Block copolymerization by a cation to anion transformation process:
1. Reaction of butyl lithium with polyTHF possessing terminal styryl groups

M. J. M. Abadie, F. Schue and T. Souel
Laboratoire de Chimie Macromoleculaire, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex, France

and D. B. Hartley and D. H. Richards
Propellants, Explosives and Rocket Motor Establishment, Ministry of Defence, Waltham Abbey, Essex EN9 1BP, UK

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A route for preparing novel block copolymers by a cation to anion transformation process is examined. The process involves reacting living polyTHF with the lithium salt of cinnamyl alcohol to prepare a polymer possessing a styryl terminal group and this has been shown to be virtually quantitative. The second stage involves reacting this product with *n*-butyl lithium in benzene to form an adduct to which monomer such as styrene or isoprene is added to prepare a block copolymer anionically. This last stage has been shown to operate with only about 20% efficiency and, although the reason for this low efficiency has not been elucidated, it is suspected that it is due to side reactions of the butyl lithium.

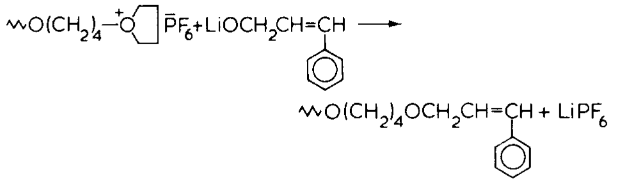
Keywords Copolymerization; cation; anion; transformation; polytetrahydrofuran; styryl groups; butyl lithium

INTRODUCTION

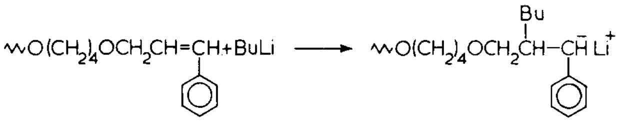
Recently, attempts have been made to synthesize block copolymers of novel combinations of monomers by the use of so-called 'transformation reactions'[1,2]. These are generally redox reactions which are employed to transform the mode of propagation best suited to the first monomer into a different mode suited to the second monomer. In all cases this transformation has to proceed *via* a relatively stable intermediate to allow isolation of the initial homopolymer so that it may be redissolved in a suitable solvent containing the second monomer before activation of the dormant end.

On the simplistic assumption that there are three main modes of polymerization—free radical, anion and cation—six transformation processes would be necessary to inter-relate these mechanisms and, in theory, thus allow block copolymers to be prepared from a large number of novel monomer combinations. Clearly such an analysis is idealistic, but the development of such reactions should greatly extend the range of block copolymers which can be prepared. Prior studies have already established methods of transforming anions to cations[1,2,5] and anions to free radicals[6–9], although the efficiencies in certain instances are lower than wished.

In this paper we describe an approach by which we have attempted to effect the transformation from cation to anion. This method involves the reaction of 'living' cationic polyTHF[10,11] with the lithium salt of an alcohol possessing a styryl unit (e.g. cinnamyl alcohol) to yield a polymer with a terminal group capable of being reacted with a strong nucleophile (equation (1)). This polymer can then be isolated, redissolved in a suitable solvent and reacted with butyl lithium (equation (2)) in order to try to create a terminal secondary benzylic anion which may be used to initiate the polymerization of further monomers, such as styrene or isoprene, to form block copolymers.



$$\sim O(CH_2)_4-\overset{+}{O}\,\bar{P}F_6 + LiOCH_2CH{=}\underset{C_6H_5}{CH} \longrightarrow \sim O(CH_2)_4OCH_2CH{=}\underset{C_6H_5}{CH} + LiPF_6 \quad (1)$$



$$\sim O(CH_2)_4OCH_2CH{=}\underset{C_6H_5}{CH} + BuLi \longrightarrow \sim O(CH_2)_4OCH_2\overset{Bu}{CH}-\underset{C_6H_5}{\bar{C}H}\,\overset{+}{Li} \quad (2)$$

EXPERIMENTAL

Materials

The purification of benzene, THF, isoprene and styrene to the standards required for ionic polymerization was carried out as described in earlier publications[12–15]. Cinnamyl alcohol was distilled before use and the purity of the distillate was shown by gas-liquid chromatography (g.l.c.) to be >98%. 1-phenyl-1-buten-4-ol was synthesized and purified according to a published method[16] by reacting ethylene oxide with the magnesium derivative of *β*-bromostyrene.

