# Block copolymer synthesis by reaction of living polystyrene with living polytetrahydrofuran

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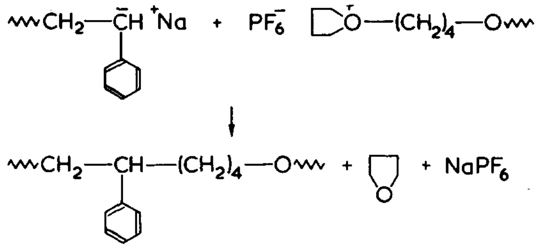
The reaction between anionic living polystyrene and cationic polyTHF has been examined and shown to result virtually quantitatively in coupling of the two polymers. The reaction has been exploited to prepare AB, ABA and (AB)$_n$ block copolymers and g.p.c. analysis has shown these materials to be free from contamination by homopolymer. Possible synthetic developments arising from this and similar reactions are discussed.

## INTRODUCTION

Techniques have been developed and are now well established for preparing polymers with terminal carbanions either at one or both ends of the chains[1]. The most commercially significant monomers which undergo these living polymerization processes are styrene, α-methylstyrene, butadiene and isoprene. In principle, living polymerization systems using a cationic mechanism may be devised to prepare polymers possessing terminal cations, either monofunctional or telechelic. In practice, however, because of the ease of proton transfer in such processes, comparatively few monomers form stable living cationic polymers and of these tetrahydrofuran (THF) is by far the best known and most studied[2,3].

It is clear that if living polymeric anion and cation solutions are mixed and the reaction between the two species is additive, then block copolymers may be readily formed. This is illustrated with polystyrene and polyTHF in equation (1), and this process may be generalized to form AB, ABA, BAB and (AB)$_n$ block copolymers by choosing the appropriate functionalities of the component homopolymers.



(1)

This synthetic approach has been previously reported, however, in only one short communication[4]. In the main example quoted in the paper, difunctional living polystyrene was reacted with monofunctional polyTHF to yield a material which could be precipitated from methanol and which was shown by i.r. spectroscopy to contain styryl and tetramethylene oxide units. Thus, since homopolyTHF is soluble in this solvent, block copolymer had been undoubtedly formed, but the efficiency of the linking process was not examined. The reaction could not have been quantitative under the authors' experimental conditions since the block copolymer could be fractionated with methanol and water to yield aliquots of substantially different relative compositions, and some homopolyTHF was observed as a methanol soluble component. Further, reaction of difunctional polyTHF with difunctional polystyrene yielded insoluble gels predominantly which could not be readily characterized, rather than the expected linear (AB)$_n$ block copolymers.

Although the techniques for preparing living polymeric anions have been established with little change for twenty years, significant developments have occurred in the synthesis of living polyTHF since the publication of that paper. The method[2] employed by the authors has been improved by later workers[3], and this has in turn been adapted in these laboratories to produce mono- or difunctional living polyTHF of narrow polydispersity with equal facility[5]. Thus, by using these more recent synthetic developments, improvements may be effected in the overall conversion to block copolymer and, as will be seen, the efficiency of the linking process may be quantified by examining the product by gel permeation chromatography (g.p.c.).

This communication examines the efficiency of the reaction between living polystyrene and living polyTHF to form block copolymers.

