# Reaction to effect the transformation of anionic polymerization into cationic polymerization: 1. Synthesis and reactivities of anionically generated bromine terminated polymers

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A method is described whereby 'living' anionic polystyrene may be oxidized via a stable intermediate stage to a polymeric cation. The process involves termination with excess bromine, and the subsequent reaction of the polymeric product with an appropriate silver salt in the presence of a second monomer. Block copolymers involving tetrahydrofuran have been prepared in this way, but the efficiency of the process is marred by a competing proton elimination reaction at the initiation stage. Nevertheless, block copolymers have been synthesized by this means with polydispersities as low as 1.04.

## INTRODUCTION

The synthesis of block copolymers by sequential addition processes has yielded materials of significant academic and commercial interest. Great stimulus was given to the preparation of these materials through the introduction by Szwarc and coworkers of the 'living' anionic polymerization technique in 1956[1], and by its subsequent development. This activity led directly to the synthesis of ABA poly (styrene-b-butadiene)[2], a thermoplastic elastomer of rapidly increasing industrial importance, much used for moulding applications[3]. Other combinations of monomers have also been block copolymerized using this technique, and a great deal of effort has been devoted to examining the properties of the resulting materials. The whole field of block copolymers has been reviewed recently[4].

Virtually all the synthetic effort has been confined to sequential polymerization by a single propagating mechanism, usually anionic, so that the number of monomers which can be copolymerized (and hence the variety of block copolymers which can be prepared from them) is limited. This restriction would be very much reduced if the mechanism of polymerization could be switched after polymerization of the first monomer to one best suited to the polymerization of the second. Ideally, the transformation should be effected via a stable intermediate so that the homopolymer initially formed can be isolated and redissolved with the second monomer in a solvent suitable for the next mechanism, before reactivation of the propagating end.

To be able to interconvert between the three main propagation mechanisms (anionic, cationic and free radical), six transformations involving one or two electron oxidations or reductions would be required. We have previously briefly outlined a method by which the anion-to-cation transformation may be carried out[5], and two methods which allow the conversion from anion to free radical[6,7]. The object of this and succeeding papers[8,9], is to consider the former two-electron oxidation process in more detail, to maximize its efficiency[8], and to provide a detailed analysis of the compositions of the products formed[9].

A direct transformation from polymeric anion to cation would not be suitable as a general method of preparing block copolymers of this type, as it would be subject to a number of difficulties. Tetrahydrofuran (THF) is the solvent most commonly used for anionic polymerization, but it is readily polymerized cationically. Linear ethers such as the glymes may be used as alternative solvents, but these are subject to cleavage reactions by the polymeric cations generated by the transformation. Even if anionic polymerization is carried out in hydrocarbon solvents, then a choice exists between introducing the second monomer before or after the transformation has been achieved. If the former method is adopted then monomers which can react directly with carbanions have to be excluded, whereas if the latter procedure is used polymeric carbenium ions will be generated in the absence of monomer, and will therefore rapidly react with solvent or their backbones by some Friedel–Craft process. It is therefore evident that these problems may be avoided only if the carbanion can be reacted suitably to create a stable but potentially reactive species which may be subsequently activated to a carbenium ion in conditions suitable for cationic polymerization.

The propagating end in all cationic polymerization processes is the polymeric salt of a strong acid such as perchloric or hexafluorophosphoric acid, and so the ideal reaction sequence would allow a two-step transformation from a 'living' polymer into such a species. A likely process could

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well involve initial reaction to form a halogen terminated polymer which would allow isolation, and which could be reacted subsequently under controlled conditions with a suitable silver salt (such as silver perchlorate) to generate the required polymeric carbenium ion. The steps envisaged are illustrated in equations (1) and (2):

$$\sim\sim M_1^- Li^+ + xsBr_2 \rightarrow \sim\sim M_1 Br + LiBr \qquad (1)$$

$$\sim\sim M_1 Br + AgClO_4 \rightarrow \sim\sim M_1^+ ClO_4^- + AgBr\downarrow \qquad (2)$$

This paper considers the synthesis of polymeric bromides by reaction of the parent 'living' polymers with elemental bromine, and their subsequent reactions with appropriate silver salts. During the course of this work it was discovered that related research was being carried out at the University of Akron and at L'Université Louis Pasteur de Strasbourg. At the former institution Dreyfuss and Kennedy had succeeded in preparing graft copolymers of polytetrahydrofuran by reacting halogenated polymers (PVC, chlorinated rubbers etc.) with silver salts in the presence of THF[10,11]. The French group had obtained evidence of block copolymer formation in systems in which they had terminated 'living' polystyrene with excess phosgene to yield an acyl chloride end group and which they had then reacted with silver salts in the presence of THF to generate oxocarbenium ions[12]. The overall efficiency of the system described was, however, not high.