Both these alcohols were converted into n-pentyl ethers by the following procedure: A benzene solution of each was reacted under nitrogen and at room temperature with

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a marginally below equimolar amount of a 2M solution of n-butyl lithium in hexane. It was demonstrated that the alcoholate is uniquely formed under these conditions, no attack on the styryl double bond being observed. The n-pentyl ether was then prepared using the Williamson reaction by adding the lithium alcoholate to n-pentylbromide in a benzene–dimethylsulphonate mixture. Yields obtained were 60% for the cinnamyl alcohol derivative and 40% for that derived from 1-phenyl-1-buten-4-ol. The ethers were purified through a silica gel column and their purity as measured by g.l.c. was >95%.

Preparation of styryl-terminated polyTHF and its reaction with n-*butyl lithium and monomer*

The polymerization of THF has been fully described previously[1–5]. After a suitable polymerization time at −10°C, an equimolar quantity of the unsaturated alcoholate prepared as outlined above was added as a solution in benzene or in a benzene–THF mixture. Samples were taken for analysis, and the polymeric product could be isolated or reacted *in situ* with n-butyl lithium. In the latter case, the lithium reagent was added at room temperature under nitrogen in a molar ratio of 0.9:1—this proportion ensuring that no excess butyl lithium was present to initiate directly the polymerization of the subsequently added monomer. Introduction of the butyl lithium resulted in the development of the red coloration characteristic of the styryl anion. After allowing 3 h for reaction to reach completion the monomer, isoprene or styrene, was added either neat or in benzene solution.

Reaction of model compounds with n-butyl lithium and monomers

The model ethers were reacted under nitrogen and at room temperature with n-butyl lithium in three different solvents, pure THF, THF–benzene mixture 2:1 v/v, or pure benzene. In all cases the ether concentration was 10^{-2} M. The products formed were examined by terminating samples removed from the reaction vessel at set time intervals with methanol, and subjecting them to g.l.c. analysis.

In experiments designed to examine the initiating efficiency of the products toward added monomer, the molar ratio of added butyl lithium to model ether was held at 0.9:1 to avoid direct initiation by any excess butyl lithium. Three hours were allowed to elapse after this addition before monomer was introduced.

Characterization of products

G.l.c. analyses were carried out on a Varian 1440 or a Pye-Unicam 1004 chromatograph.

G.p.c. traces were obtained using a Waters Associates ALC/GPC 301 apparatus possessing u.v. and differential refractometer detectors. Styragel columns of porosity 10^2 to 10^5 Å were employed.

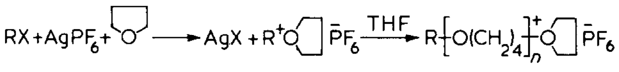
N.m.r. spectra were recorded on a Jeol PS100 or a Varian EM390 spectrometer.

RESULTS AND DISCUSSION

The overall efficiency of the proposed transformation process is a product of the efficiency of the reactions depicted in equations (1) and (2), and these may be tested separately.

Formation of polyTHF possessing terminal styryl units

The cationic polymerization of THF may be carried out under living non-transfer conditions by reacting silver hexafluorophosphate with a variety of organic halides in THF at −10°C[12] (equation (3)). The molecular weight distribution of the product is narrowest when the rate of initiation greatly exceeds the rate of propagation, and the most efficient initiators are consequently alkyl halides which possess labile carbon–halogen bonds. Such a species is cinnamylbromide which reacts with silver salts within seconds even at −78°C[17], and use of this compound as initiator, therefore, might be considered an ideal means of introducing a terminal styryl group on to the polymer. However, the lability of the bromide is undoubtedly related to the high degree of resonance stabilization of the generated carbenium ion derived from the two canonical forms I and II, shown below without THF solvation, and since it is likely that the resonance structure possesses a large contribution from form II, the terminal groups produced by reaction with THF would have a high probability of being a mixture of olefinic and vinylic structure. This approach was therefore not examined experimentally since it was decided that a styryl terminal unit could best be introduced uniquely by reaction of living polyTHF generated through use of a conventional benzylic bromide with an appropriately structured alcohol III (equation (1)).