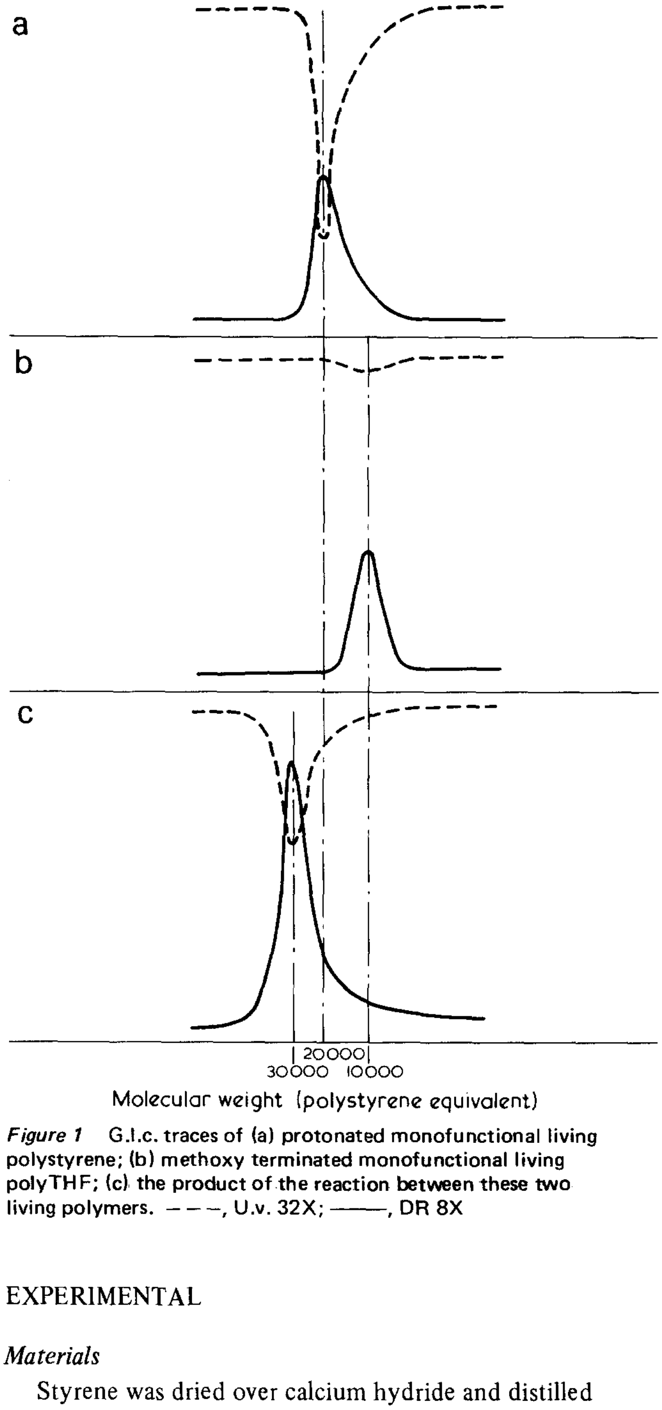


*Figure 1* G.l.c. traces of (a) protonated monofunctional living polystyrene; (b) methoxy terminated monofunctional living polyTHF; (c) the product of the reaction between these two living polymers. – – –, U.v. 32X; ———, DR 8X

## EXPERIMENTAL

### *Materials*

Styrene was dried over calcium hydride and distilled under reduced pressure before use. Tetrahydrofuran, stabilized with 0.1% quinol, was freshly distilled under nitrogen after sufficient 0.7 M sodium naphthalene solution in THF had been added to produce a permanent green colour. n-Butyllithium (Koch–Light) was obtained and used as a 2 M solution in hexane. Benzyl bromide (BDH) was distilled and stored over molecular sieve. *p*-Xylylene dibromide (Koch–Light) was recrystallized from benzene. Silver hexafluorophosphate (Pfaltz and Bauer) was supplied as a free flowing powder which was used without purification.

### *Polymer synthesis*

*Polystyrene.* Monofunctional living polystyrene was prepared under nitrogen by a method described by Burgess *et al.*[6], and difunctional living polystyrene was prepared in the conventional manner[1] using sodium naphthalene as catalyst. Samples were removed by syringe for g.p.c. analysis, protonated and precipitated by addition to methanol, filtered and dried before being used to prepare 0.1% w/v solutions in THF for injection.

