Reactions of living polytetrahydrofuran with amines: 1. Pyridine

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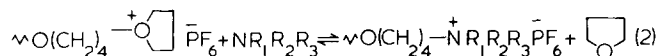*(Received 1 June 1980)*

Pyridine has been shown to react rapidly and quantitatively with living cationic polyTHF to yield terminal pyridinium groups. These ionic groups interact with the matrix of gel permeation chromatography columns to give traces with asymmetric peaks at retention times longer than those obtained with THF polymers of the same molecular weight not possessing polar terminal units. This reaction has also been applied to pyridine units attached to polymer chains to yield graft copolymers quantitatively.

INTRODUCTION

Recent work has succeeded in defining conditions under which tetrahydrofuran (THF) may be polymerized cationically as a living system free from termination and transfer reactions[1,2]. The living conditions have allowed good yields of block copolymers to be synthesized either by the employment of an appropriate anion to cation transformation reaction[3,4] or by direct coupling with anionic living polystyrene[5]. A suitable initiating system to produce monofunctional polyTHF is the combination of silver hexafluorophosphate with an organic halide such as p-methylbenzyl bromide[6], which gives the initiating species I (equation 1):

$$CH_3-\langle\bigcirc\rangle-CH_2Br+AgPF_6 \longrightarrow CH_3-\langle\bigcirc\rangle-CH_2^+PF_6^-+AgBr\downarrow \quad (1)$$
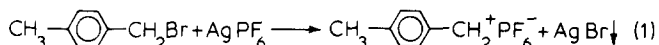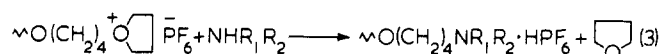
The combination of living polyTHF with base ions suggests that coupling might also occur with bases such as tertiary amines to form polymeric quaternary ammonium salts (equation 2):

$$\text{wO(CH}_2)_4\overset{+}{-}\overset{\diagup}{\text{O}}\rfloor \ \bar{P}F_6+NR_1R_2R_3 \rightleftharpoons \text{wO(CH}_2)_4\overset{+}{-}NR_1R_2R_3\bar{P}F_6+ \ \langle_O\rangle \quad (2)$$

The reaction is envisaged as one of displacement of the THF coordinated onto the end of the polymer chain by the more basic tertiary amine. Quaternary ammonium salts are generally stable compounds and to the extent that the reaction, written as an equilibrium between molecules of different base strengths, lies to the right, it is expected that polymerization will stop. The effect of any exchange between the quaternary ammonium salt and the oxonium structure would be to allow polymerization to

occur at a rate proportional to the average time fraction spent by the molecules in the latter state.

This paper considers the reaction of living polyTHF with pyridine. Apart from interest in the reaction itself, it could serve as a useful model for the formation of graft copolymers by the reaction of living polyTHF with poly(vinylpyridine), and of block copolymers by reaction with pyridine terminated polybutadiene[7]. Part 2 in this series of papers[8] describes the reactions of polyTHF with other tertiary amines; it is of interest to note that triphenyl phosphine, a phosphorus analogue of a tertiary amine, has been reported to trap the cationic propagating species in copolymerizing systems of cyclic ethers to form the terminal phosphonium grouping $\sim P^+Ph_3$[9]. Subsequent papers in the series report the reactions of living polyTHF with secondary and primary amines, and with ammonia — the reactions being of the type shown for a secondary amine in equation 3.

$$\text{wO(CH}_2)_4\overset{+}{\overset{\diagup}{\text{O}}}\rfloor \ \bar{P}F_6+NHR_1R_2 \longrightarrow \text{wO(CH}_2)_4NR_1R_2\cdot HPF_6+ \ \langle_O\rangle \quad (3)$$

EXPERIMENTAL

Materials

Tetrahydrofuran (Fisons, unstabilised) was purified by refluxing over sodium wire for several days, distilling and refluxing further over fresh sodium for up to 48 h. Addition of naphthalene permitted the green sodium–naphthalene complex to form, and the THF was distilled under nitrogen through a packed column immediately prior to use.

Styrene (British Drug Houses Ltd) was washed with sodium hydroxide and water, dried initially with sodium sulphate and finally with calcium hydride from which it was fractionally distilled under vacuum prior to use.

