Reactions to effect the transformation of anionic polymerization into cationic polymerization: 2. Synthesis and reactivities of anionically generated xylelene bromide-terminated polymers

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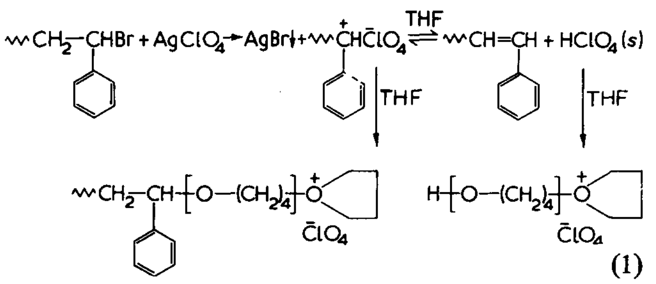
A method is described whereby 'living' anionic polymers may be transformed via a stable intermediate stage into polymeric cations. The process involves termination with excess xylylene dibromide, and the subsequent reaction of the polymeric product with an appropriate silver salt in the presence of a second monomer. Living polystyrene and polybutadiene may be transformed by this technique, and block copolymers have been prepared with tetrahydrofuran from both these starting materials. The efficiency of initiation in this system at room temperature is considerably greater than that obtained from 'living' polymer terminated with elemental bromine but some transfer process still occurs. 'Living' cationic AB block copolymers have been synthesized, which have subsequently been coupled using disodium resorcinate to yield ABA blocks with 70% efficiency.

INTRODUCTION

Part 1 of this series[2] described a method of preparing block copolymers via an anion-to-cation transformation process which required the synthesis of an intermediate polymeric bromide by termination of an anionic 'living' polymer with excess elemental bromine. It was shown with polystyrene that this intermediate (PSBr) could be prepared virtually quantitatively by prior conversion of the 'living' polymer into a polymeric Grignard compound.

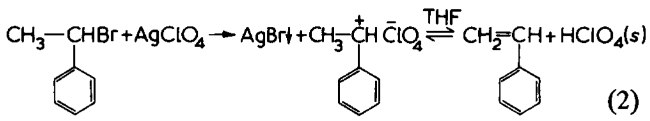
PSBr was then reacted in THF with silver salts, such as the perchlorate or hexafluorophosphate, to generate polymeric carbenium ions which polymerized the solvent to form block copolymer. This initiating process was, however, shown to be inefficient, especially at room temperature, suffering from a competing β-elimination reaction which terminated the polymer and generated the appropriate acid. The reaction scheme involved in these processes is shown in equation (1) for silver perchlorate.



(1)

The incidence of this elimination reaction controls the amount of homopolymer which contaminates the required block copolymer. The percentage block copolymer formation varied from about 75% at –78°C down to about 20% at room temperature. The sole observable contaminant was homopolystyrene and, surprisingly, no homo polyTHF was found under the prevailing experimental conditions, indicating that the catalytic activity of the generated acid may be neglected. It is clear from these results, however, that methods to improve the efficiency of block copolymer formation must be devised if this process is to be a viable synthetic method.

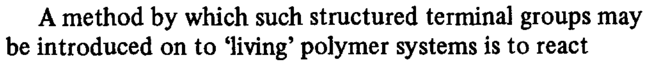
An approach to this problem may be made if the truism be considered that a β-hydrogen elimination reaction can only occur if the β carbon possess hydrogens to eliminate. Thus, the model compound (1-bromoethyl) benzene on reaction with, say, silver perchlorate can eliminate perchloric acid to yield styrene (equation 2):



(2)

whereas this course is not open to benzyl bromide because its β carbon is aromatic and possesses no hydrogen. If, therefore, a similarly structured end-group could be generated on an anionic polymer chain, then the facile proton elimination experienced by the directly brominated materials should be avoided.

A method by which such structured terminal groups may be introduced on to 'living' polymer systems is to react these species with excess of a xylylene dihalide (equation 3):



(3)

Apart from the prevention of the β-elimination reaction, this approach would have two further advantages over the direct bromination reaction considered in part 1. Firstly, this reaction may be applied to 'living' polydienes, whereas

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direct bromination would result in extensive attack on the polymer double bonds. Secondly, the reactivity of the terminal bromide would be predominantly controlled by the adjacent moiety (in this case a xylylene residue) and it should therefore be insensitive to the nature of the polymer to which it is attached. Thus it is possible that a number of experimental parameters may be optimized using one polymeric system, and that these may then be broadly applicable to similar systems using different polymeric initiatiors.

It is an examination of the preparation and properties of polymers prepared using this approach that forms the subject of this communication.

EXPERIMENTAL

Materials

Most of the materials employed were the same as those used in part 1 and the purification procedures were identical to those described therein[1]. *m*- and *p*- xylylene dibromides (Koch-Light) were recrystallized from petroleum spirit (60°–80°C) and benzene respectively. The resorcinol was of Analar grade (BDH Ltd) and was used without further purification.