*PolyTHF.* Monofunctional or difunctional living polyTHF was prepared in bulk under nitrogen by initiation with $AgPF_6$ solution and alkyl monobromide or dibromide respectively. This method has also been described[5]. Samples were taken immediately before the remainder was used for block copolymer preparation, and injected into methanol to terminate the polymer with methoxy groups. One of two work-up procedures was used depending on the availability of the g.p.c. equipment. If this was immediately available, the solution was evaporated down to dryness and a 0.1% w/v THF solution prepared for injection. If g.p.c. analysis was delayed, the solution volume was reduced by evaporation before extracting the acid present ($HPF_6$ complex) with successive aliquots of an ether–brine mixture. The ether solution was dried with $MgSO_4$, and evaporated to dryness before preparing the standard 0.1% w/v THF solution for analysis.

*Block copolymer.* By suitable manipulation of the nitrogen gas pressure, the THF solution of living polystyrene (10 to 15% v/v) was introduced into an enclosed burette, and the polyTHF solution in its own monomer (0.01 M) into the attached flask. The temperature of the latter solution was maintained below –10°C throughout the titration by an appropriate external coolant. The polystyrene solution was then added to the polyTHF solution until a permanent red tinge appeared indicating completion of the titration. The titre was invariably within 3% of that expected theoretically. In certain cases, particularly when both component polymers were difunctional so that a large molecular weight was expected of the block copolymer, the viscosity of the solutions increased markedly as titration proceeded, and powerful stirring had to be supplied to prevent laminar flow and to ensure complete mixing of the reagents. The product was isolated by precipitation from methanol, filtered, dried and made up to a 0.1% w/v solution in THF for g.l.c. analysis. No detectable organic material was observed on evaporating the methanol, indicating the virtually complete reaction of homopolyTHF.

### *Gel permeation chromatography*

Gel permeation chromatography (g.p.c.) was carried out on a Waters Associates model ALC/GPC 301 chromatograph fitted with a differential refractomer (thermostatically controlled at 25°C) and ultraviolet (254 nm) detectors. Two styragel columns in sequence with porosities of $10^4$ and $10^3$ Å were used for simplicity to monitor the medium and low molecular weight products (*Figures 1* and *2*) although a four column set with porosities $10^6$, $10^5$, $10^4$ and $10^3$ Å was used in the high molecular weight product experiments (*Figure 3*). Elutions were carried out at ambient temperature with THF as solvent and with a flow rate of 1 $cm^3$/min. A 2 ml aliquot of 0.1% w/v THF solutions of the polymers was injected. The retention time was sometimes compared with those of a series of polystyrene standards under the same conditions to obtain an apparent polystyrene molecular weight.

## RESULTS AND DISCUSSION

The efficiency of block copolymer formation in the reaction of polystyrene anions with polyTHF was determined by the use of dual detector g.p.c. only. This technique is of parti-