4-Vinyl pyridine (Aldrich) was dried over calcium hydride before vacuum distilling as required.

n-Butyllithium (Koch–Light) was supplied as a 15% w/w solution in hexane and was used as received.

Silver hexafluorophosphate (Ozark–Mahoning) was obtained as a free flowing powder from Fluorochem Ltd. It was stored under nitrogen and used as supplied.

p-Methylbenzyl bromide (α-bromo-p-xylene) (Aldrich 99+%) was held in a vacuum desiccator over silica gel.

p-Xylylene dibromide (α,α'-dibromo-p-xylene) (Koch–Light) was recrystallized from benzene.

Pyridine (AR grade) was distilled then treated with calcium hydride under vacuum until degassing was complete. A middle fraction was obtained by distillation through a glass wool plug, and the clear liquid was stored under nitrogen.

Methods

Preparation of living polyTHF and its reaction with pyridine Experiments were conducted under nitrogen and, as far as possible, exposure of prepared reagents to air was avoided. Initiation was induced by adding p-methylbenzyl bromide to a stirred THF solution of $AgPF_6$ in a 3-necked flask at $-10°C$ to give equivalent concentrations of 2×10^{-2} M. After 1 h, with the initiating reaction complete[6], the solution was diluted to 10^{-2} M with further THF, cooled to between $-20°$ and $-25°C$, and separated from the AgBr precipitate by lifting through a sintered glass filter into an adjacent cooled 3-necked flask.

This prepared solution of living polymer with a molecular weight ~ 3000 was used to investigate the reaction with pyridine. 2.0 ml of a 0.1 M solution of pyridine in THF (nominally equivalent to a 20 ml sample of living polymer) was prepared in a small flask under nitrogen and set in the cooling bath alongside the main polymer solution together with a similar empty flask. 20 ml Aliquots of the polymer solution were then introduced to each flask and a similar amount was simultaneously terminated with methanol to provide initial reference material.

A different equivalence of pyridine was added to the balance of the solution in the main flask. The three flasks were maintained at $-10°C$ for 3–4 h, sufficient time to allow the observation subsequently by gel permeation chromatography (g.p.c.) of any remaining chain growth, before terminating with excess methanol. The solvent was then removed from the samples using a rotary evaporator followed usually by pumping overnight before preparing solutions for g.p.c. analysis.

Preparation of AB poly(styrene-b-4-vinyl pyridine) and its reaction with living polyTHF A reaction vessel containing 0.1 mol styrene in 100 ml THF under nitrogen was cooled to $-78°C$, and 1 ml of 1.55 M n-butyllithium added. The red colour characteristic of the living polystyryl anion developed rapidly and the solution was allowed to warm up to ambient temperature over a 45 min period. The reaction vessel was then cooled to about $-100°C$ and 0.1 mol of 4-vinyl pyridine was slowly added dropwise over 15 min before again allowing the system to warm up gradually to room temperature.

A 10^{-2} M solution of living polyTHF of molecular weight ~ 3300 in THF had been prepared at $-10°C$ by the method described previously, and 5.5 ml of the living vinyl pyridine copolymer solution was added to 90 ml of

this solution. The whole was then allowed to stand at $-10°C$ for a further hour before terminating with methanol. The solvent was removed by rotary evaporation and the residue was partitioned in an ether–aqueous sodium bicarbonate mixture. The polymer was isolated by evaporation of the separated ether layer. Samples of the intermediate polymer solutions had been also taken during the experiment and the polymeric materials isolated. All these were subjected to analysis by g.p.c.

Gel permeation chromatography (g.p.c.)

The chromatograph employed was a Waters Associates model 301 instrument equipped with differential refractometer and ultraviolet detectors, the latter operating at 254 nm. High resolution was not necessary in this work, and two Styragel columns with porosities of 10^4 and 10^3 Å were used in series. THF was employed as the mobile phase, eluting at 1 cm^3 min^{-1}. Samples were injected from a 1.7 ml sample loop normally charged with a 0.1% w/v THF solution of polymer, but other concentrations were also used. For calibration, the polystyrene equivalent molecular weights were derived from a set of polystyrene standards and, by multiplying by 0.556[10], converted to absolute polyTHF molecular weights.