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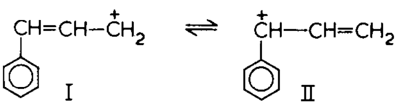
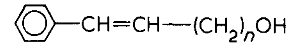
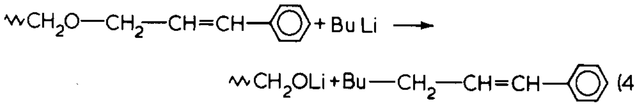




III

Two such reagents, with $n = 1$ and 2, were accordingly selected; the first, cinnamyl alcohol, is commercially available whilst the second, 1-phenyl-1-buten-4-ol, was synthesized. The latter was prepared since it was felt that cinnamyl alcohol might form an adduct in which the ether linkage might be weakened by the proximity of the styryl unsaturation and thereby allow a scission reaction to occur with butyl lithium (equation (4)) as an alternative to the required addition reaction. Insertion of an extra methylene unit between the ether and the styrene moiety should prevent such interactions and thus minimize the probability of scission occurring.



(4)

Preliminary experiments had indicated that rapid termination of polyTHF by these alcohols could only be effected if the reagent were in large excess, and so their basicities were increased by prior reaction, using butyl lithium to form the lithium alcoholate. An experiment in which the lithium salt of cinnamyl alcohol was reacted under equimolar conditions with living polyTHF gave the g.p.c. traces shown in *Figure 1*. Here the product resulting

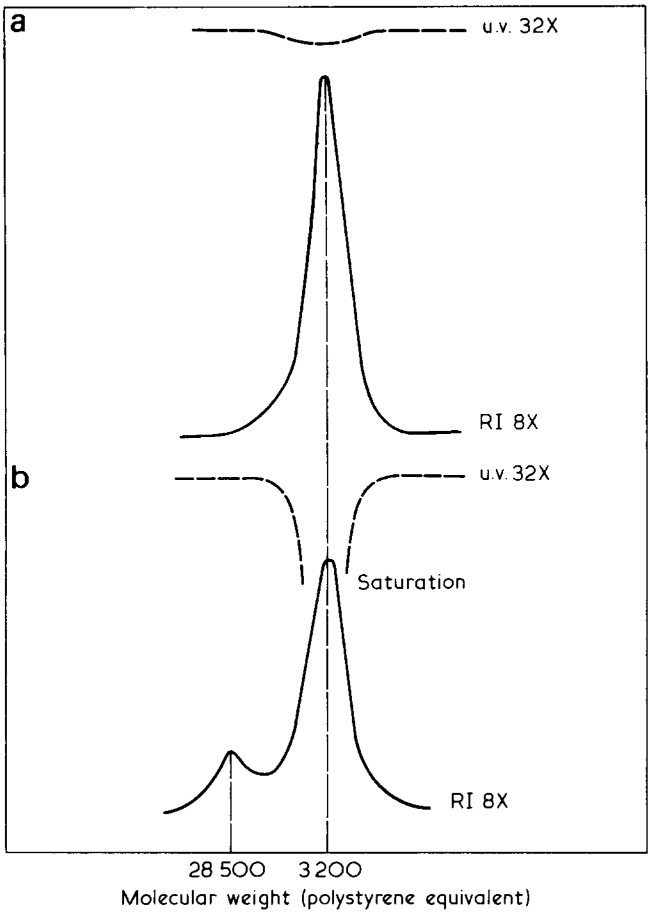


Figure 1 **G.p.c. traces of polyTHF samples (a) terminated with methanol at the time of addition of cinnamyl alcoholate to a parallel sample, (b) terminated with methanol 3.5 h after addition of nominally equimolar cinnamyl alcoholate**

from maintaining the reaction mixture for 3.5 h at $-10°C$ before adding methanol is compared with that of a control obtained by terminating identical polyTHF with excess methanol at the time of mixing of the two reagents. It is clear that the bulk of the living polyTHF has been rapidly terminated with the cinnamyl derivative since the major RI peak in the trace coincides with that of the control. Moreover, the very strong u.v. absorbance associated with this product contrasts with the control and indicates the presence of a u.v. absorbing adduct—undoubtedly the terminal styryl grouping, and this was subsequently confirmed by ^1H n.m.r. spectroscopy. The small u.v. transparent peak also seen in *Figure 1b* represents unreacted polyTHF chains which have continued to grow over the 3.5 h period before termination with methanol. These are almost certainly present because of experimental inaccuracy in adding exact molar equivalence of the alcoholate to the living polymer. In any case they represent less than 3% of the total number of chains originally present (the RI signal is proportional to the weight of material present and so the relative areas of the peaks have to be multiplied by the ratio of the molecular weights of the polymers causing them in order to assess the proportion of unreacted chains).