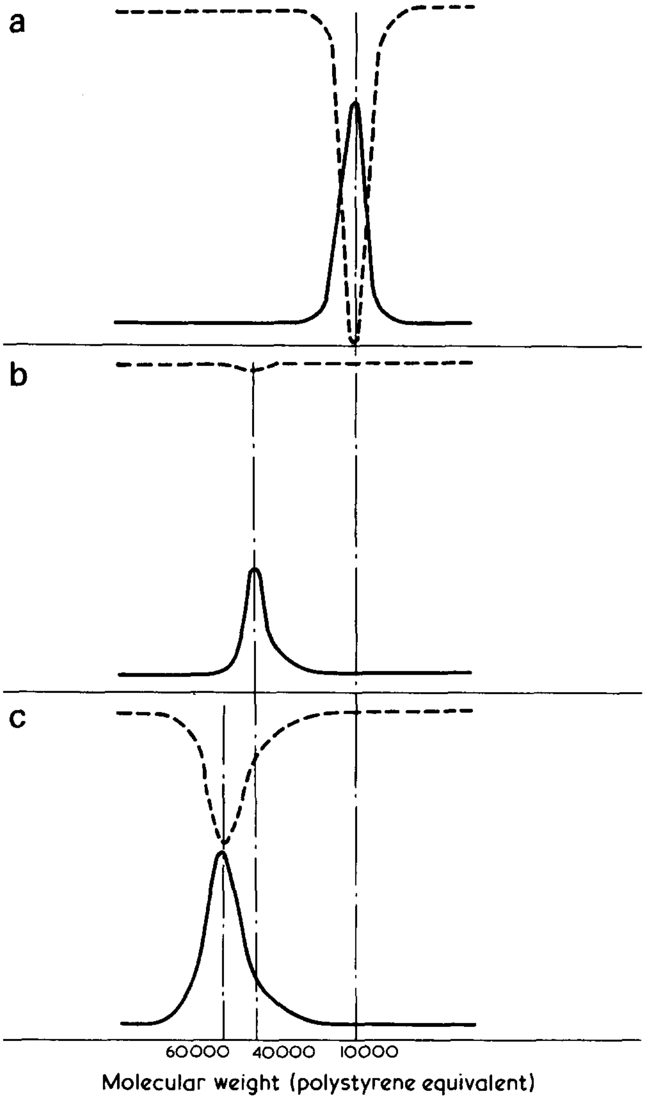


*Figure 2* G.l.c. traces of (a) protonated monofunctional living polystyrene; (b) methoxy terminated difunctional living polyTHF; (c) the product of the reaction between these two living polymers. – – –, U.v. 32X; ———, DR 8X

cular value when, as in this work, one ot the component polymers, polyTHF, is transparent at the u.v. detector wavelength of 254 nm and the other, polystyrene, strongly absorbs. In such systems block copolymer formation can be quantified not only by comparison of the product molecular weight and its distribution with those of the terminated constituent homopolymers, but also by a similar comparison of the relative responses of the u.v. and differential refractometer detectors. The latter technique has been previously applied to an examination of the efficiencies of anionic to cationic transformation reactions[7], and is outlined below.

The relative response ($r$) of the differential refractometer to polyTHF compared with polystyrene is determined by comparing the areas of the responses to equal concentrations of the two homopolymers. The relative response ($s$) of the differential refractometer and u.v. detectors to polystyrene is measured similarly. Then, if the observed responses of the differential refractometer and u.v. detectors to the reaction product are $a$ and $b$ respectively, the area of the differential refractometer signal derived from polystyrene is $bs$, and that derived from polyTHF is $a - bs$. The weight ratio of polyTHF to polystyrene in the product is therefore $[(a/bs) - 1]\,1/r$, and this value may be compared with that predicted from the observed molecular weights and functionalities of the component polymers; the conversion factor 0.592 was used to obtain the true molecular weight of polyTHF from its g.p.c. polystyrene equivalent[7].

A series of experiments were carried out to examine the efficiency of the metathetical reaction between polystyryl anions and polyTHF cations. The molecular weights of the component polymers were chosen to be as low as was consistent with obtaining a significant change in the retention times between the reactants and the products. Monofunctional living polystyrene was reacted with monofunctional living polyTHF to give an AB block copolymer and with difunctional polyTHF to give an ABA block copolymer. Lastly, difunctional polystyrene was reacted with difunctional polyTHF to give an $(AB)_n$ block copolymer. The g.p.c. traces of these products, together with their methanol terminated components are shown in *Figures 1, 2* and *3* respectively, the columns used are reported in the Experimental section.

The homopolyTHF samples in all three g.p.c. traces show small u.v. absorption. This is due to the aromatic initiator