^1H n.m.r. spectroscopy. ^1H n.m.r. spectra were recorded on a Jeol PS 100 spectrometer at 100 MHz in the external lock field sweep mode. Spectra were obtained as solutions in $CDCl_3$ or hexadeuteroacetone at ambient temperature, and chemical shifts were measured relative to tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

Reaction of living polyTHF with pyridine

Figure 1 shows the g.p.c. curves obtained from an experiment in which equimolar and 0.6 relative molar quantities of pyridine were added to samples of living polyTHF at $-10°C$ 1 h after initiation and allowed to react for a further 3.5 h at that temperature before being terminated with excess methanol. They are compared with the traces of polyTHF killed directly with excess methanol at the two time intervals specified. The addition of pyridine is seen to stop polymerization close to the initial molecular weight (trace a) whilst a proportion of chains inversely dependent on the amount of amine used continues to grow at the normal rate, shown by trace d. The terminated fractions exhibit a strong u.v. absorption, indicating incorporation of pyridine into the polymers.

The number of chains represented by the high molecular weight fractions in traces b and c is less than that suggested by the areas drawn out by the refractometer, which measures the total weight of polymer in each peak. Allowing for the difference in molecular weight, the number of chains continuing to grow after the addition of 1 nominal equivalent of pyridine (trace b) is estimated to be only $\sim 4\%$. This small amount of residual growth was also observed in other experiments, but disappeared with a slightly larger quantity of amine, and when the addition was made to the main reaction flask. These facts suggest a systematic error in sampling the reaction vessel with consequent errors in calculating the amine equivalences required. It seems likely that the error arises through volume contraction of the polymerization solution which
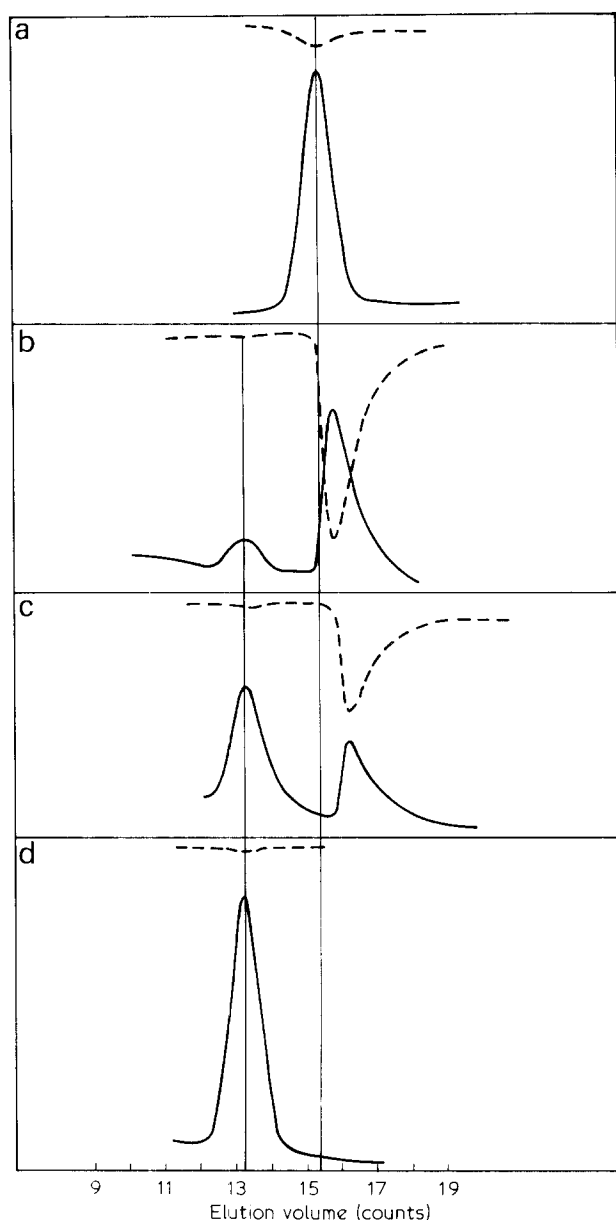
Figure 1 Reaction of pyridine with living polyTHF at −10°C.
(a) Starting polymer (methanol-killed); (b) and (c), polymer reacted
with pyridine (1.0 and 0.6 nominal equivalents, respectively) for
3.6 h; (d) control, terminated with methanol after 3.6 h:
— — — —, u.v. 64x; ———, R I 4x

counts). The third and major peak, also with u.v. absorbance, is of intermediate molecular weight. This trace clearly illustrates the results of a statistical distribution of a limited amount of pyridine between the available ends, with the most probable product at this equivalence, namely polymer terminated at one end only, growing at half the rate of difunctional polyTHF in the presence of smaller amounts of unterminated and completely terminated polymer.