## 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-Butyl lithium (Aldrich Chemical Co.) was obtained and used as a 2.3 M solution in hexane.

Benzene was dried by azeotropic distillation before immediate use.

All small molecule halides were distilled before use.

Silver perchlorate was dried at 120°C and stored over $P_2O_5$ in a desiccator. Note that silver perchlorate is a powerful oxidizing agent which, when mixed with organic fuels such as THF or benzene, forms an explosive mixture. A sample of silver perchlorate wetted with THF was shown by the Sensitiveness and Hazard section of our Establishment to be very sensitive to impact and friction. Great care was therefore taken to avoid organic solutions containing silver perchlorate or mixtures of solid silver perchlorate and solvents from being trapped in ground-glass joints.

Silver hexafluorophosphate (Pfaltz and Bauer Inc.) was supplied as a free-flowing powder which was used without further purification.

### *Polymer synthesis*

The polymerization to form polystyryl lithium of about 2000 molecular weight, was carried out under nitrogen using an adaptation of a high vacuum technique described by Altares *et al.*[13]. This adaptation has been reported previously[5], as has the termination of the 'living' polymer with excess bromine either directly[5], or via the Grignard intermediate[14]. The reaction of this product with silver salts in the presence of THF has also been outlined[5], so that no further elaboration of the techniques employed need be made here, although specific experimental points are covered in the text.

### *Apparatus*

Gel permeation chromatography (g.p.c.) was carried out on a Waters Associates model ALC/GPC 301 chromatograph fitted with differential refractometer (thermostatted at 25°C) and ultra-violet (254 nm) detectors. Styragel g.p.c. columns, 4 ft (1.2 m) in length and 3/8 in (9.5 mm) o.d. were used in sets of four and were selected from porosities ranging from $10^2$ to $10^6$ Å. The two sets most frequently used were [$10^4$ Å, $10^3$ Å, $10^3$ Å, $10^2$ Å] and [$10^4$ Å, $10^4$ Å, $10^3$ Å, $10^3$ Å]. Elutions were conducted at ambient temperature with THF as the solvent and with a flow rate of 1 $cm^3$/min. The retention volume (1 count = 5 $cm^3$), and hence the molecular weight of a given component of the reaction mixture, was calculated from the initial point of injection to the appearance of the peak height maximum. In this paper and in part 2[8], the molecular weight values quoted are based on calibration curves derived from polystyrene standards supplied by Waters Associates. They do not represent the true molecular weights when applied to block copolymers of styrene and other monomers. In part 3[9], where a detailed analysis of the g.p.c. traces is given, more sophisticated methods of deriving the true molecular weights and dispersities of these block copolymers are described.

$^1H$ n.m.r. spectra were recorded on a Jeol PS-100, 100 MHz spectrometer using approximately 10% solutions in deuterochloroform with tetramethylsilane as internal standard.

Gas–liquid chromatography (g.l.c.) was carried out using a Pye Unicam Series 104 dual column chromatograph with flame ionization detectors. For analytical separations 7 ft (2.1 m) glass columns of 4 mm i.d. were packed with 80/100 mesh 'Chromosorb G' coated with 2½% OV1, and temperature programmes in the region 100° to 300°C were used. For preparative separations for $^1H$ n.m.r. analysis a 3 ft (0.9 m), 7 mm i.d. column packed with 10% OV1 on 80/100 mesh 'Chromosorb G' was used.

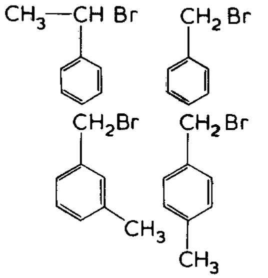
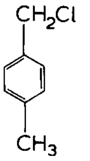
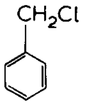
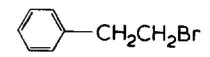
## RESULTS AND DISCUSSION

### *Model compounds*

The transformation process being considered requires for maximum efficiency that the reaction of the silver salt with the polymeric precursor be very rapid, so that all active species are generated at virtually the same instant. Strong indications of the likelihood of such a situation arising are given by a qualitative examination of the reactivities of variously structured small molecule organic halides toward silver perchlorate under the conditions proposed for the block copolymerization experiments. The results of a series of experiments carried out at room temperature on solutions of such compounds in THF are reported in *Table 1*; similar observations were made when benzene was used as a solvent.