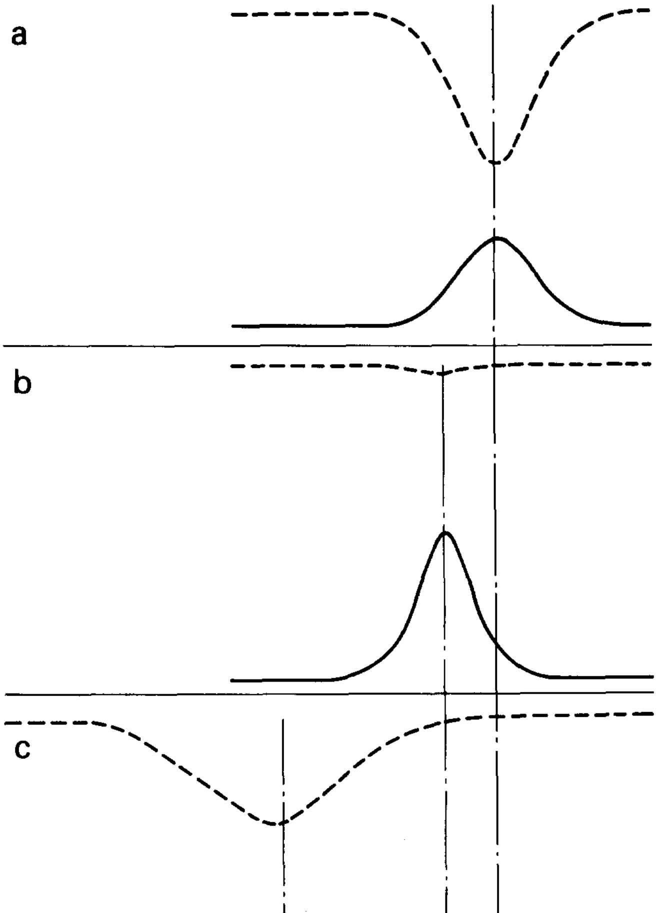


*Figure 3* G.l.c. traces of (a) protonated difunctional living polystyrene; (b) methoxy terminated difunctional living polyTHF; (c) the product of the reaction between these two living polymers. – – –, U.v. 32X; ———, DR 8X

used, benzyl bromide for monofunctional and *p*-xylylene dibromide for difunctional polymer, which is then included as a group either terminal or central to the polymeric chain[5]. Allowance for this small absorbance was not made in the calculation of block copolymer composition from detector responses described above.

In *Figure 1,* as in the other two figures, the product at a molecular weight higher than the component polymers shows significant absorption in the u.v., indicating the presence of a polystyrene component which can only have resulted from the formation of AB block copolymer. The low intensity refractometer signal exhibited by the product at 10 000 molecular weight indicates that the polyTHF component has been effectively coupled. It is difficult in this case to come to the same conclusion with equal certainty about the efficiency of the polystyrene coupling, as residual uncoupled material at 20 000 molecular weight could be buried under the copolymer envelope.

Analysis of the reaction to form ABA poly(styrene–*b*–THF) (*Figure 2*) indicates, however, that the coupling efficiency of living polystyrene is very high. In this case the retention time of this homopolymer is sufficiently different from the resulting block copolymer to avoid any overlapping peaks, and it is evident that no detectable polystyrene remains after reaction with polyTHF.

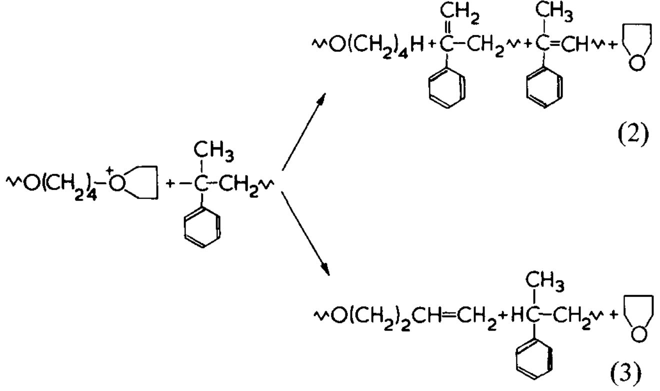
Finally, confirmation of the high efficiency of the linking process may be observed most dramatically by examining the traces obtained from the reaction of the two polymeric components when they are difunctional (*Figure 3*). In this case the molecular weight of the resulting $(AB)_n$ block copolymer is understandably broad since it is created as a result of a polycondensation reaction, but the efficiency of the process may be estimated from it. If the peak molecular weights are taken as an approximation of the number-average molecular weights, (this approximation is reasonable as the number-average is related to the peak molecular weight ($M_p$) by the relation $M_p = (M_w M_n)^{1/2}$, and so $M_n$ lies at lower values in all three cases and errors tend to cancel) then the number of linking reactions per chain is 22, and the linking efficiency is consequently greater than 90%. Even higher estimates of the efficiency are obtained if calculations are carried out based on the residual differential refractometer signals at 12 000 and 6000 molecular weight. A value of greater than 95% is also obtained for the difunctional polyTHF/monofunctional polystyrene system by the analysis described above involving a comparison of the u.v. and differential refractometer signals.