It may be noted that the precise position of the pyridinated polymer on the g.p.c. traces lies at longer retnetion times than the equivalent methanol terminated material. This, coupled with the presence of a pronounced tail, suggested that the product was degrading to lower molecular weights. More detailed work described below, however, shows that the chain lengths are unaffected by reaction with pyridine and that these features are due to interaction of the sample with the g.p.c. column.

In summary, these g.p.c. results imply the occurrence of a terminating addition of pyridine to living polyTHF ends which has a stoichiometry which is probably exactly
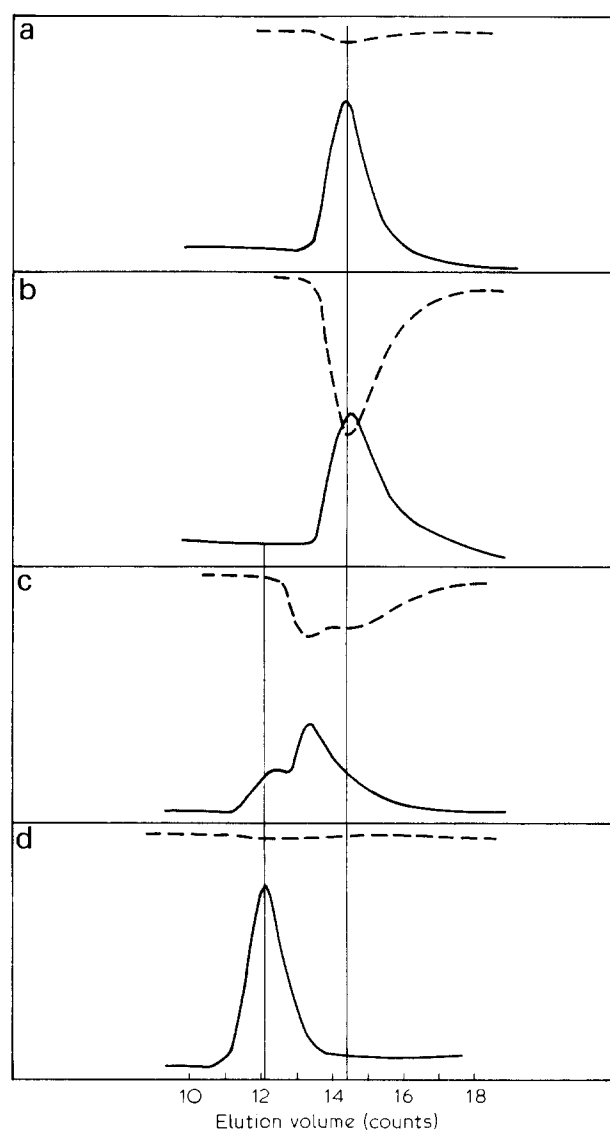
was not allowed for, and it is concluded that the reaction is in fact quantitative.

The presence of two distinct peaks in trace c, one at high retention time absorbing strongly in the u.v. and the other at a retention time corresponding to the high molecular weight standard with virtually no u.v. signal, indicates that there is not exchange between pyridine terminated polyTHF and the living material.

In an experiment carried out in a similar way but using *p*-xylylene dibromide to initiate a difunctional polyTHF[2], the traces shown in *Figure* 2 were obtained. Complete killing was observed with 1 equivalent of added pyridine (curve b), but with a fractional amount of amine (0.5 equivalents) the more complex picture of curve c is obtained. This shows evidence of 3 components, one (with u.v. absorbance) corresponding to complete termination at the original molecular weight (14.3 counts) and a second (without significant u.v. absorbance) which has grown at the normal rate within experimental error (12.1

Figure 2 Reaction of pyridine with living difunctional polyTHF
at −10°C. (a) Starting polymer (methanol-killed); (b) and (c),
polymer reacted with pyridine (1.0 and 0.5 nominal equivalents,
respectively) for 3.5 h; (d) control, killed with methanol after
3.5 h: — — —, u.v.; ———, RI; unspecified sensitivities

Table 1 ¹H n.m.r. chemical shift data on poly THF—pyridine materials and related compounds