It is apparent that bromides are more reactive than the corresponding chlorides. Although this observation is not unexpected, it is contrary to some results obtained on similar systems by Dreyfuss[15]. Iodides were not included in this study as they were considered to be too light sensitive for the polymer analogue to fulfil the further requirement of stability during isolation and protracted storage. Those bromides which can generate resonance stabilized carbenium ions (benzylic or allylic) are very reactive indeed, and allow

*Table 1* Qualitative assessment of reactivity of various alkyl halides to silver perchlorate in THF at room temperature

| Halide | Observation on silver halide appearance |
|---|---|
| <br>$(CH_3)_3C\,Br$ $CH_3—CH=CH—CH_2Br$ | Virtually instantaneous precipitation |
| $CH_2=CH—CH_2Br$ | Very slight delay in precipitation |
| $CH_3—CH_2—CH_2—CH_2Br$ | Slow precipitation over 30 min |
|  | Precipitation over 5 min |
|  | Precipitation over 10 min |
| $CH_2=C(CH_3)CH_2Cl$<br><br>$CH_3CH_2CH_2CH_2Cl$ | Precipitation > 30 min |
| $CH_2Cl_2$ | Slight haziness overnight |

virtually instantaneous and complete precipitation of silver bromide. These compounds are, respectively, structurally analogous to bromine terminated polystyrene and polydienes, and so these preliminary trials strongly suggest that such polymers may be rapidly and quantitatively converted into the polymeric carbenium ions necessary for the second stage of the block copolymer synthesis.

Lastly, it should be noticed that saturated aliphatic halides react only very slowly with silver salts, and that in particular methylene chloride exhibits a stability sufficient for it to be considered as a potential solvent for these polymerization systems.

### *Synthesis of bromine terminated polystyrene (PSBr)*

The principle technique used to examine the polymeric products formed by the transformation reaction was g.p.c. and, as the instrument employed possessed both differential refractive index (r.i.) and ultra-violet (u.v.) detectors, use was made of the differing responses of these to evaluate the efficiency of block copolymer formation. Thus the characteristics of this instrument were borne in mind when choosing the nature and degree of polymerization of the polymer to be prepared anionically, and the monomer to be subsequently polymerized cationically.

Styrene was chosen as the most suitable monomer for the anionic block for a number of reasons. First, it is readily polymerized by well-established techniques to a material of predetermined and narrowly distributed molecular weight and, secondly, after termination it is conveniently isolated by precipitation from methanol; thirdly, polystyrene has a strong absorbance at the wavelength (254 nm) of the u.v. detector. Clearly, in order to examine the transformation reaction as accurately as possible, the molecular weight should be reduced to a minimum, and 2000 was chosen as being suitable because below about 1500 polystyrenes are oils and consequently difficult to handle. It was further decided that, since the Wurtz condensation reaction was an expected side reaction in the bromination step (equation 3):

$$\sim\sim M_I^- \overset{+}{Li} + \sim\sim M_I Br \rightarrow \sim\sim M_I{-}M_I \sim\sim + LiBr \qquad (3)$$

monofunctional rather than difunctional 'living' polystyrene should be prepared, as the condensation product would then appear on the g.p.c. trace as a discrete peak at double the molecular weight of the required PSBr product. This inert material could, in fact, be useful as an internal marker for the experiments, although for improved efficiency of the transformation step this side reaction should be minimized.

Experiments were carried out where monofunctional 'living' polystyrenes of about 2000 molecular weight were prepared, samples protonated with methanol and the remaining portions reacted with excesses of bromine up to a hundred-fold at various rates of stirring. G.p.c. traces of the protonated and brominated product resembled those shown in *Figures 1a* and *b*. Although the protonated material invariably gave a single sharp peak, the brominated material always exhibited an extra peak at double the molecular weight due to coupled material. The amount of this inert component was relatively insensitive to changes in the reaction parameters, and the yield of PSBr obtained by this method never exceeded 72%.

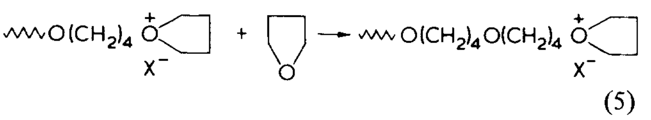
It was felt that this significant irreducible amount of coupling was due to the extreme reactivity of the 'living' polymer causing reaction to take place before efficient mixing could occur, and so this reactivity was reduced by prior reaction of the 'living' polymer with excess magnesium bromide to form the polymeric Grignard (equation 4):

$$\sim\sim M_I^- \overset{+}{Li} + MgX_2 \rightarrow \sim\sim M_I MgX + LiX \qquad (4)$$

The details of this method have been recorded elsewhere[14], and this reduction in reactivity caused the bromine reaction to proceed in a more controlled manner to give products which were at least 95% brominated (*Figure 1c*). Thus the modification allows virtually quantitative production of PSBr but, because this method was developed late in the research programme, the bulk of the experiments to be described were carried out using the partially brominated material prepared by the direct reaction with 'living' polystyrene.

