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Block copolymerization by a cation to anion transformation process:
2. Polymerization of styrene by polyTHF possessing terminal secondary nitranions

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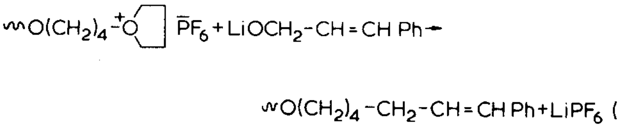
A route for preparing block copolymers by a cation to anion transformation is examined. PolyTHF possessing a terminal secondary amine group is prepared by reacting living polymer with excess of the primary amine, then metallated with potassium to create a terminal nitranion. This is then used to initiate the anionic polymerization of styrene, but initiation is relatively slow and, although all the styrene is consumed, only about 30% of polyTHF chains form a block copolymer.

Keywords Copolymerization; cation; anion; transformation; polytetrahydrofuran; polystyrene; polymer amine

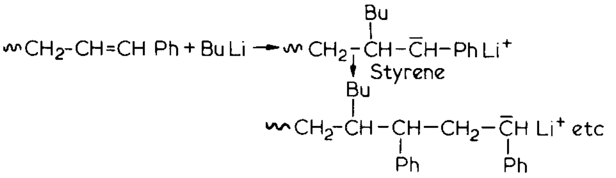
Introduction

For a number of years we have been examining methods of synthesizing novel block copolymers by developing so called transformation reactions in which the mode of propagation of the first monomer is transformed *via* a 3 stage process into a different mode suited for the polymerization of the second. These processes have been recently reviewed[1], and it is evident that certain transformations may be achieved with greater efficiencies than others. Thus the anion to cation process has been carried out with overall efficiencies in excess of 90%[2-4], whereas the reverse reaction, cation to anion, has to date achieved an efficiency of only about 20%[5]. Alternative, more efficient transformation reactions are therefore still being sought, and one such approach to the cation to anion transformation forms the subject of this communication.

The method reported previously[5] used tetrahydrofuran (THF) as the cationically polymerizable monomer, and required a quantitative reaction of the living polyTHF with lithium cinnamate to form a polymer with a terminal styryl unsaturation (equation (1)). This was achieved, but the subsequent process which involved reacting the polymer with n-butyl lithium to form a terminal carbanion and then using this species to initiate the polymerization of a monomer such as styrene (equation (2)), yielded only small amounts of block copolymer. The reasons for this low efficiency were not fully elucidated, and it seemed desirable to seek an alternative method of effecting this transformation.

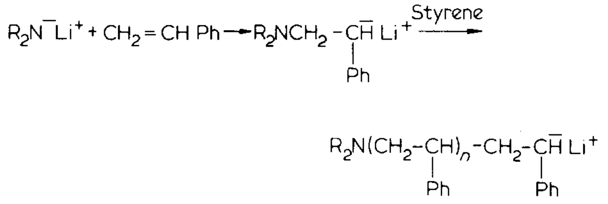


$$\sim O(CH_2)_4-\overset{+}{O}\ \bar{P}F_6 + LiOCH_2-CH=CH\,Ph \rightarrow \sim O(CH_2)_4-CH_2-CH=CH\,Ph + LiPF_6 \quad (1)$$



$$\sim CH_2-CH=CH\,Ph + BuLi \rightarrow \sim CH_2-\underset{}{\overset{Bu}{C}}H-\bar{C}H-Ph\,Li^+ \xrightarrow{Styrene} \sim CH_2-\overset{Bu}{C}H-\underset{Ph}{C}H-CH_2-\underset{Ph}{\bar{C}}H\,Li^+ \text{ etc} \quad (2)$$

Elsewhere, studies had been carried out on anionic initiation by alkali metal salts of amines[6-8], and these had shown the species to be active in the polymerization of monomers such as styrene or butadiene (equation (3)),



$$R_2\bar{N}Li^+ + CH_2=CH\,Ph \rightarrow R_2NCH_2-\underset{Ph}{\bar{C}}H\,Li^+ \xrightarrow{Styrene} R_2N(CH_2-\underset{Ph}{C}H)_n-CH_2-\underset{Ph}{\bar{C}}H\,Li^+ \quad (3)$$

although the initiation process was found to be slow relative to propagation. It seemed possible, however, that this approach could be adapted to carry out the cation to anion transformation required.

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We had been carrying out a general study of the reactions of living polyTHF with amines[9-12], and had shown in particular that reactions could be effected with primary amines under controlled conditions to generate polymers possessing terminal secondary amine groups with yields up to 98%[12] (equation (4)). Thus a polymer


(4)

amine was available which could in principle be converted to the alkali metal salt, and which in turn could be used, as in equation (3), to polymerize a second monomer anionically to create block copolymers.