Sample	Chemical shifts of pyridinium and adjacent protons (δ)			
	ortho	*meta*	*para*	$-CH_2-N\underset{\ll}{\overset{+}{\diagdown}}$
Pyridine	8.60	7.62	7.23	—
n-Butylpyridinium bromide	9.70	8.80	8.30	5.04
n-Butylpyridinium hexafluorophosphate	9.14	8.77	8.28	4.81
PolyTHF pyridinium bromide	9.40	8.68	8.16	5.01
PolyTHF pyridinium hexafluorophosphate	8.80	8.56	8.08	4.70

equimolar. Further, the product is not in equilibrium with living polyTHF. These facts are consistent with the reaction given in equation (2), but its validity must be confirmed by identification of the terminal group formed.

Identification of the product

Formation of a pyridinium salt was established by ¹H n.m.r. carried out on polymer prepared using sufficient pyridine to ensure complete termination, the excess being removed by pumping. *Table* 1 shows the chemical shift values of pyridinium terminated polymers and several related molecules — n-butyl pyridinium bromide being synthesized by refluxing n-butyl bromide with pyridine in ethanol, and the hexafluorophosphate prepared by reacting this with $AgPF_6$.

A comparison of the quaternary salts with pyridine itself indicates that the effect of the positive charge is to cause the aromatic protons of the pyrdinium salt to exhibit a pronounced downfield shift. The methylene adjacent to the pyridinium moiety absorbing at about 5.0 δ establishes the polyTHF–pyridinium link, and the relative areas of these protons, the aromatic pyridinium protons and the aromatic benzyl protons of the initiator all indicate that the ratio of pyridinium salt to initiator is 1.0 ± 0.1. Thus within the accuracy of the measurement, the n.m.r. results confirm that the reaction is quantitative.

Table 1 also shows that the chemical shifts of the pyridinium unit are sensitive to the nature of the counterion. Thus on changing the counterion in the polymer from PF_6^- to Br^- by stirring with a THF solution of lithium bromide, the *ortho* protons in particular were moved 0.6 ppm downfield. That this is caused by the change in counterion is demonstrated by considering the n-butyl pyridinium model compounds in which the changes in chemical shift on going from the PF_6^- ion to the Br^- ion are similar to those of the analogous polymers (the absolute shifts of the model compounds are displaced relative to those of the polymer, but this is reasonable since the THF units in the polymer would be expected to affect the solvation of the ions).

In support of the n.m.r. results the u.v. spectra of the polymer pyridinium salts and the n-butyl pyridinium salts were found to be closely similar.

Rate of reaction

Experiments were carried out to determine the approximate time scale for the reaction of pyridine with the

polymeric ends. Samples were withdrawn at intervals soon after introduction of pyridine to the living polymer and quenched immediately with methanol. The traces obtained are shown in *Figure* 3. All the traces of samples with reaction times greater than 40 s (traces c–f) show a single asymmetric peak with the high u.v. absorbance of the pyridinated product at a retention time longer than that of the reference polymer (trace a). The invariance of the position and shape of this peak with time indicates that the increased retention time is not caused by degradation of the polymer chains through reaction, which should be progressive, but must be due to some interaction of the pyridinium-terminated polymer with the g.p.c. columns. The constancy of the chain lengths on reaction was confirmed in a separate experiment in which the intrinsic viscosities of pyridine-terminated and of methanol-terminated materials were shown to be the same.

The trace of the material at 40 s reaction time (trace b) exhibits an additional small u.v. transparent peak coincident with the position of the reference polymer, and this clearly represents polymer (10% total) which has not yet reacted with pyridine. Since this peak has disappeared in the subsequent trace at 2.5 min, this experiment establishes that the reaction between living polyTHF and pyridine is rapid, being probably complete in 1 to 2 min at $-10°C$ under these conditions.

Reaction of living polyTHF with poly(4-vinyl pyridine)

Having established the quantitative nature of the reaction of living polyTHF with pyridine to form polymers with terminal pyridinium salts, it was of synthetic interest to extend this approach to analogous reactions with pyridine units attached to polymer chains. In this way novel graft copolymers with ionic bonds could be prepared.