### *Transformation reaction*

The monomer most favoured for this study of the transformation to cationic polymerization is THF. Ring opening occurs by an oxonium ion mechanism (equation 5):



(5)

to yield poly(tetramethylene oxide), more usually called polyTHF, and the monomer is unusual among those poly-

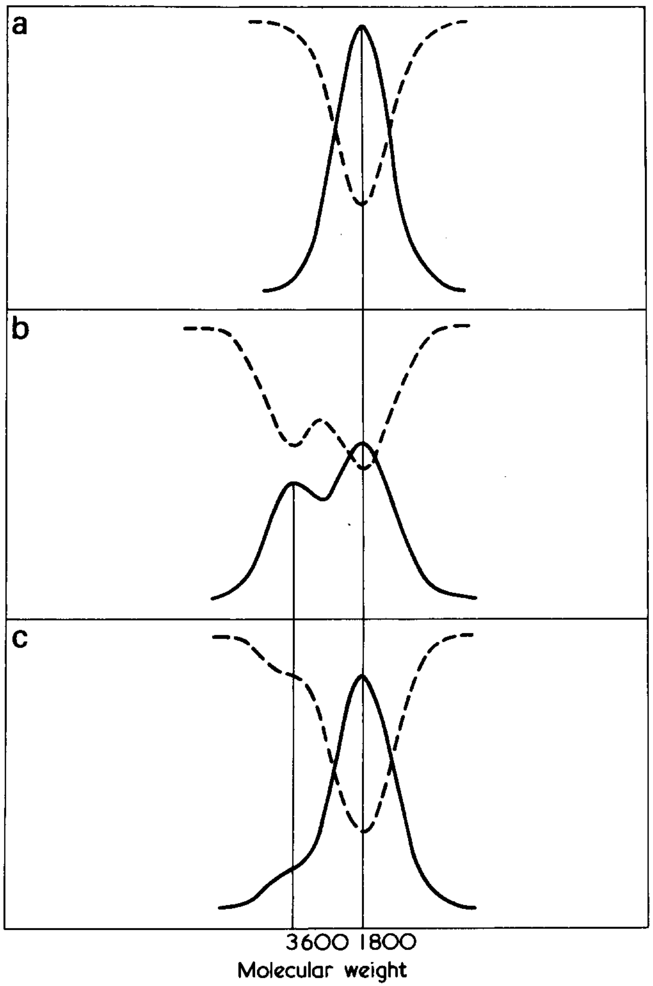
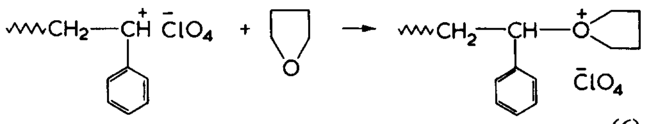


*Figure 1* G.p.c. traces showing the degrees of coupling in the preparation of PSBr. (a) methanol terminated polystyryl lithium; (b) bromine terminated polystyryl lithium; (c) bromine terminated polystyryl magnesium bromide. — — — —, u.v. 32X; ———, r.i. 4X

merizable cationically in that it exhibits very little chain transfer during propagation, particularly at low temperatures[16,17]. Furthermore, polyTHF is transparent at 254 nm and, as will be seen, this allows the r.i. and u.v. detectors on the g.p.c. to be used to estimate the efficiency of block copolymer formation when the other block component, like polystyrene, is a u.v. absorber. All the polymerizations involving THF were carried out in bulk.

Preliminary experiments showed that reaction of PSBr with silver perchlorate in THF resulted in rapid precipitation of silver bromide, both at room temperature and at –78°C and it was decided to carry out the initiation at –78°C to avoid possible side reactions. Brominated material containing 59% PSBr was used, and precipitation was carried out in bulk THF. After a period of 6 days at –78°C, an aliquot was removed and the polymerization terminated with methanol. $^1$H n.m.r. analysis of the isolated product showed that on average only two or three molecules had added to each of the active chain ends. G.p.c. traces of the starting material and this product are shown in *Figures 2a* and *b*, and confirm that very little copolymerization had occurred. The main feature of the product trace is that the peak originally due to PSBr has moved slightly toward higher molecular weights so that a greater degree of overlap now occurs with that of the coupled material. This is consistent with a picture of the reaction of PSBr with silver perchlorate to generate a very reactive carbenium ion which rapidly attacks THF to form the much more stable oxonium ion (equation 6), the rate of propagation of which is very low at –78°C.