Polymer synthesis

The polymerization to form polystyryl lithium, usually of about 2000 molecular weight, was carried out under nitrogen, and is an adaptation of a high vacuum technique described by Altares *et al.*[2]. This adaptation has been reported previously[3], as has the termination of this polymer with excess xylylene dibromide either directly[3], or via the Grignard intermediate[4]. The preparation of AB poly(styrene-*b* butadienyl) lithium has not been reported and will therefore be briefly outlined.

8 ml (~0.1 mol) of butadiene, measured at –78°C, were collected in a graduated tube, and allowed to distil under nitrogen into a flask containing a solution of 2000 molecular weight polystyryl lithium (10 mmol) in 250 ml benzene/THF[3]. The butadiene was added over a period of 15 min and the solution then stirred for a further 1.5 h at room temperature. The introduction of the butadiene caused the colour of the solution to fade to a pale yellow characteristic of polybutadienyl lithium in THF. 5 ml of the solution were removed and terminated with methanol for g.p.c. analysis. The remaining solution was then reacted with the chosen terminating agent.

The reaction of these polymeric species with silver salts in the presence of THF has also been previously reported, so that no further elaboration need be made here, although specific experimental points are covered in the text.

Apparatus

The equipment used for gel permeation chromatography (g.p.c.), gas liquid chromatography (g.l.c.) and proton magnetic resonance spectroscopy (^{1}H n.m.r.) has all been described in part 1, and will therefore not be detailed here.

RESULTS AND DISCUSSION

Model compounds

One of the important experiments in establishing the presence of the β-elimination reaction with directly brominated polystyrene (PSBr) was that involving the model compound (1-bromoethyl)benzene[1]. This compound was reacted in bulk THF with silver perchlorate and, almost immediately, methanol was added to terminate the reaction. The presence of styrene, as shown by g.l.c. and ^{1}H n.m.r. analysis, confirmed that proton transfer had taken place.

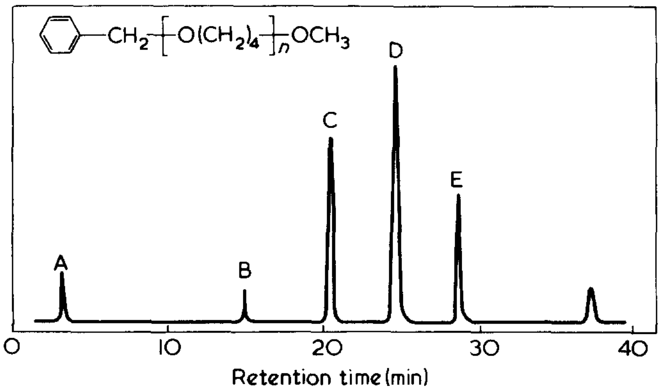
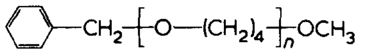


Figure 1 G.l.c. trace of the products obtained from the reaction at room temperature of THF, benzyl bromide and AgClO$_4$, terminated with methanol: A, n = 0; B, n = 1; C, n = 2; D, n = 3; E, n = 4

A similar experiment was carried out using benzyl bromide as a model for a xylylene bromide terminated polystyrene (PSXBr), and the g.l.c. trace of the products obtained at room temperature is shown in *Figure 1*. Again, the products were individually isolated and identified by ^{1}H n.m.r. spectroscopy as being oligomers of structure I, where n = 0, 1, 2, 3 and 4. The compound



(I)

giving rise to the peak at highest retention time was too involatile to be separated by preparative g.l.c., but is probably structure I with n = 5. This remarkably clean trace indicates that initiation by addition takes place exclusively. No elimination was observed in circumstances in which this reaction was seen to account for 63% of the (1-bromoethyl) benzene initiator[1].

Thus there seem to be good grounds for supposing that xylylene bromide-terminated polymers will be significantly more efficient at forming block copolymers than were their directly brominated counterparts.

Synthesis of m*-xylylene bromide-terminated polystyrene (PSmXBr)*

For the reasons outlined in part 1, it was decided that the investigation should mainly involve the material resulting from the preparation and subsequent termination of 2000 molecular weight monofunctional 'living' polystyrene.

Of the three xylylene dibromide isomers which could be used in the synthesis, the *para* isomer appeared to be the most suitable as the resulting PSpXBr should possess the most accessible bromine. However, *p*-xylylene dibromide has only a low solubility in THF and in benzene so that the amount of reagent required to provide a molar excess of at least tenfold was such that inordinately large volumes of solvent would have had to have been introduced to the 'living' system. This would have created a situation in which inadvertent impurities from the solvent could have terminated a significant proportion of the 'living' ends, and so in these circumstances it was decided to use the much more soluble *meta* isomer for the bulk of the terminations.