Thus this and similar experiments confirm that the above technique may be employed to prepare with greater than 97% efficiency polyTHF chains with terminal styryl units. Equally high efficiency coupling was obtained when the lithium salt of 1-phenyl-1-buten-4-ol (structure III, $n=2$) was reacted with living polyTHF under equimolar conditions.

Reaction of butyl lithium with model compounds possessing terminal styryl units

Having established an efficient method of preparing polymer possessing terminal styryl units, it was then necessary to examine its reaction with butyl lithium to create terminal benzylic anions (equation (2)). Since there are difficulties in carrying out quantitative examination of reaction efficiencies on polymeric systems, it was decided that the conditions for maximizing the desired reaction could best be established by the use of model compounds. Such small molecules, in order to simulate the polymer chain end as closely as possible, should possess an ether grouping at the appropriate position as well as a terminal styryl group. The n-pentyl ethers of the alcohols of structure III with $n=1$ and 2 were therefore prepared, the former to represent polyTHF with a cinnamyl ether terminal group and the latter polyTHF terminated by 1-phenyl-1-buten-4-ol.

Reactions of these ethers with butyl lithium were carried out at ambient temperature and at concentrations identical with those to be used for the reaction with the functionalized polymers. Three solvent systems were employed: pure THF, pure benzene, and a 2:1 v/v mixture of THF and benzene—the last corresponding to the solvent composition in which the functionalized polyTHF was prepared. Samples of the reaction mixture were removed at regular intervals, terminated with methanol and analysed by g.l.c.

It is apparent visually that the solvent is important in determining the rate of reaction; in both systems containing THF the onset of the red colour characteristic of the styryl anion is rapid, occurring before addition of butyl lithium is complete, whereas in pure benzene the onset of colour is much more gradual. G.l.c. analysis of methanol killed samples indicates that the course of the reaction is also very much solvent dependent. A number of products are obtained from the reaction in THF-containing solvents at retention times lower and higher than that of the reacting ether (*Figure 2*), the former suggesting that there are decomposition products formed. In pure benzene, however, the reaction proceeds more smoothly and predictably; g.l.c. traces show that the peak due to the unsaturated ether is slowly reduced and replaced by a single product at longer retention time

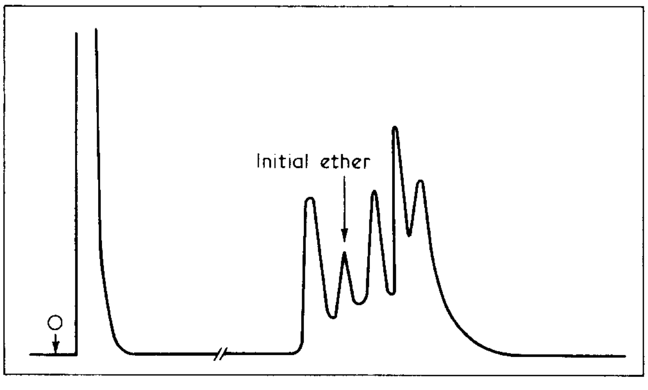


Figure 2 **G.l.c. trace of the reaction products in THF of pentyl cinnamyl ether and butyl lithium after 45 min**

