus the symmetrical free diamine shows only two types of hydrogens giving a very characteristic $(AB)_2$ pattern with peaks at about 7.5 δ and 8.75 δ. On monoquaternization the reduction in symmetry results in four types of hydrogen with two $(AB)_2$ patterns, one for each ring. The expected shifts are 9.1 δ and 8.5 δ for the quaternized ring and 8.8 δ and 8.5 δ for the non-quaternized ring. Allowing for slightly different shifts due to solvent effects and different counterions, the spectra observed with the product at equimolar reaction are in excellent agreement with these predictions. Virtually pure mono-adduct was obtained when excess bipyridyl was reacted with living polyTHF (*Table* 1).

When 0.5 molar equivalents of diamine are added, the expected two peaks in the aromatic region corresponding to di-quaternization appear. These are much broader than the signals obtained from the product from equimolar reaction so that the doublet splitting of the $(AB)_2$ spin system is lost. This effect has been observed previously with polymer systems possessing highly polar 'end-groups' and is believed to be caused by the limited solubility of the polar species in $CDCl_3$, the chains being held in solution by the abundant polyTHF units. The

$-CH_2N^+$ group of the THF unit bonded to bipyridyl is clearly observed as a broad multiplet at 4.7 δ, and the relative areas of the bipyridyl $-CH_2N^+$ and initiator peaks all indicate quantitative formation of the di-adduct.

It was not possible to observe all the peaks of interest in the spectra of TMEDA adducts because of the masking effect with aliphatic amines already discussed. The methyl peaks are, however, readily observed as sharp singlets well-removed from polyTHF peaks. When excess TMEDA was employed the product exhibited methyl peaks due to the quaternized and unquaternized forms at 3.1 δ and 2.32 δ, respectively, and their relative areas show that the mono-adduct is virtually exclusively formed.

The analysis of spectra of the pyrazine products is similar to that of bipyridyl products since the diamine and the di-adduct are symmetrical whereas the mono-adduct is unsymmetrical. Pyrazine itself gives a singlet at 8.6 δ, the mono-adduct gives an $(AB)_2$ spectrum with doublets at 8.8 δ and 9.4 δ, and the diadduct would be expected to produce a singlet from four equivalent hydrogens at about 9.5 δ. No evidence was found for the di-adduct in any samples tested. However, the product of the equimolar reaction shows peaks at 9.4 δ and 8.8 δ (with $(AB)_2$ structure) and a triplet of 4.6 δ characteristic of $-CH_2-N^+$. Relative areas again indicate complete conversion to the mono-adduct.