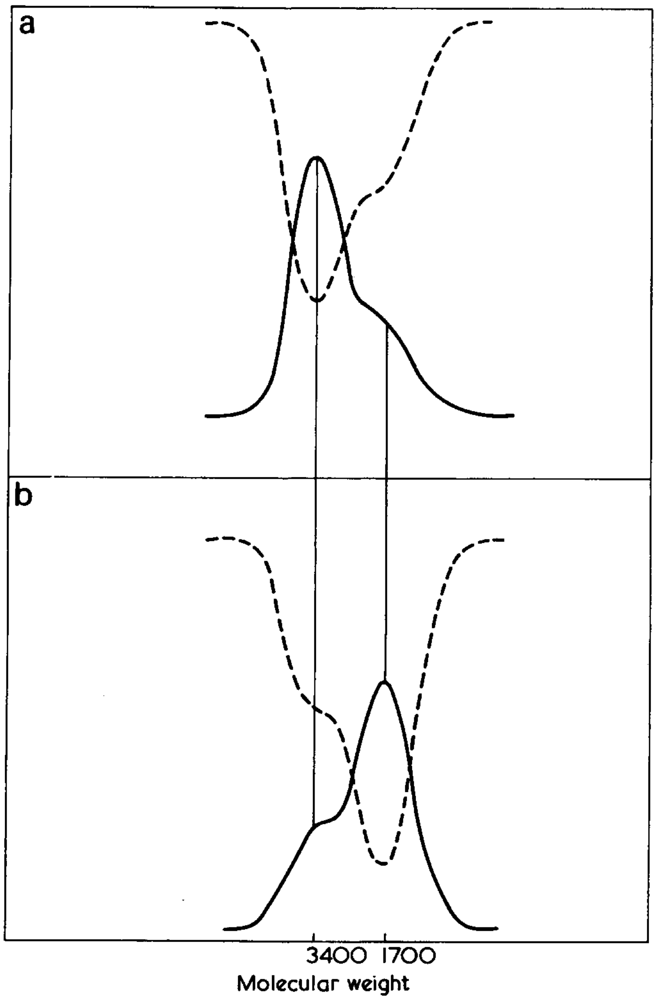
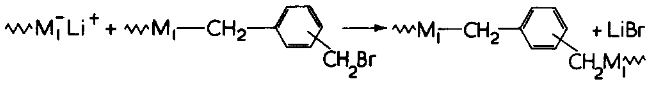


Figure 2 G.p.c. traces showing the degrees of coupling in the preparation of PSmXBr from (a) polystyryl lithium and (b) polystyryl magnesium bromide. — — —, U.v. 32X; ——, r.i. 4X

As in the experiments involving direct bromination the reaction of 'living' polymer with excess reagent resulted in significant amounts of coupling taking place (equation 4):



(4)

Again, this unwanted reaction was minimized by converting the polymer anion into its Grignard analogue[4]. *Figure 2* shows g.p.c. traces which contrast the product obtained by direct reaction with 'living' polymer and that obtained after reaction via the Grignard intermediate. By this means the percentage PSmXBr formed has been increased from 26 to 77% and, undoubtedly, the yield could be pushed still higher if the reaction conditions were studied more stringently. Nevertheless, this material may be conveniently used to examine the initiating efficiency of the *m*-xylylene end-group.

Transformation reaction

Again, THF was the monomer principally used to study the transformation reaction. It was found, however, that the rate of reaction of PSmXBr with silver perchlorate in THF was very slow at –78°C. There was no instantaneous precipitation of silver bromide and, after 40 min at that temperature, only a faint cloudiness was apparent. This is in contrast to the behaviour of PSBr which reacts rapidly with silver perchlorate at –78°C, and it may be due to the lower reactivity of a primary *versus* a secondary benzyl halide.

At room temperature, however, the precipitation proceeded quickly and the mixture gradually became viscous as the polymerization of THF ensued. A g.p.c. trace of the products isolated after initiation and polymerization at room temperature for two days is shown in *Figure 3*, where it is compared with that of the initiating material. It can be seen that a new peak has appeared at high molecular weight characterized by a very strong signal from the r.i. detector and a less intense but still very definite signal from the u.v. detector. As homo poly(tetramethylene oxide) is transparent at the wavelength (254 nm) of the u.v. detector, this is a positive indication that block copolymer has been formed. The dispersity of the copolymer peak is, however, quite broad and this will be discussed[4] in part 3[6].

Of more immediate interest, however, is the observation that a much larger proportion of PSmXBr has been converted to block copolymer at room temperature than when PSBr was used (80% *versus* 20%). This result strongly supports the argument that PSmXBr cannot undergo a facile β-hydrogen elimination. Nevertheless *Figure 3* does show a