(6)

The reaction mixture was then allowed to warm up to and remain at room temperature, and after 24 h it became viscous. Aliquots were removed at intervals and analysed by g.p.c. Traces are shown in *Figures 2c* and *d* and in both examples a large peak appeared in the r.i. trace at high molecular weight (in the range 50 000 to 70 000 polystyrene equivalent). The u.v. detector also gave a smaller but significant peak at these high molecular weights, and this can only be attributed to a polystyrene component derived from the starting material. Furthermore, the area of the PSBr peak had diminished to about a quarter of its original value. The reproducibility of these observations was confirmed by repeating the experiment with a different source of starting material containing 72% PSBr, when very similar traces were obtained.

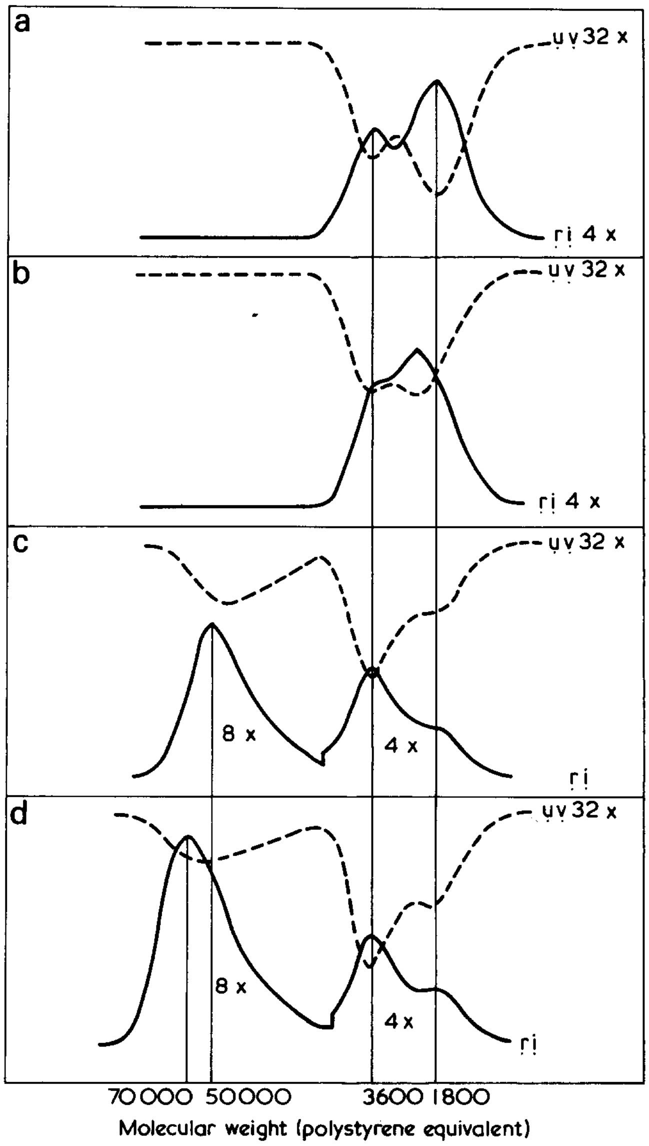


*Figure 2* G.p.c. traces of the block copolymerization of THF initiated by PSBr and $AgClO_4$ at –78°C. (a) PSBr; (b) product after 6 days at –78°C; (c) product after 1 day at room temperature; (d) product after 6 further days at room temperature