To this end, poly(4-vinyl pyridine) was prepared but was found to be insufficiently soluble in THF, the preferred solvent, to carry out conveniently the grafting reactions with living polyTHF contemplated. An equimolar AB poly(styrene-b-4-vinylpyridine) copolymer of nominal molecular weight 13 500 was therefore prepared anionically and was found to be soluble in the THF solution. This was therefore reacted at $-10°C$ with sufficient living polyTHF of molecular weights 3300 to consume about 20% of the total pyridine units on the polymer chains (weight ratio of polyTHF to block copolymer 4:1), and then stirred at that temperature for a further hour before terminating and isolating.

The product and its constituent polymers were subjected to g.p.c. analysis and the small peak due to free polyTHF found on the product trace demonstrated that a grafting efficiency of at least 95% had been achieved. Furthermore, since the peak position corresponded to a molecular weight of 3300 rather than the 6900 expected if the unconsumed polyTHF has continued to propagate during the 1 h reaction time allowed, it is likely that this peak merely represents a small amount of inadvertently terminated polymer and that the reaction is in fact quantitative. Solubility tests on the reaction product and its parent block copolymer were carried out, and the differences in behaviour (*Table* 2) confirmed that grafting had occurred.

It may be remarked that the retention time of the g.p.c. peak of the polyTHF graft was much longer than that expected from its theoretical molecular weight. Moreover,

Table 2 Differences in solubilities in some common solvents of AB poly(styrene-b-4-vinylpyridine) (I) and ABC poly(styrene-b-4-vinylpyridine-g-THF) (II)

Solvent	I	II
Ether	Insoluble	Soluble
Acetone	Insoluble	Soluble
Methanol	Partly soluble	Insoluble
Isopropanol	Partly soluble	Insoluble
Cyclohexane	Insoluble	Soluble

the shape of this peak was variable, indicating considerable column interaction. This is discussed in the next section.

G.p.c. column effects

The appearance of a new characteristic g.p.c. distribution immediately on formation of the pyridine complex and its apparent stability with time (*Figure* 3) suggests a difference in behaviour of the pyridinated polymer on the g.p.c. columns from that of its methoxy-terminated analogue — presumably related to the ionic character of the terminal group of the former. The effect of sample concentration on the elution characteristics is shown in *Figure* 4 where it is seen that the shifts increase as the concentration is reduced.

Broadly, this behaviour is the reverse of that described for multiply charged polymers (polyelectrolytes) which tend to elute early with a diffuse front and an abrupt trailing edge[11], the effect of decreasing concentration being to reduce the retention volume[12]. The behaviour conferred by the pyridinium grouping is not therefore that of a polyelectrolyte. The skew distributions and greater retention times observed with these polymers are characteristic of adsorption on the column substrate, and closely parallel to the behaviour noted elsewhere of poly(propylene oxide) glycol in toluene on Styragel[13].

Column interaction and partition have been demonstrated in a weak solvent when a polymer may prefer the gel environment to the mobile phase[14]. For polyTHF in THF, however, it seems more likely that the interaction is between the ionic terminal groups and specific polar adsorption sites on the column. These may be the carbonyl and hydroxyl groups which are known to develop in small concentrations on crosslinked polystyrene columns on use. The observed behaviour is consistent with interaction of the polymer with a limited number of such sites which might possess a range of interaction energies.

