# Block copolymer synthesis:
# 2. Reaction of living poly(α-methylstyrene) with living polytetrahydrofuran

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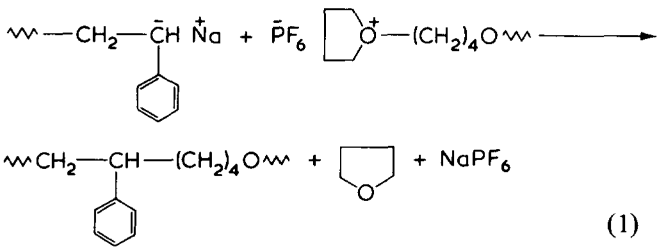
The reaction between anionic living poly(α-methylstyrene) and cationic living polyTHF has been examined using g.p.c. techniques. The efficiency of the coupling reaction was shown to be only about 20%, and this efficiency was relatively insensitive to the temperature of the reaction. The competing reaction was identified as one of β-proton transfer resulting in a hydrogen-terminated poly(α-methylstyrene) chain and a polyTHF molecule possessing terminal unsaturation. Transformation of the living poly(α-methylstyrene) into a polymeric Grignard prior to reaction seemed to have no significant effect on the efficiency of the linking process.

## INTRODUCTION

An examination was recently published of the reaction of living anionic polystyrene with cationically generated living polytetrahydrofuran (polyTHF) in which it was found that the reaction was quantitatively additive and that block copolymer was the exclusive product[1] (equation 1).



This result quantified the observations of previous workers[2], and g.p.c. techniques were used to demonstrate that AB, ABA and $(AB)_n$ block copolymers could be cleanly prepared with equal facility by appropriate permutation of the functionality of these two reagents.

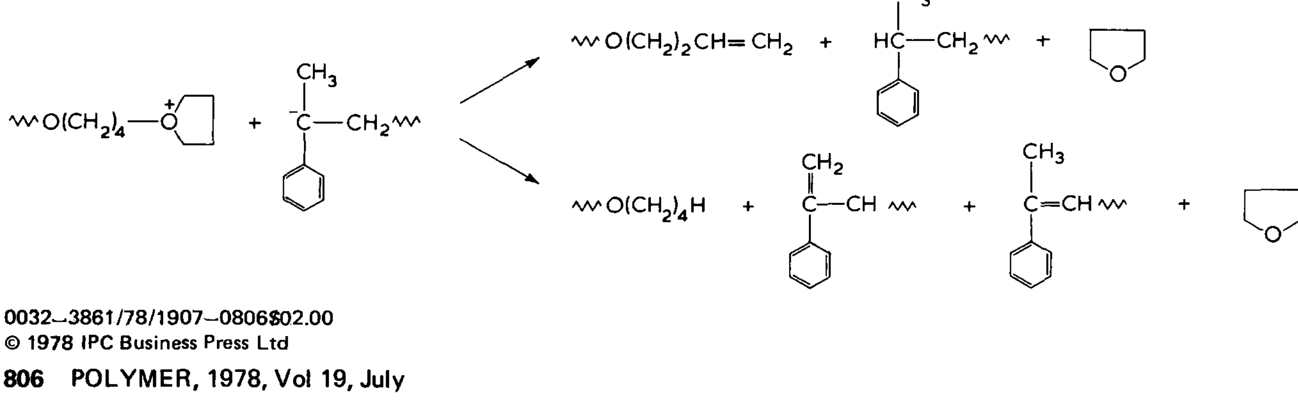
Preliminary results, recorded in that communication, indicated, however, that the equivalent reaction between living anionic poly(α-methylstyrene) and living cationic polyTHF was not exclusively additive, and that significant quantities of the component homopolymers remained in the reaction mix. It was suspected that the interfering side reaction was either that of proton transfer (equation 2) or that of hydride transfer (equation 3), with the former reaction being favoured on energetic grounds.

This paper details the experiments carried out on this system to identify the nature of the metathetical reaction, and to quantify the efficiency of the linking process. As in the previous communication, g.p.c. was the tool principally employed in these investigations.

## EXPERIMENTAL

### *Materials*

α-Methylstyrene was dried over calcium hydride and distilled under reduced pressure before use. Tetrahydrofuran (THF), stablized 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



(2)

(3)

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and used as a 2 M solution in hexane, and benzyl bromide (BDH) was distilled and stored over molecular sieve. Silver hexafluorophosphate (Pfaltz and Bauer) and silver hexafluoroantimonate (Ventron Alfa Products) were supplied as free flowing powders which were used without further purification.