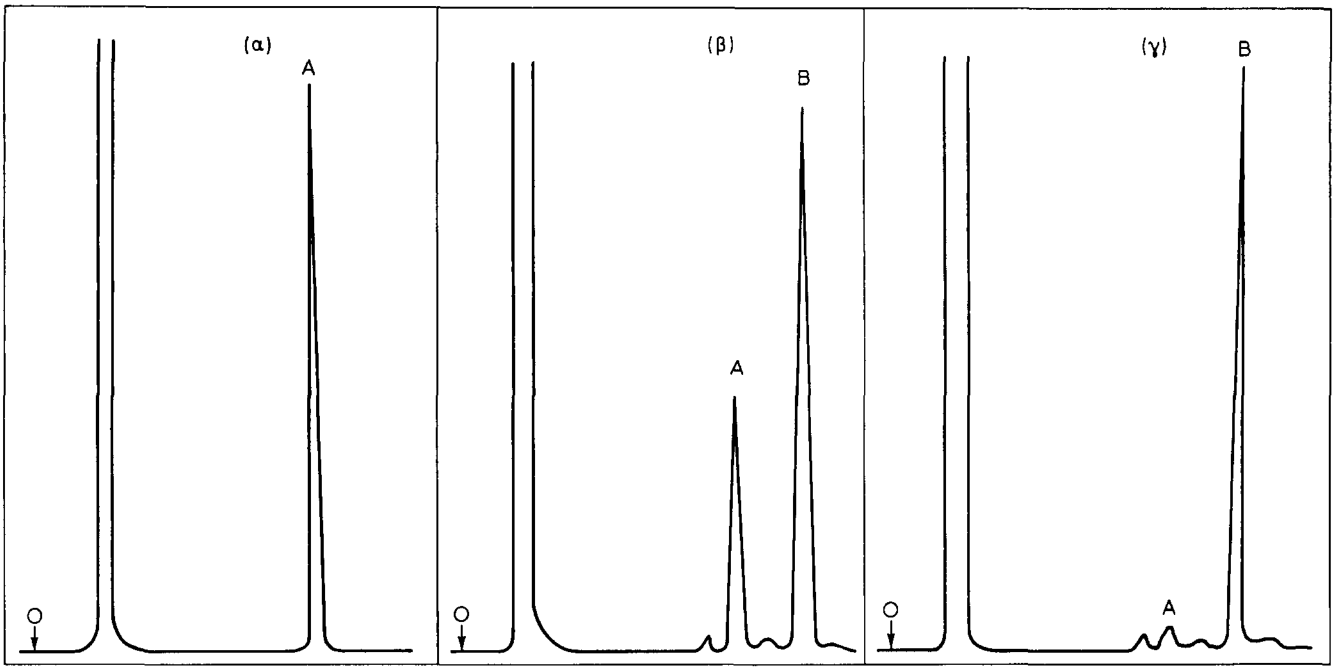
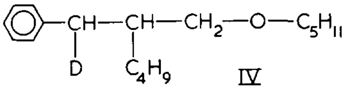


Figure 3 G.l.c. traces of (α) pentyl cinnamyl ether, and its reaction products with butyl lithium in benzene after (β) 1 h, and (γ) 3 h

(*Figure 3*). Reaction with the cinnamyl ether is essentially complete in 3 h and a sample taken after this time was terminated with D_2O and analysed by ^1H n.m.r. This analysis confirmed the product to be of structure IV with


$C_6H_5\text{—}CH(D)\text{—}CH(C_4H_9)\text{—}CH_2\text{—}O\text{—}C_5H_{11}$

IV

only a trace of starting material still present. By using the retention time observed for this product to identify it in the multiple-peaked traces obtained from the products of the THF-containing solvents, the yield of the desired adduct in such systems was shown not to exceed 60%.

The virtually quantitative yield of the model anion obtained in benzene with the cinnamyl ether means that the cleavage reaction feared (equation (4)) is not significant in this solvent, although it might contribute to the complexity of products observed in THF containing systems. Reaction of the pentylether of 1-phenyl-1-buten-4-ol was equally clean with butyl lithium in benzene, but slower—only 60% yield of the adduct being obtained after 3 h. It was decided, therefore, to concentrate on the behaviour of cinnamyl-terminated polyTHF in these circumstances, and the cinnamyl pentyl ether was consequently used as the model compound.

Polymerization experiments were carried out using as initiator the product of 3 h reaction in benzene of cinnamyl pentyl ether and butyl lithium in a molar ratio of 1:0.9 (to avoid unreacted excess butyl lithium initiating the system). Isoprene and styrene were used as monomers and, with the former, a small quantity of THF (1% v/v) was added some minutes after addition of monomer to accelerate propagation, at which point the colour of the solution turned to the distinct yellow characteristic of the isoprenyl anion.

G.p.c. analysis of the products showed that, with styrene, the molecular weight of the polymer was 8 700 compared with a calculated value, assuming complete initiation, of 3 500. Thus an initiating efficiency of only ~40% was obtained. Similar experiments with isoprene resulted in a polymer of 7 500 polystyrene equivalent molecular weight which on application of published conversion data[18] gave an actual molecular weight of about 5 600. Since the value assuming quantitative initiation was calculated to be 3 000, this again gave an initiating efficiency of about 50%. It therefore appears that with either monomer only about half the number of chains are initiated compared with the amount of butyl lithium used.