External factors can, of course, contribute to an apparent diminution in the efficiency of the linking process. Any inadvertent termination of the living polymers, by adventituous impurities in the case of polystyrene or by a small amount of chain transfer in the case of polyTHF, would act in this way and, since these materials were prepared under nitrogen rather than under the more clinical high vacuum conditions normally employed, it is very likely, especially in the former system, that termination could become the limiting feature. The g.p.c. trace of polystyrene in *Figure 1* exhibits a low molecular weight tail which is characteristic of this phenomenon and this tail is seen also in the block copolymer trace. The g.p.c. trace for the difunctional polystyrene in *Figure 3* is also broader than expected for living polymer and, again, spurious side reactions could account for this.

Furthermore, the rate of addition of the solution of one living component to the other can be critical in maximizing the molecular weight of the $(AB)_n$ block copolymer. In this case, although no gelling occurred as had been reported previously[4], the rapid increase in polymer molecular weight occurring as the equivalence point is approached results in a correspondingly rapid increase in the viscosity of the solution. Thus, even under powerful stirring conditions it is difficult to avoid laminar flow and, although the reaction between the polymer components is intrinsically extremely rapid, the titration has to be slowed down to allow sufficient time for the reagents to diffuse to each other and complete the reaction before a further aliquot is introduced. Failure to control this would result in an overshoot of the titre with the result that the molecular weight of the block copolymer would be controlled by this excess.

Despite the potential pitfalls inherent in these systems, however, the g.p.c. traces show the process to be remarkably specific, and the authors consequently claim that, within the accuracy of the experiments, the linking reaction appears to be quantitative.

Quantitative linking need not, however, be a feature of all reactions between polymeric cations and anions. Preliminary experiments of a nature similar to those described in this paper involving living polyTHF with living poly(α-methylstyrene) and with polystyrene possessing living terminal 1,1-diphenylethylene units indicate only partial linking in the former case and no detectable linking in the latter. These results have still to be confirmed, but suggest that reaction can also proceed through an alternative elimination route. The two most probable reactions occurring in these cases are illustrated with poly(α-methylstyrene) in equations (2) and (3).



The first involves a hydride transfer from poly(α-methylstyrene) to polyTHF whilst the second involves a proton transfer in the reverse direction. The latter reaction appears to be the more likely because firstly, proton transfer is a more facile process than hydride transfer and secondly, because hydride transfer would result in the vinyl polymer possessing a terminal conjugated unsaturation which would exhibit a greatly enhanced u.v. absorption[8], and no such increase was observed in the g.l.c. traces.

Further work is continuing on these systems and on ones involving polyTHF and polydienes to quantify and, if necessary, to try to increase their linking efficiencies by various means. The results of these investigations will be reported later.

The virtually quantitative nature of the linking reaction between polyTHF and polystyrene opens up the opportunity of combining this process with the anion to cation transformation process reported previously[7–9] to synthesize specifically structured novel block terpolymers. For example, monofunctional living anionic polybutadiene has been oxidized via a stable intermediate to a living cationic polybutadiene which has efficiently initiated the polymerization of THF to produce a cationic AB block copolymer[9]. Titration of this living solution with monofunctional living polystyrene would yield uniquely an ABC poly(butadiene–*b*–THF–*c*–styrene) which should have interesting morphological properties. Other structural possibilities are readily envisaged by permutation of this theme, and it is hoped to report on some of these in later communications.

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