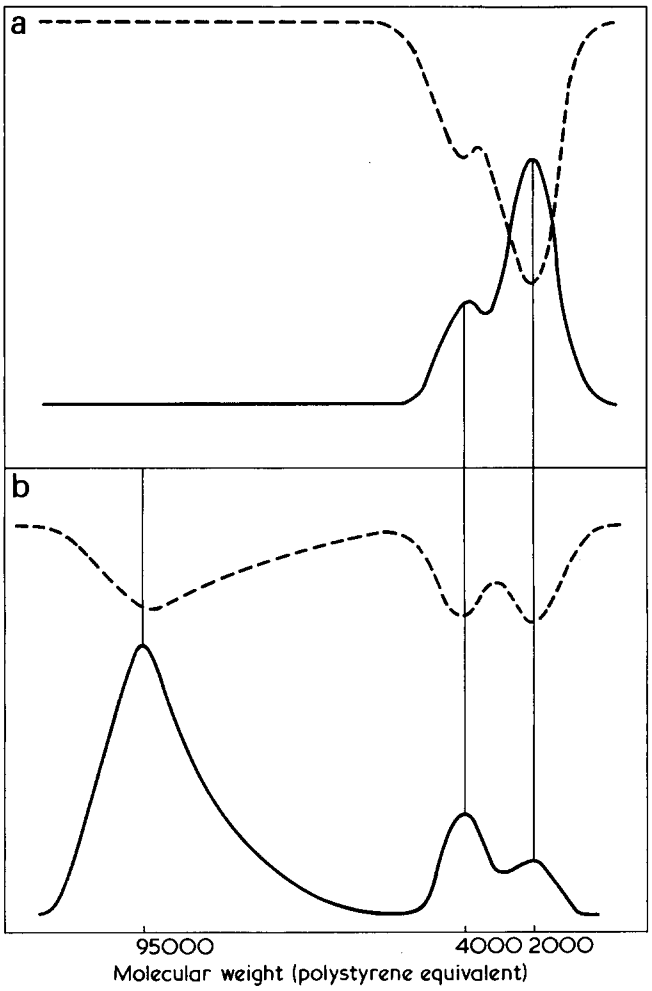


Figure 3 G.p.c. traces of (a) PSmXBr and (b) the products from the polymerization of THF by this material and $AgClO_4$ at room temperature for two days. — — —, U.v. 32X; ——, r.i. 4X

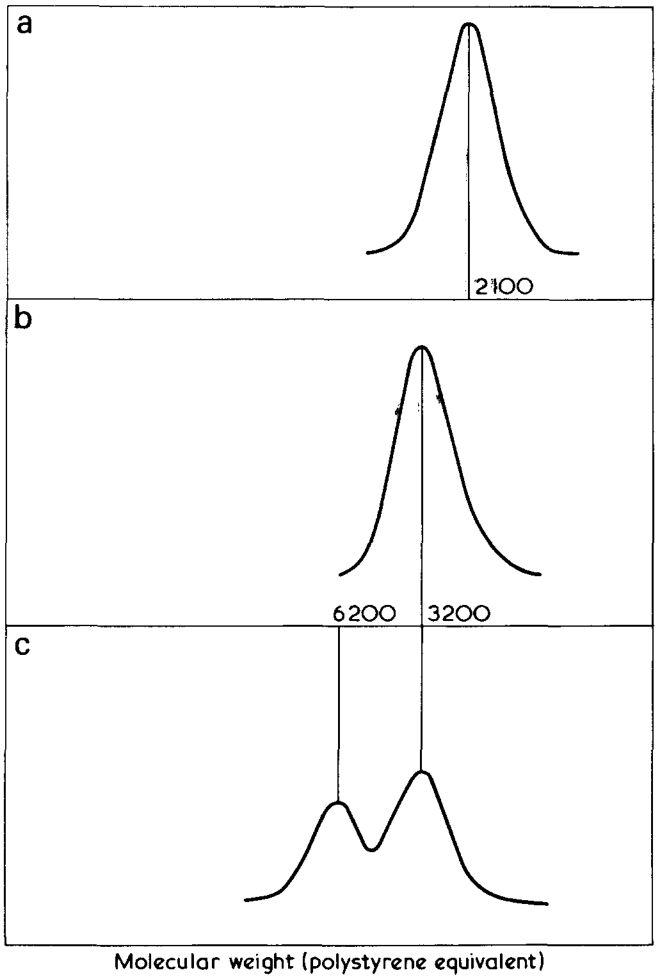
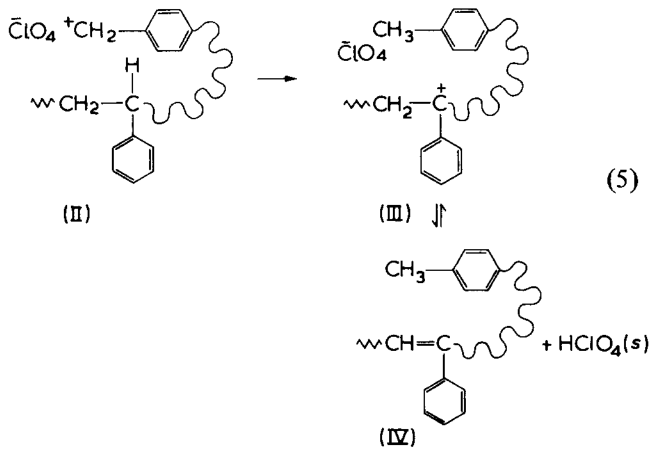


Figure 4 G.p.c. traces showing the three stages in the preparation of PSBmXBr: (a) methanol-terminated polystyrene; (b) methanol-terminated poly(styrene-*b*-butadiene); and (c) PSBmXBr. ——, r.i.

small but very definite peak remaining at 2000 molecular weight. This peak could be explained by the presence of inert polymer produced during the preparation stage through the reaction of 'living' polystyrene with adventitious impurities. More significantly, the increased u.v. absorbance of this residual material suggests that some other species may be present.