Reaction of butyl lithium with polyTHF possessing terminal styryl units

The feasibility of the cation to anion transformation having been established by using model compounds, experiments were planned involving polyTHF with cinnamyl terminal units as co-initiator. Reactions with butyl lithium were carried out either directly in the solvent in which the polymer was prepared (2:1 THF:benzene), or in pure benzene. In the former case the dark red colour due to the styryl anion appeared immediately, and in the latter case more slowly; the monomer was then added in bulk or in benzene solution.

Of the many experiments carried out under different conditions, two typical reactions are described; the first involving styrene as monomer in a 2:1 THF: benzene mixture, and the second involving isoprene in pure benzene.

In the first, polyTHF of 1 900 polystyrene equivalent molecular weight and terminated with the cinnamyl ligand (*Figure 4a*) was reacted at ambient temperature with 0.9 mol equivalent of butyl lithium, and after 3 h styrene was added. The predicted molecular weight was 6 000 but the g.p.c. trace of the product after complete consumption of the styrene indicated a peak at 20 000 molecular weight with a shoulder remaining at 1 900 (*Figure 4b*). This residual peak is almost certainly uninitiated polymer still possessing unsaturated styryl

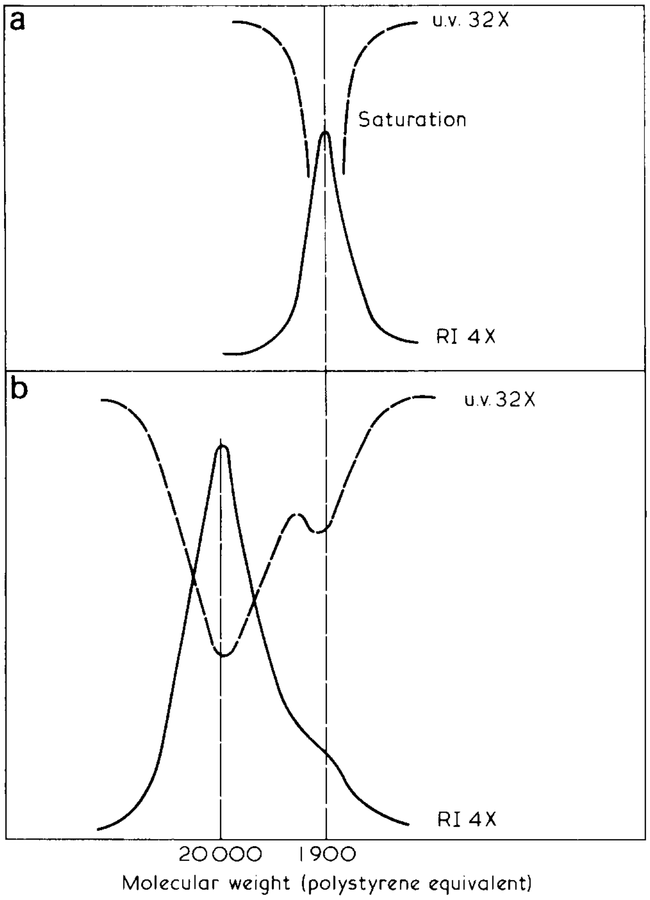


Figure 4 **G.p.c. traces of (a) polyTHF terminated with cinnamyl alcoholate, and (b) the product of its reaction with butyl lithium and, subsequently, styrene**

terminal groups because of its relatively large u.v. absorption (see General Discussion), and it indicates that the overall transformation process in this mixed solvent system is inefficient (20% maximum if all the high molecular weight component is block copolymer).

PolyTHF terminated with the cinnamyl ligand and 3 500 polystyrene of equivalent molecular weight was similarly reacted in pure benzene with butyl lithium, and isoprene subsequently added. Polymerization was allowed for some hours until 60% conversion had occurred before the system was terminated. G.p.c. traces of the materials obtained at the various stages of the process are shown in *Figure 5*. Most importantly, the final product (*Figure 5d*) shows two peaks in the RI trace, the larger at 80 000 polystyrene equivalent molecular weight (60 000 polyisoprene molecular weight[18]) with a small but significant u.v. signal, and a residual peak at 3 500 with a more prominent u.v. signal indicating unitiated polyTHF. The presence of u.v. absorbance in the high molecular weight material demonstrates that some block copolymer has been formed, since homopoly-isoprene is transparent at 254 nm. However, the anticipated molecular weight of the product assuming quantitative initiation was only 8 000, so that the initiating efficiency on this basis is only about 15%.