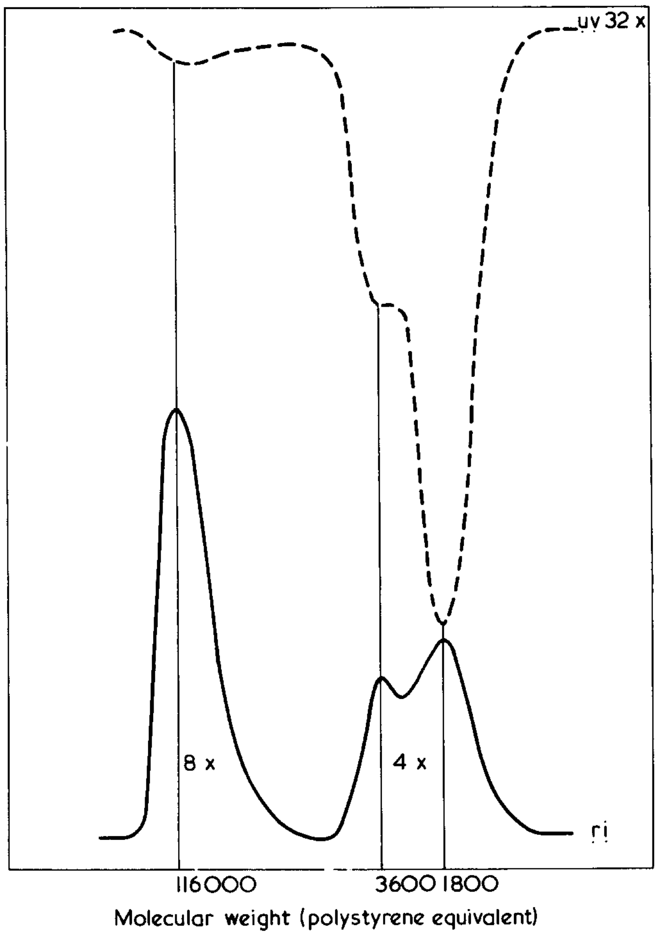
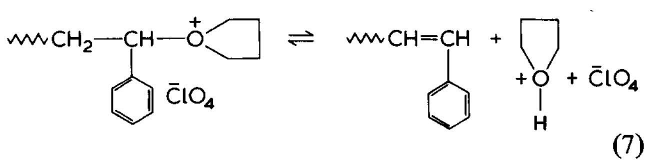


*Figure 3* G.p.c. traces of the block copolymerization of THF initiated by PSBr and $AgClO_4$ at room temperature

If block copolymer initiation had been quantitative, however, the PSBr peak should have been totally eliminated rather than very substantially reduced. Two possibilities could account for this: either the residual material could be inactive polystyrene created by inadvertant reaction of the 'living' polymer with spurious impurities at the preparation stage, or the initially generated oxonium ion may undergo a β-hydrogen elimination to yield solvated perchloric acid and a polystyrene chain with an unsaturated end group (equation 7).

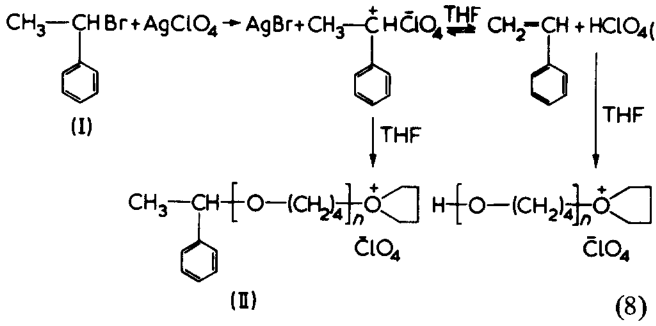


(7)

If this latter process was happening then the terminal unsaturation should cause an increase signal from the u.v. detector. (Styrene monomer has an extinction coefficient at 254 nm approximately two orders of magnitude greater than that of ethyl benzene.) The traces shown in *Figures 2c* and *d* do show small increases in the relative intensities of the 2000 molecular weight peaks when signalled by the u.v. detector over those signalled by the r.i. detector. In general, however, transfer reactions occur with increasing ease as the temperature is raised, so that if the transformation process were carried out at room temperature the amount of proton transfer resulting and hence the intensity of the u.v. signal from the residue should be enhanced.

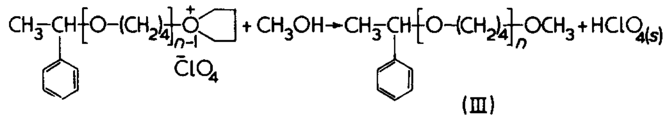
Initiation and polymerization of bulk THF was therefore carried out at room temperature using the 59% PSBr material. The g.p.c. trace of the resulting polymeric mixture is shown in *Figure 3*; the difference between this trace and those in *Figure 2* is readily apparent. It may be calculated from the diminution of the r.i. peak at 2000 molecular weight that only about 20% of the brominated peak has formed block copolymer (cf. ~75% at –78°C). Nevertheless the u.v. response of the residue has increased threefold, thereby substantiating that the β-elimination reaction predominates at room temperature.

The transformation reaction may also be studied by use of model compounds, and (1-bromoethyl)benzene (I) was chosen as a compound likely to simulate the behaviour of PSBr. The sequence of reactions expected from using I to initiate THF polymerization is given in equation (8):



(8)

β-elimination with this compound would result in styrene generation which can be detected and measured by g.l.c. Furthermore, the rate of initiation of THF polymerization by the perchlorate derivative of I is expected to be much faster than that by perchloric acid[18], so that if the polymers were to be quenched with methanol almost immediately after initiation, it should be possible to isolate low molecular weight oligomers derived from II, i.e. of structure III (equation 9).