A mechanism which would account for these observations is that depicted in equation (5):



(5)

The terminal primary carbenium ion (II) could abstract a hydride ion intermolecularly or, more probably, intramolecularly from the polystyrene backbone to generate a tertiary carbenium ion (III) which may then eliminate a β hydrogen to form an in-chain styryl unit (IV). Thus the increased conjugation generated in this way would explain the presence of residual material at 2000 molecular weight with enhanced u.v. absorbance. This scheme may also be developed to account for the higher dispersity of block copolymers observed generally in these systems when compared with those obtained with PSBr. This aspect will be considered in detail in the later section on the synthesis of 'living' block copolymer.

Synthesis of m-*xylylene bromide-terminated AB poly (styrene-*b*-butadiene) (PSBmXBr)*

The technique of terminating 'living' polystyrene with xylylene dibromides to produce a polymeric intermediate for the anion-to-cation transformation can be extended to 'living' polydienes. Butadiene was selected as a suitable monomer, but homopolymers derived from butadiene or from isoprene suffer two major disadvantages so far as the approach used in this present work is concerned: first, they do not absorb appreciably at the wavelength (254 nm) of the g.p.c. u.v. detector, so that the technique of contrasting the responses of the two detectors cannot be used to estimate any block copolymer formation with THF as was done with polystyrene initiator; secondly, low molecular weight polydienes are tacky liquids difficult to isolate free from contaminants.

Both of these problems were overcome by using polystyryl lithium of 2000 molecular weight in place of butyl lithium to initiate the polymerization of butadiene. In this way an AB poly(styrene-*b*-butadiene) block copolymer was prepared which permitted the study of a suitable functionally terminated polybutadiene in the transformation reaction yet also possessed the advantage of u.v. absorption and, by careful choice of the ratio of styrene to butadiene, allowed precipitation from methanol as an easily handled powder.

G.p.c. traces showing the three stages in the preparation of PSBmXBr are shown in *Figure 4*. The narrow molecular weight distributions shown by the polystyrene precursor and by the protonated block copolymer indicated that butadiene had been efficiently polymerized on to the polystyrene ends. In this experiment the 'living' block copolymer was reacted directly with ten-fold excess *m*-xylylene dibromide and, perhaps surprisingly, 57% PSBmXBr was produced (c.f. 26% PSmXBr under similar conditions). This increased yield could be explained by a lower reactivity of butadienyl lithium toward the dibromide than polystyryl lithium. Although the yield could almost certainly have been increased further by reacting via the Grignard intermediate, it was considered high enough to allow examination of the efficiency of this material in the transformation reaction.

Transformation reaction

As with PSmXBr, reaction of PSBmXBr with silver perchlorate was very slow at –78°C. However, when the reaction was carried out at room temperature, a precipitate of silver bromide quickly formed and the viscosity of the mixture increased as the THF polymerized.

Figure 5 shows the g.p.c. traces of the starting material and the products formed after 24 h bulk polymerization of THF at room temperature. Again a new rather broad peak has appeared at high molecular weight which is signalled principally by the r.i. detector, although the weaker response from the u.v. detector shows that block copolymer formation has taken place. It was estimated from the traces that

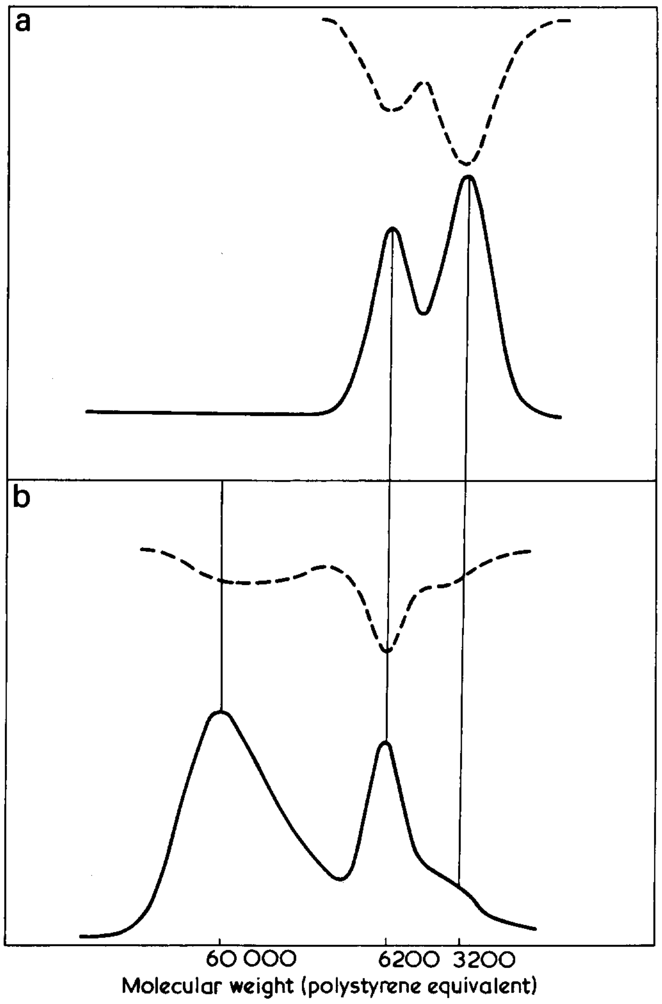
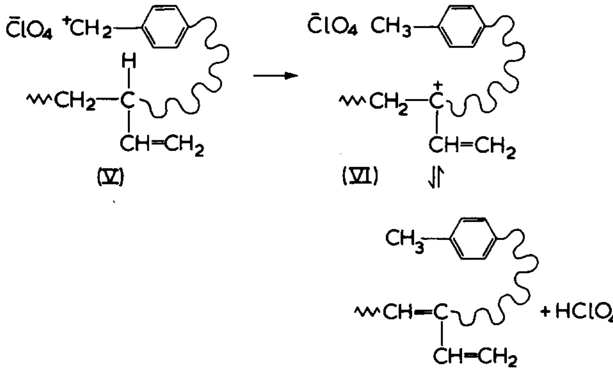