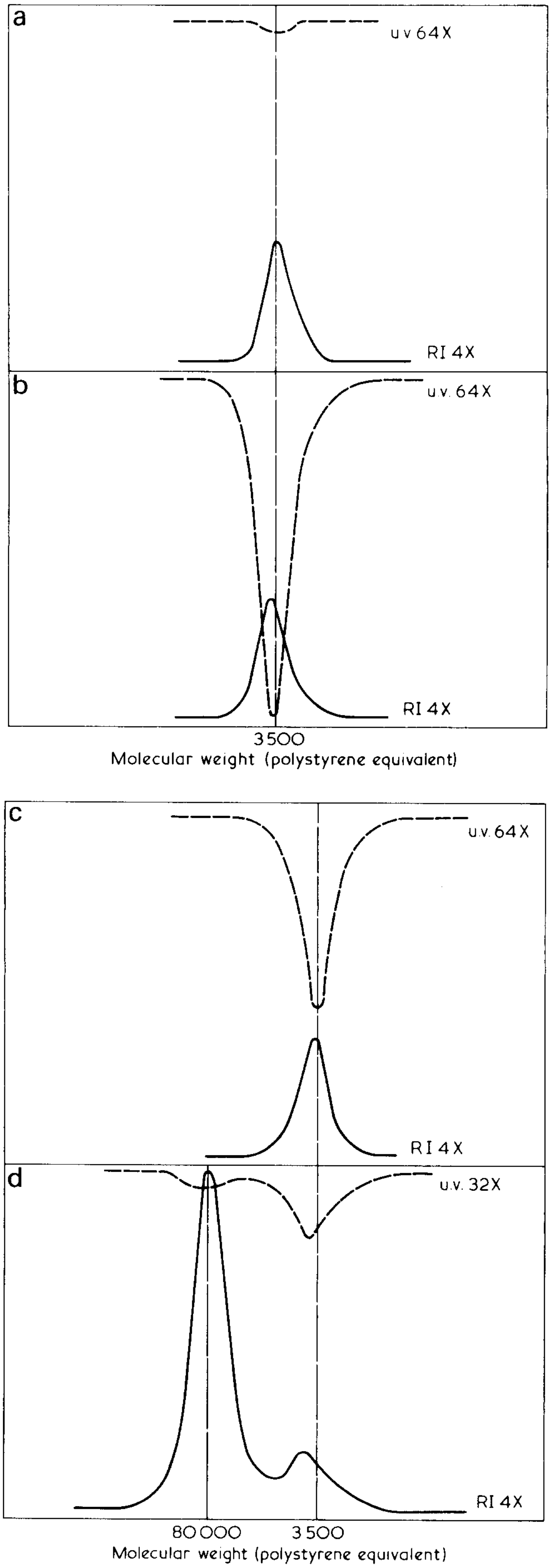


Figure 5 **G.p.c. traces of polyTHF (a) terminated with methanol, (b) terminated with cinnamyl alcoholate, (c) terminated with cinnamyl alcoholate, then reacted with butyl lithium and terminated with methanol, and (d) terminated with cinnamyl alcoholate, then reacted with butyl lithium and subsequently, isoprene**

GENERAL DISCUSSION

In summary, the experimental results indicate that cinnamyl alcohol terminated polyTHF may be prepared virtually quantitatively; it reacts with butyl lithium to form a species giving a red colour characteristic of the styryl anion, but addition of monomer results in an initiating efficiency of only 15–20%, as estimated from the molecular weight of the product. In contrast, similar reactions with model compounds result in initiating efficiencies of about 50%.

From the g.l.c. traces shown in *Figure 3* it is evident that the addition of butyl lithium to the cinnamyl pentylether goes smoothly to form the adduct in high yield, so that the 50% efficiency observed with these species cannot be ascribed to incomplete formation of the styryl carbanion, but rather to its anomalous behaviour in initiating polymerization of the added monomer. Alternatively, the presence of a terminating impurity in the monomers could account for these observations, but the similar efficiencies obtained with isoprene and with styrene would require the unlikely condition that the impurity was present to the same degree in both systems. Further, these monomers, purified in an identical manner for conventional anionic polymerizations in THF, had been initiated with very high efficiencies. This last explanation is therefore considered unlikely, although a satisfactory chemical reason for this behaviour cannot currently be given.