(9)

The g.l.c. trace of the products of such an experiment carried out at 0°C is shown in *Figure 4*. The individual components were isolated where possible by preparative g.l.c. and their identities established by $^1H$ n.m.r. spectroscopy. They were shown to be styrene and oligomers of structure III where $n = 2, 3$ and 4. The material giving rise to the final peak was too involatile to be separated by preparative g.l.c. but probably has the structure III with $n = 5$. Undoubtedly one of the small peaks at low retention time corresponds to structure III with $n = 1$, but insufficient material was present for positive identification. The remaining small peaks may be ascribed to oligomers initiated by perchloric acid, but in any event their areas are relatively very small, confirming that perchloric acid is an inefficient initiator.

Similar model compound experiments were carried out at room temperature and at –78°C, and measurement of the styrene evolved showed that β-elimination accounted for 63% of the initiator at room temperature, 33% at 0°C and <5% at –78°C. These values are lower than those obtained from direct measurement on PSBr but that is to be expected as β-elimination in polystyrene necessitates removal of a secondary hydrogen whereas it requires removal of the

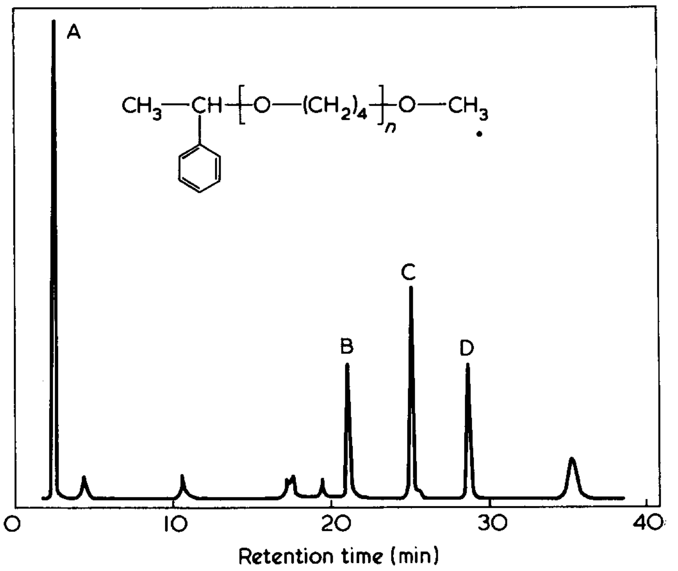


*Figure 4* G.l.c. trace of the products obtained from the reaction at room temperature of THF, (1-bromoethyl) benzene and $AgClO_4$, terminated with methanol. A, styrene; B, $n = 2$; C, $n = 3$; D, $n = 4$

more tightly bound primary hydrogen in the model compound.

*Synthesis of 'living' AB poly(styrene-*b*-THF)*

All the experiments so far described have made use of silver perchlorate as the precipitant, so that the subsequent propagation has always involved the perchlorate gegen ion. It is well known that the nature of the gegen ion can influence the polymerization characteristics of a given system, controlling the rate of propagation, chain transfer and even termination[19,20]. In particular, a recent publication by Croucher and Wetton[21] described a method of polymerizing THF in which transfer was reduced to negligible proportions, and the system could be essentially regarded as 'living' over a period of hours. In this system the gegen ion was generated from the initiator *p*-chlorophenyldiazonium hexafluorophosphate. Although initiation was induced at elevated temperatures (95°C), the mix was rapidly cooled to −10°C where propagation was allowed to proceed to low conversions (~10%) to produce a low-dispersity polymer.

We therefore carried out an experiment based on these observations in which 2000 molecular weight PSBr was reacted with silver hexafluorophosphate at −30°C in bulk THF. The solution was kept at that temperature for thirty min to ensure complete initiation, and then warmed to −10°C for polymerization to ensue. Samples were removed as a function of time and analysed by g.p.c. A typical trace is shown in *Figure 5* where the narrowness of the block copolymer peak (shown to have $M_wM_n \approx 1.04$, see part 3[9]) is strong indication of the absence of transfer. The 'living' nature of this system was confirmed by a plot of the molecular weight of the polyTHF component of the block copolymer (based on polystyrene calibration) as a function of time (*Figure 6*). The linearity of the plot at −10°C again indicates no significant chain transfer. The intercept is close to 2000 because the rate of propagation at −30°C over the initiation period is much slower. Analysis of the g.p.c. traces indicates that only about 50% of the PSBr chains initiated additively to form block copolymer. Nevertheless, the acid generated by the chain transfer mechanism does not appear to have caused any observable homopolymerization of THF over the experimental period. Thus, block copolymers of very low dispersity may be prepared by this technique.