Figure 5 G.p.c. traces of (a) PSBmXBr and (b) the products from the polymerization of THF by this material and $AgClO_4$ at room temperature for 24 h. – – –, U.v. 32X; ——, r.i. 4X

about 80% of the PSBmXBr chains had been converted to block copolymer (c.f. 78% for PSmXBr under identical conditions) so that again some side reaction seems to prevent about 20% of the active ends from initiating additively. The reaction analogous to equation (5) for PSBmXBr is shown in equation (6) for the 1,2-butadienyl moiety:



(6)

and a similar scheme could be also drawn for a 1,4-structured unit. In this instance the terminal primary benzyl carbenium ion (V) abstracts a hydride ion from the polydiene backbone to generate a tertiary allylic carbenium ion (VI) which may then eliminate perchloric acid to form an in-chain butadienyl unit. Again, the effect of this mechanism on the molecular weight broadening observed will be discussed in the next section.

Whatever the slight differences in behaviour between PSBmXBr and PSmXBr, however, the reactivity and mode of polymerization of these species are very similar, and appear to be controlled principally by the *m*-xylylene units rather than by the nature of the polymers to which they are attached.

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

Part 1 describes[2] how a method devised by Croucher and Wetton[5] to produce 'living' polyTHF was adapted to produce living AB poly(styrene-*b*-THF) from PSBr. This involved initiating in bulk THF at –10°C using silver hexafluorophosphate. Although only about 50% efficiency was achieved in block copolymer formation, the dispersity of 1.04 obtained and the linear relationship observed between molecular weight and time at low conversions established the 'living' nature of the system and the absence of appreciable chain transfer.

It was therefore decided to repeat this experiment using PSmXBr to see whether the block copolymer yield could be increased using this material. After initiation at –10°C samples were removed at hourly intervals, and the polymer extracted for analysis by g.p.c. and ^1H n.m.r. The g.p.c. trace obtained after 5 h polymerization is shown in *Figure 6*, from which it was calculated that the efficiency of block copolymer formation had been raised to about 80%. A more detailed analysis of all the traces is given[6] in part 3, where it is shown that the peaks at high molecular weight consist entirely of block copolymer and possess a dispersity of about 1.15.

Although this dispersity is low, it is significantly greater than that observed with PSBr and, as a slight broadening of the distribution appears to be a general feature of block copolymers prepared from xylylene-terminated materials, it is instructive to consider the possible causes of this effect. First, chain transfer cannot be invoked to explain this behaviour as a linear relationship with time was found with both molecular weight and conversion (*Figure 7*), and in any case transfer is equally likely with propagating block copolymers initiated by PSBr. The difference in behaviour could well be related to the back-biting mechanism postulated at the initiation stage.

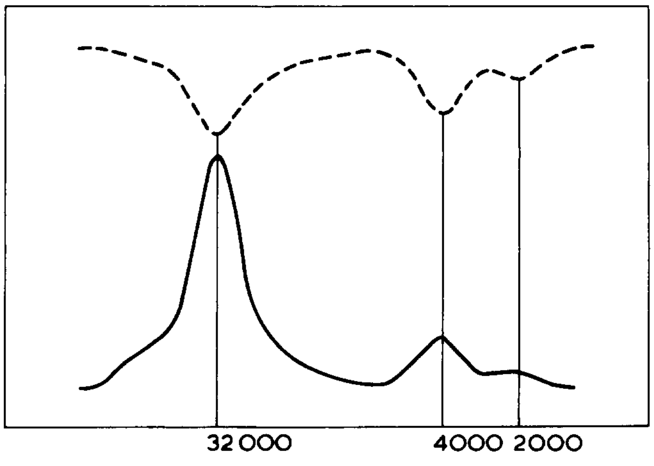


Figure 6 G.p.c. trace showing the products from the polymerization of THF by PSmXBr and $AgPF_6$ at –10°C for 5 h. – – –, U.v. 32X; ——, r.i. 4X