Because of the dynamic nature of the adsorption, which permits movement of the sample along the column, it seems likely that the leading polymer in the advancing front will become attached to the more strongly adsorbing sites and suffer greater delay in elution. Over the full length of the column this would have the effect of removing the leading wing of the normal elution profile and increasing the average time spent on the column. Molecules remaining adsorbed after the main polymer fraction has passed will contribute an extended tail to the trace. At lower concentrations, with less competition for
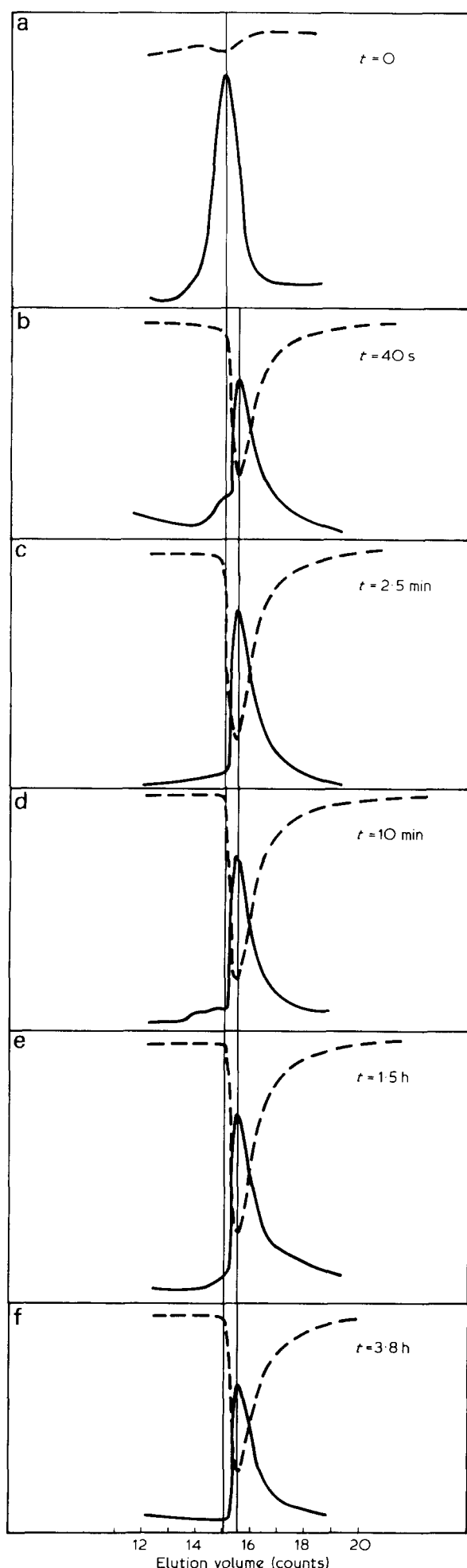
Figure 3 Time-sampling of a 1:1.1 living polyTHF—pyridine mixture. Samples injected into methanol at the times indicated. G.p.c. sample concentration 0.1% w/v: — — — —, u.v. 64x; ———, RI 4x
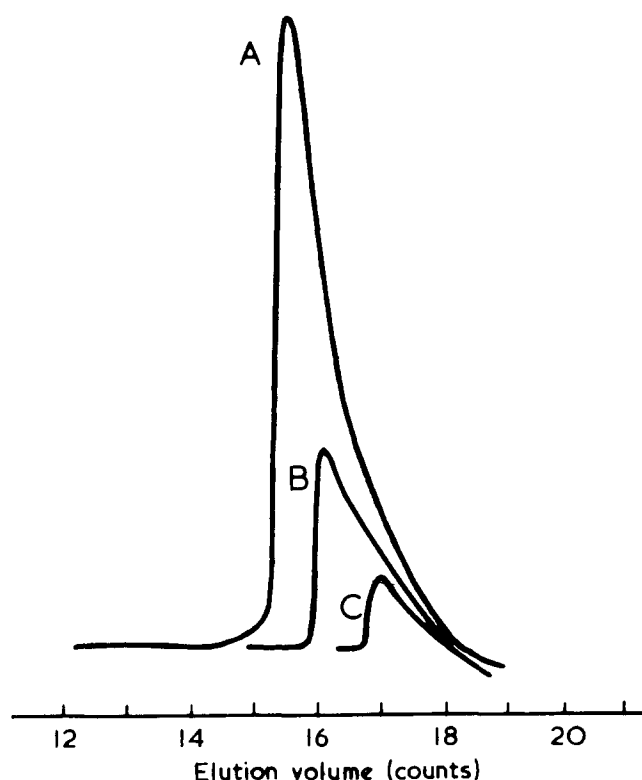
Figure 4 Dependence of peak position of pyridinated polyTHF on concentration injected. (A) 0.1% w/v; (B) 0.05% w/v; (C) 0.025% w/v: RI trace only, 2x

sites, a greater proportion of interactions will take place at the more tightly binding sites, thus accounting for the increased elution time observed.

With a limited number of adsorption sites, increase in the polymer concentration should lead eventually to saturation conditions when a large proportion of polymer is unaffected by adsorption. Under such circumstances (2.0% w/v injection concentration) we have observed a symmetrical profile very much resembling that of the methoxy-terminated polymer at the same concentration, with a closely similar retention time.