Experimental

Materials. Styrene, THF and other materials were purified to the standards required for ionic polymerization by techniques described previously[13-16].

Synthesis. Previous publications[13-16] outline the experimental procedures involving greaseless high vacuum systems and break seal techniques also used in this investigation. A summary only of the methods used are given here.

Standard conditions were employed to prepare living polyTHF[17], using *p*-methylbenzyl bromide and silver hexafluorophosphate as the initiating system. The living polymer was then terminated with tenfold excess n-butylamine[12], the solvent removed by rotary evaporation and the residue pumped under high vacuum for 12 h to remove unreacted amine. This material was then redissolved in THF and reacted with a potassium film for 24 h at room temperature. After filtering through a sinter, the solution was cooled to −45°C and styrene added, either directly *via* a breakseal or by distillation over a period of an hour. Thereafter the solution was allowed to warm to ambient and remain at this temperature for 24 h before terminating with methanol.

Cationic oligomers of THF ($DP \sim 2$) were prepared at −78°C using a technique described previously[12]; they were then aminated and processed as described above.

Characterization. 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 Varian HA 100 or a Varian EM 390 spectrometer.

Results and Discussion

It was shown previously that living polyTHF could be prepared in bulk at −10°C using *p*-methyl benzyl bromide and silver hexafluorophosphate as initiating reagents[17], and that such polymers could be reacted with excess primary amines to yield chains possessing terminal secondary amine groups virtually quantitatively[12]. Three primary amines, n-butylamine, cyclohexylamine and aniline, were examined and, although reaction of all three with living polyTHF proceeded equally efficiently, it was decided that the polyTHF/n-butylamine product would be the most effective as a reagent to examine the cation to anion transformation; the nitranion generated was thought to be the most basic and least sterically hindered of the three and therefore likely to be the most active initiator.

Three ways of metallating the polymer as a solution in THF were examined; reaction with a solution of n-butyl lithium in heptane, with a solution of sodium naphthalene in THF, or with a potassium metal film. It was difficult to use the first reagent to effect exact neutralization because of the possibility of side reaction with THF and/or direct anionic initiation of the subsequently added monomer by any excess or unreacted n-butyl lithium. Sodium naphthalene solution, being coloured, could be visually titrated into the polymer amine solution and was therefore a better alternative, but the method ultimately chosen was the direct reaction with potassium film since the reaction could be allowed to go to completion and the solution then filtered to remove excess metal.

On introduction of the polymer amine solution on to the potassium film, hydrogen gas was seen to evolve and the originally colourless solution developed a yellow-orange colouration which deepened with time. The conditions for quantitative reaction were determined by comparison of the ^1H n.m.r. spectrum of oligo THF ($DP \sim 2$) terminated with n-butylamine metallated with potassium with the spectrum of the product of its subsequent reaction with methanol (*Table 1*). Analysis showed that the nitranion was exclusively formed, and that reaction was complete after 12 h at ambient temperature. These conditions were therefore applied to the reaction involving the aminated polymer.

Two types of polymerization experiments were carried out. In the first, styrene was added as a THF solution at −40°C to a solution of the totally metallated polymer in THF, and the temperature allowed to return to, and remain at ambient. In the second, styrene was distilled into the metallated polymer solution, held at −40°C, over a period of about 1 h before the solution was allowed to return to ambient temperatures. As the styrene was added and as the solution warmed, the colour changed to a deep orange which intensified as reaction proceeded. After 24 h reaction the solution was added to methanol, the precipitate was filtered off, washed and dried, and the filtrate was worked up on a rotary evaporator to yield a polymeric residue. Both materials were weighed and were then analysed by ^1H n.m.r. and by g.p.c.