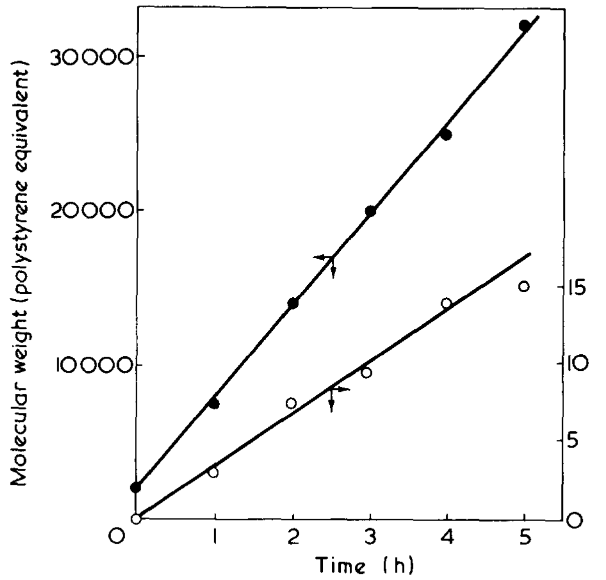


Figure 7 Plots of molecular weight of block copolymer (●) and percentage conversion (○) as functions of reaction time

Equations (5) and (6) have been invoked to explain the small fraction of initiating polymer which does not participate in the block polymerization process, and these reactions require the transient formation of the carbenium species III and VI in which the charge resides on a carbon atom along the polymer chain. It is reasonable to suppose that these species are also capable of initiating THF polymerization and, to a degree dependent on their rates of deprotonation, must therefore contribute to the production of copolymer. With these initiators, however, the products which result will be graft copolymers and, for a given degree of polymerization of the THF component, they will possess a smaller radius of gyration than their block copolymer analogues. G.p.c. traces of products resulting from such systems should therefore exhibit low molecular weight tails even under conditions which may be described as 'living' and in which chain transfer reactions are absent.

The idea that dispersity figures derived from g.p.c. traces may not reflect the molecular weight distribution of the copolymer material but rather its graft copolymer composition is an interesting one, and it is tempting to ascribe this explanation to the tailing observed. Rough calculations based on monodisperse models with maximum permissible differences in radii of gyration show, however, that this effect is not sufficient to account for the broadening observed. It is necessary to assume further that propagation from these species is slower, at least in the initial stages, than that obtaining when growth is occurring at the ends of the polymer. Although steric crowding may be invoked to support this hypothesis, further evidence is certainly needed before it can be accepted, but it is difficult, however, to visualize any other mechanism which will explain these observations. Finally, it should be stressed that although broadening does occur with xylylene-terminated materials, the copolymer product molecular weight distribution is still very sharp when compared to polymers prepared by other routes.

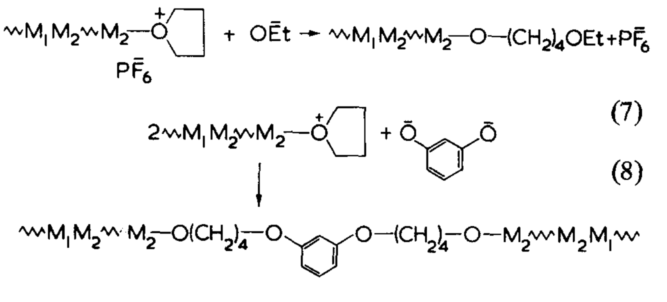
Finally, polystyrenes terminated with *m*-xylylene bromide ligands (PSmXBr) and with *p*-xylylene bromide ligands (PSpXBr) were prepared from a common source of 'living' polymer of 2000 molecular weight in order to compare their initiating efficiencies. Initiation was carried out at −10°C with $AgPF_6$ and polymerization continued at that temperature for 5 h. Analysis of the g.p.c. traces showed that the efficiency of PSmXBr initiation was 81% and that of PSpXBr was 77%. These values assume that there is no protonated material present at 2000 molecular weight caused by inadvertent termination of the 'living' polymer and therefore represent the lower limit for additive initiation. The figures quoted are within the accuracy of the analysis employed and so it may be presumed that products obtained with either isomer are equally effective in inducing block copolymer formation.

The absence of chain transfer under these experimental conditions opens up the possibility of using linking agents to prepare ABA block copolymers in which the central unit is polyTHF.