Moving to the much lower initiating efficiency of the polyTHF adduct system, the following points may be considered. *Figures 4*(*b*) and *5*(*d*) show that a considerable proportion of the polyTHF remains at the molecular weight of the starting polymer. This could be because (a) the polymer terminal group had not reacted with butyl lithium for some reason, or (b) reaction had taken place to form an adduct, but the adduct had not reacted with monomer, or had reacted anomalously to terminate the polymer chain.

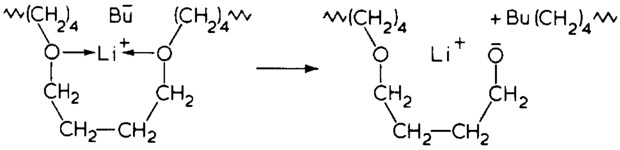
Of these two possibilities the former is favoured because of the high u.v. absorbance of the residual peak. The styryl grouping has a very much higher extinction coefficient of 254 nm than the benzyl derivative which would be generated by reaction of butyl lithium with the terminal group (ε_{254} styrene$\gg\varepsilon_{254}$ ethyl benzene). Indeed, the measure of benzyl absorbance may be observed in *Figure 5*(*a*) in which the u.v. absorption is due to the *p*-methyl benzyl ligand of the initiator; in this case the u.v./RI ratio at the listed sensitivity settings is 0.07, whereas that of the cinnamyl adduct (*Figure 5*(*b*)) is 2.8, that of this material after reaction with butyl lithium (*Figure 5*(*c*)) is 1.5, and that of the unpolymerized polyTHF in *Figure 5*(*d*) is 2.2 (at u.v. = 64x). The limitations of the g.p.c. detectors makes quantitative evaluation of these figures suspect; nevertheless the trends shown are real and may be commented upon.

Firstly, the high value of the u.v./RI observed in *Figure 5*(*c*) compared with *Figure 5*(*a*) indicates that all the styryl double bonds have not reacted with butyl lithium to form the adduct—if total reaction had taken place and the extinction coefficients of the resulting terminal benzyl group were similar to that of the initiator, the ratio would have been reduced to about 0.2. An assessment of the reaction based on a comparison of the u.v./RI ratios of *Figures 5*(*b*) and *5*(*c*) indicates that only about 50% of the adduct had been formed. The increase in the ratio of the residual peak after polymerization (*Figure 5*(*d*)) supports this view, suggesting that the peak is principally due to the strongly u.v. absorbing unreacted unsaturated starting material.

If the reactivity of butyl lithium to the double bonds in these polymeric systems is mirrored by the model compound studies then it is high, and it is therefore unlikely that the presence of unreacted polymer is caused by incomplete reaction; about half of the added butyl lithium must therefore have been consumed by some alternative process.

A possible identification of this alternative reaction may be obtained from the model compound studies in which it was found that a number of side products were formed during the butyl lithium reaction when carried out in THF and the yield of adduct did not exceed 60%. Undoubtedly such side reactions involved attack on and scission of the THF molecule since these are well established and have been found to occur under experimental conditions similar to those employed in this study[19].

This suggests an essential difference between the model compound and the polymer reactions when carried out in benzene. In the former case the high yield of adduct showed there to be little reaction with ether grouping of the model compound, probably because the molar ratios of ether to butyl lithium never exceeded unity, and any interaction through ether solvation of the cation would be in close proximity to the styryl double bond and thus promote nucleophilic additive attack by the 'solvent' separated butyl anion. Neither of these conditions apply in the polymer system since the polyTHF chains introduce a relatively high concentration of ether groupings which undoubtedly participate in the solvation of the lithium cation. This could create a situation analogous to that observed in the reactions in THF where solvation, by increasing the nucleophilicity of the reagent, allows the butyl anion to cleave the chain (equation (5)).



(5)

Whilst this hypothesis could account for the observed inefficient initiation through destruction of significant amounts of butyl lithium, the cleavage reaction if random, should also result in an appreciable reduction in the molecular weight of the polyTHF. Comparison of g.p.c. traces such as *Figure 5*(*b*) and *5*(*c*), however, show that there is no readily observable diminution in molecular weight or broadening in its distribution after reaction with butyl lithium.

The reasons for the low efficiency of the polymerization reaction, therefore, remain unclear, although it is evident that, until these reasons are elucidated and the difficulties overcome, this approach to the development of a cation to anion transformation scheme will not become an attractive route to the synthesis of novel block copolymers.

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