G.p.c. traces of the methanol soluble and the methanol insoluble fractions obtained in both types of experiments are shown in *Figure 1*. The molecular weights of the methanol soluble components are very much lower than those of the methanol insoluble counterparts, and the shapes and positions of their traces are similar to those of the amine terminated starting materials. Further, their

Table 1 ^1H n.m.r. spectral data of oligoTHF terminated with n-butylamine and subsequently metallated with potassium metal, and this product terminated with methanol

Peaks δ ppm (TMS)	Assignment	Metallated amine	After terminating with methanol
2.90	$-\underline{CH_2}-NH-\underline{CH_2}-$	Peak slightly shifted to higher field due to the negative charge on the nitrogen	Peak at normal position (2.90 ppm)
0.95	$-N\underline{H}-$ and $\underline{CH_3}-(CH_2)_3-$	3 protons inferred from integral	4 protons inferred from integral

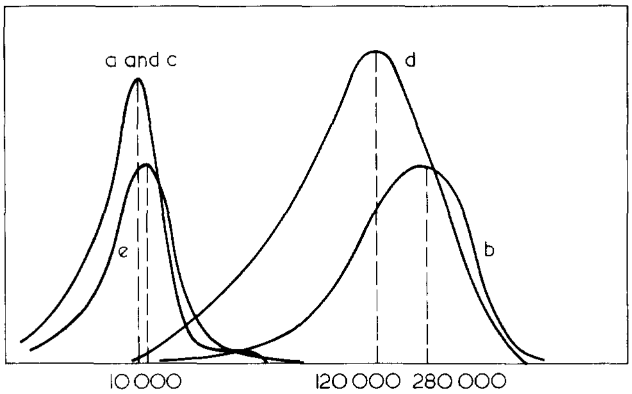

Figure 1 G.p.c. traces of products obtained by initiating styrene polymerization with polyTHF possessing a terminal nitranion (a) methanol soluble and (b) methanol insoluble components of system into which total styrene was introduced initially, (c) methanol soluble and (d) methanol insoluble components of system into which styrene was distilled over 1 h, (e) aminated polyTHF starting material

Table 2 ^{1}H n.m.r. spectral data of the methanol soluble and methanol insoluble components of the product obtained by initiating styrene polymerization with polyTHF possessing a terminal anion

Peaks δ ppm (TMS)	Assignment	Methanol soluble polymer	Methanol insoluble
7.05 and 6.50	aromatic protons	not observed	observed
3.40	$-O-C\underline{H}_2-$	observed	observed

u.v. absorbances at 254 nm (not shown) are very low, commensurate with the presence of the *p*-methyl benzyl ligand of the initiator only. Thus, on this basis the methanol soluble materials seem to consist predominantly of unreacted polyTHF.

In contrast the methanol insoluble samples are at very much higher molecular weights, have broad molecular weight distributions, and exhibit very strong u.v. absorptions at 254 nm (not shown). This high absorbance can only be caused by the presence of a polystyrene component whether as homopolymer or as copolymer. Therefore methanol precipitation appears to fractionate polystyrene-containing polymer from unreacted homopolyTHF.

^{1}H n.m.r. analysis of the two product fractions (*Table 2*) confirmed the conclusions arrived at from the g.p.c. traces. The spectra of the methanol soluble components showed no detectable aromatic absorbance, whilst those of the insoluble fraction revealed signals from polystyrene and from polyTHF. This is strong evidence that the insoluble material consists principally of polyTHF–polystyrene block copolymer, and therefore that polymerization resulting from the cation to anion transformation has taken place.

The total weight of polymeric product obtained in the experiments indicated that the added styrene had been polymerized quantitatively. Thus, measures of the initiating efficiency of the nitranion could be derived in two ways, both of which being based on the assumption that the methanol insoluble component contained none of the homopolyTHF and all of the polystyrene containing component. The first was derived from the weight fractions of the two polymer fractions, and the second was calculated from the ratio of the observed number average molecular weight (M_n) of the block copolymer to its calculated molecular weight assuming 100% initiating efficiency. The experimental and derived data are given in *Table 3*.

Table 3 Block copolymer formation as a function of the mode of styrene addition

Mode of styrene addition	Block copolymer calculated M_n	Methanol insoluble polymer M_n	 M_p	Initiating efficiency (%) by weight	 by M_n
Immediate total addition	20 000	140 000	295 000	10	14
Distillation over 1 h	20 000	67 000	175 000	25	30

The estimates of efficiency calculated by the weight fraction method are consistently lower than those derived from the molecular weights of the product components. This could be explained by invoking a chain transfer process during the propagation stage, but is more likely to reflect the inaccuracies inherent in both methods of estimation. Despite these shortcomings, however, it is evident from *Table 3* that the efficiency of block copolymer formation is relatively low, but that it can be improved by adding the monomer slowly to the polymerizing system. These observations confirm the picture that the initiation step, in which a nitranion is converted to a carbanion, is slow relative to propagation, and the broad molecular weight distributions and the long low molecular weight tails observed with the copolymers is further support for this view.

These results therefore show that a cation to anion transformation capable of preparing block copolymers can be achieved by this route, but that the stability of the intermediate nitranion is too great to allow quantitative conversion.

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