Linking reactions to form ABA poly(styrene-b-THF)

There are two prerequisites for a linking reaction to take place efficiently. First, all the polymer chains must be active and, secondly, the reaction between the coupling agent and the oxonium ions must be quantitative. The former criterion appears to be met in the system described above, and the latter could well be met by using phenol derivatives analogous to those described by Saegusa and Matsumoto[7–8]. Employing sodium phenoxide as an efficient terminating agent, they used the optical density of the terminal phenoxide chromophore to give an accurate measure of the active centre concentration of the original cationic polymer system. In this case, excess phenoxide was used to ensure that the reaction was driven to completion, but it did suggest that difunctional phenols might act as effective linking agents if they were added slowly as the disodium salts to the 'living' THF block copolymer solutions.

PSmXBr of 1000 molecular weight, possessing 77% brominated chains, was initiated in THF at −10°C with $AgPF_6$ and allowed to polymerize for four hours before being divided into two portions. One was terminated with excess alcoholic potassium hydroxide solution whilst the other was slowly titrated with a THF solution of the disodium salt of resorcinol. The reactions expected to take place in these two instances are illustrated in equations (7) and (8):



G.p.c. traces of the initiator and the products of these two reactions are shown in *Figure 8*. The alcohol-terminated product shows a peak at 18 000 molecular weight (polystyrene equivalent) signalled by both detectors. The linked material shows peaks at 38 000 and 21 000 indicating that significant coupling has occurred, estimated from the r.i. trace to be about 70%. The small deviations in the molecular weight at the peaks in the coupling reaction are due to the degree of overlap of the coupled and uncoupled materials.

The coupling reaction is under continued study to increase its efficiency further. It is hoped that the use of crown compounds will increase the nucleophilicity of the

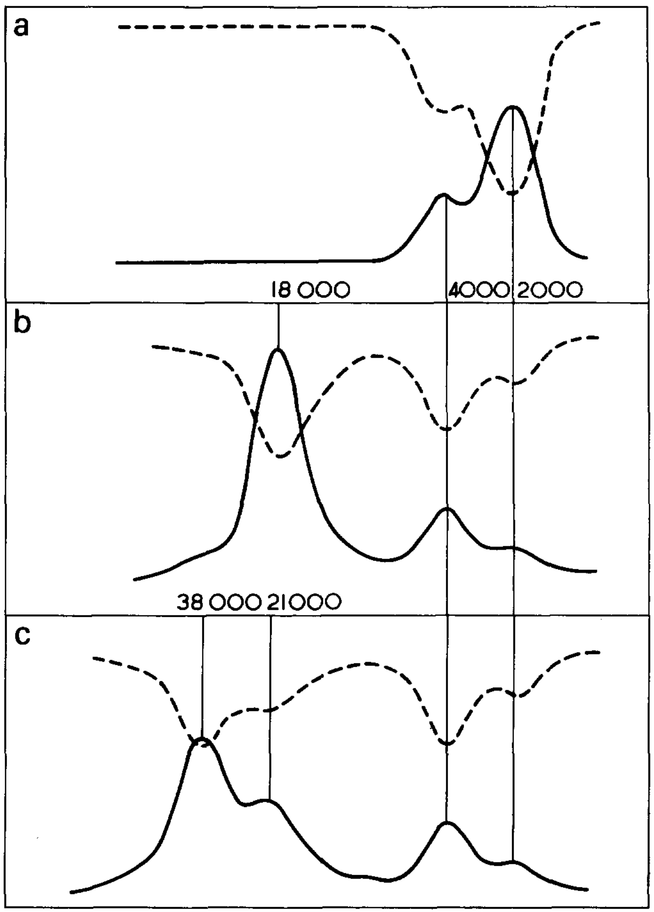


Figure 8 G.p.c. traces showing the product (c) from coupling 'living' poly(styrene-*b*-THF) (b) prepared from PSmXBr. (a) ––––, U.v. 32X; ——, r.i. 4X

phenate derivative to a point where quantitative coupling will ensue[9].

CONCLUSIONS

The following conclusions may be drawn from the experiments reported in this communication:

(a) A high, although not quantitative, conversion of 'living' polystyrene into xylylene bromide-terminated material (PSXBr) has been achieved by its reaction to form a polymeric Grignard compound prior to addition to excess of the dihalide. This process is equally applicable to polydienes.

(b) PSmXBr and PSpXBr were shown to initiate block copolymer formation with about the same efficiency, and both were very much more efficient than PSBr under the same conditions. With neither of these polymers, however, was the initiation quantitative.

(c) The side reaction at the initiation stage with PSXBr was suspected to be intra-molecular hydride transfer which could lead to graft copolymer formation as well as β-elimination.

(d) Xylylene bromide-terminated polybutadienes also initiate THF polymerization with an efficiency similar to that obtained with the polystyrene derivative.

(e) Conditions have been developed in which 'living' block copolymers have been prepared, and attempts to carry out linking reactions using resorcinol have resulted in about 70% formation of ABA block copolymer.

Clearly, further work is necessary to improve the initiation process, and to make the linking process more efficient. Work has started on developing this method to prepare block copolymers with monomers other than THF. Similarly, the use of small molecule mono- and dibromides as convenient cationic initiators for preparing homopolymers and block copolymers is also being explored. The findings in these areas will be reported in later communications.

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