## CONCLUSIONS

The following facts emerge from experiments to effect the transformation of the terminal groups of polymers from anion to cation via an intermediate terminally brominated polymer.

(a) A nearly quantitative conversion of 'living' polystyrene into the required terminally brominated material (PSBr) may be carried out by converting the 'living' polymer into the polymeric Grignard compound prior to reaction with excess bromine.

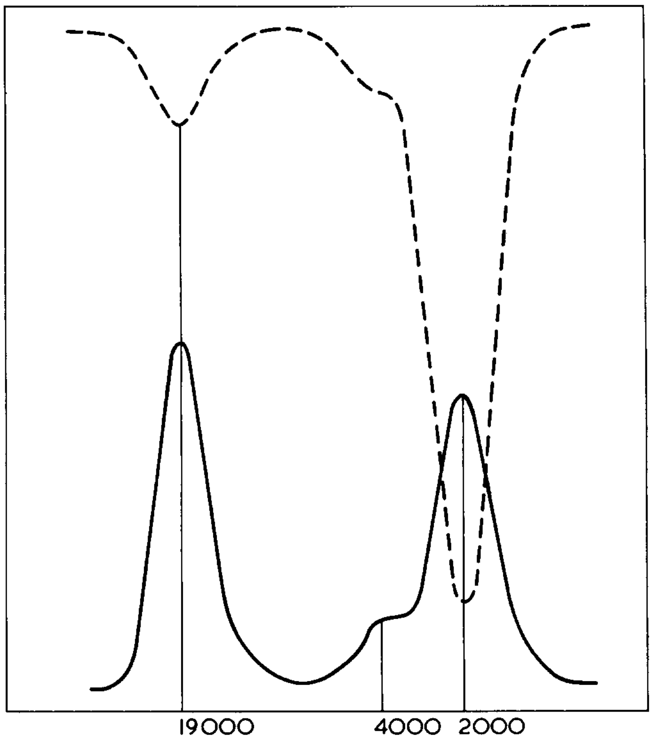


*Figure 5* G.p.c. trace of the block copolymerization of THF initiated by PSBr and $AgPF_6$ at −30°C and polymerized at −10°C for 2 h. – – – –, u.v. 32X ; ———, r.i. 4X

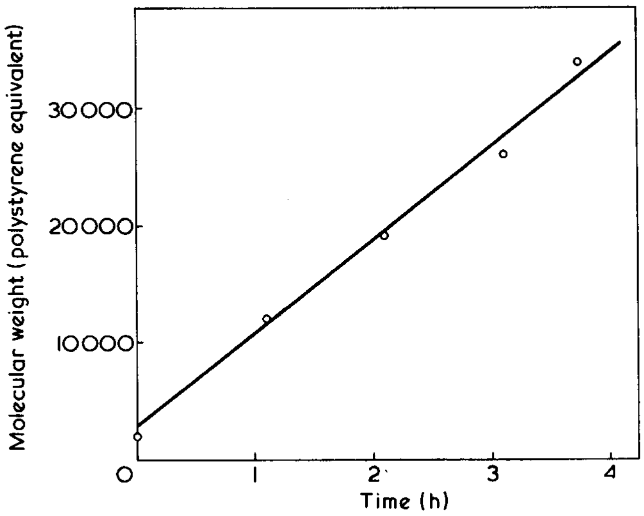


*Figure 6* Rate of block copolymerization of THF initiated by PSBr and $AgPF_6$ at −10°C

(b) Cationic initiation by PSBr on reaction with silver salts is very rapid even at −78°C although, with THF, propagation is slow at this temperature.

(c) The initiation step is not entirely additive, and an appreciable amount of $\beta$-elimination takes place, thereby reducing the efficiency of block copolymer formation.

(d) The proportion of ends initiating additively is an inverse function of temperature (with the perchlorate gegen ion the value decreases from about 75 to 20% as the temperature is raised from −78°C to room temperature).

(e) Despite the presence of the elimination reaction, conditions have been found in which the growing chains exist under 'living' conditions, producing copolymers with very low dispersities.

Part 2 of this series[8] is concerned with developing an alternative, more efficient method of initiating the cationic polymerization so that block copolymers may be prepared in higher yield.

## ACKNOWLEDGEMENT

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