The ionic nature of the polymer end-groupings suggests the additional possibility of an association–dissociation equilibrium as an alternative or merely a contributory cause of the g.p.c. characteristics observed. Two such equilibria are feasible, the dissociation of the terminal ion pairs into free ions, or the association of the ion pairs to from aggregates. If it is assumed that in either equilibrium the dissociated form is the more strongly adsorbed on to the matrix sites, then the concentration dependence of the equilibria will ensure a greater interaction in the more dilute solutions on either side of the peak. This will lead to the sort of asymmetry and the delay in elution observed, and such equilibria will give rise to the inverse dependence of the peak position on sample concentration.

If association of the polymer ends is primarily responsible for the effects observed, then this may be confirmed in principle by viscosity measurements. Such measurements showed THF solutions of pyridine-terminated polymers to have viscosities slightly higher than those of the methoxy-terminated reference materials, but the differences did not appear to be sufficient to account for the large effects observed. Furthermore, when large amounts of pyridine-terminated polymer are loaded on to the columns so that saturation conditions prevail, the retention time of the symmetrical peak obtained should

be lower than that of the reference material if association predominates. This has not been observed, and so it would appear that any significant contribution to the adsorption effects through polymer aggregation may be discounted. The detailed mechanism of adsorption is therefore still unresolved; the relative importance of sites of different adsorptive strengths and ion pair–free ion equilibrium being undetermined. What is established, however, is that the effects are due to physical interaction of the terminal groups of the polymers with the matrix rather than chemical degradation of the product.

Living end concentration by reaction with pyridine

The rapid, apparently quantitative addition of pyridine to living polyTHF to form a stable terminal group absorbing strongly in the u.v. suggests its use as a possible alternative to the method of Saegusa and Matsumoto[15,16] for determining the concentration of propagating species in such systems. This method relies upon the addition of sodium phenoxide, prepared under anhydrous conditions to avoid the formation of other base impurities, for tagging the reactive ends. Excess phenoxide must be removed by an aqueous extraction procedure in order to avoid its interference with the u.v. absorption of the resulting phenyl ether terminal group. The concentration of the terminal group is then determined from its known extinction coefficient, correction being applied for absorption by the polyTHF chains.

Using pyridine to tag the active ends, prior synthesis of the reagent would not be required — indeed we have found that reaction of living polyTHF with water is slow so that direct use of pyridine without special drying is probably justified. Moreover, the excess amine could be simply removed by pumping. The pyridine method has the further advantage that the extinction coefficient of the pyridinium salt at $\lambda_{max} = 259$ nm is approximately 4.8×10^3 l mol^{-1} cm^{-1} so that the sensitivity of the method would compare favourably with that of the phenoxide technique ($\varepsilon = 1.93 \times 10^3$ l mol^{-1} cm^{-1} for the –OPh group at $\lambda_{max} = 272$ nm). Further, the absorbance of the pyridinium salt at 254 nm is about 7.5 times that of the phenyl ether, which means that generation of the former species is favoured for adapting the method in order to determine the active end concentration directly by dual detector g.p.c.

Physical characteristics

It is of interest to note that the introduction of a pyridinium end grouping has little apparent effect on the physical characteristics of polyTHF. Visually the material is indistinguishable from the equivalent methoxy-terminated polymer; in particular there is no observable difference in their bulk viscosities.

This is in marked contrast to the dramatic increases in viscosity which have been observed on quaternization of terminal pyridine units attached at the 4-position to one or both ends of polybutadiene chains[7]. These changes were ascribed to association of the ionic ends into micelles in the presence of the non-polar polymer matrix, thereby producing with monofunctional polybutadiene a material with the physical characteristics of a high molecular weight product, and with the two ended species a pseudo-crosslinked network.

PolyTHF, however, being a polyether is a good cation solvating agent and participates in the solvation of the

quaternary ammonium group. This interaction, therefore, limits the association of polymer molecules both by minimizing the ion pair interactions electrostatically and by blocking, at least partly, the approach of another ion pair.

CONCLUSIONS

The quantitative addition of pyridine to living polyTHF can be regarded as a prototype of the addition of organic bases to the propagating species of THF and other cyclic ethers. With the lower order amines the products after an alkaline work-up (equation 3) would themselves be polymers possessing amine groups capable, in principle, of reacting with further living polyTHF. If a complete sequence of such reactions can be obtained starting from ammonia, it would be possible to build up 4-branch star polymers of cyclic ethers on a positively charged nitrogen atom.

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