### *Polymer synthesis*

*Poly(α-methylstyrene).* Monofunctional living poly(α-methylstyrene) of low molecular weight was prepared under nitrogen, as in the following example. THF (250 ml) was added to a three-necked round bottom flask fitted with a rubber septum and a stirrer, and a slow stream of nitrogen was bubbled through. α-Methylstyrene (30 ml, 0.23 mol) was introduced by syringe and the solution was cooled to −78°C before injection of butyllithium (2.5 ml, 0.005 mol). An immediate onset of the characteristic deep red colouration ensued and the reactants were held at −78°C for 1 h before a sample was extracted. This was terminated and precipitated in methanol, filtered and dried for examination by g.p.c. of its molecular weight and its distribution. The remaining living polymer solution was transferred by nitrogen into a burette preparative to titrating into the living polyTHF solutions.

In circumstances where prior conversion of the living polymer into the diGrignard was required the solution was reacted with a solution of magnesium bromide in THF prepared in the manner described by Burgess and Richards[3].

*α-Methylstyrene tetramer.* The tetramer was prepared as a THF solution of the disodium salt as follows. α-Methylstyrene(5.9 g, 0.05 mol) was introduced into THF (150 ml) in a three-necked flask though which nitrogen was bubbling. Excess sodium metal (1.2 g, 0.05 mol) was washed with petroleum ether and pressed into the solution as 2 mm diameter wire, the flask resealed and stirred at 0°C during the reaction period of 2 h. The intense red colour characteristic of the anion rapidly developed on the metal and diffused into the solution. An aliquot was withdrawn by syringe, protonated with methanol and submitted to g.l.c. and g.p.c. analysis, and shown by comparison with an authentic tetramer sample to be the tetramer with only a trace of contaminating dimer.

The living tetramer solution was then transferred into a burette and cooled to the temperature required for the reaction with living polyTHF. Alternatively it was transformed into the diGrignard adduct in the manner described previously[3].

*PolyTHF.* THF solutions of this living polymer were prepared at −10°C using benzyl bromide and silver perfluorophosphate or silver perfluoroantimonate in the manner described previously[1]. Under these conditions it has been shown that no appreciable chain transfer reactions occur in the time scale of the experiments[4].

*Titration procedure.* Details of this technique have been outlined previously[1]. The living anion solution was always used as the titrant and the end-point was marked by the onset of a very faint permanent red colouration to the solution. The titration values observed were invariably within ±3% of those predicted by theory.

### *Gel permeation chromatography (g.p.c.)*

G.p.c. was carried out on a Waters Associates model ALC/GPC 301 chromatograph fitted with a differential refractometer (thermostatically controlled at 25°C) and ultra-violet (254 nm) detectors. Two styragel columns with porosities $10^4$ and $10^3$ Å were deemed sufficient to monitor the medium and low molecular weight polymeric products produced. Elutions were carried out at ambient temperature with THF as solvent and with a flow rate of 1 $cm^3$/min. 2 ml aliquots of 0.1% w/v THF solutions of product were injected. The retention times were compared with those of a series of polystyrene standards to obtain an apparent polystyrene molecular weight.

### *$^1H$ n.m.r. and gas liquid chromatography*

$^1H$ n.m.r. spectra were recorded at 100 MHz on a Joel PS100 spectrometer. $CDCl_3$ solutions were used with tetramethylsilane as internal standard. G.l.c. analysis was conducted using a Pye series 105 instrument with an Apiezon K column. The temperature programme for the tetramer analysis has been described previously[5].

## RESULTS AND DISCUSSIONS

Monofunctional living anionic poly(α-methylstyrene) may be prepared by initiating the monomer with butyllithium, but the temperature at which the polymerization is carried out is important. At 0°C the monomer concentration in equilibrium with polymeric living ends is 0.8 M (refs 6 and 7) so that quantitative polymerization is not possible; polymerization was therefore carried out at −78°C where the equilibrium monomer concentration is $<$0.005 M (ref 6) and the living polymer solution was reacted at that temperature to avoid problems due to depropagation.

The results of typical experiments involving monofunctional living poly(α-methylstyrene) and monofunctional living polyTHF are shown as g.p.c. traces in *Figures 1* and *2*. *Figure 1* compares the g.p.c. traces of the two methanol-terminated reagents with that of the product of their direct mutual reaction. *Figure 1a* indicates the strong signals obtained from the ultra-violet (u.v.) and the differential refractometer (d.r.) detectors; the trace is sharp indicating a narrow dispersity material centred at about 5500 molecular weight calibrated with polystyrene. PolyTHF (*Figure 1b*) is also reasonably sharp at 10 000 molecular weight (polystyrene based) but is signalled principally by the d.r. detector – the very small peak shown on the u.v. trace is due to the benzyl moiety from the initiator. It is evident from the trace of the reaction products (*Figure 1c*) that the bulk of the poly(α-methylstyrene) remains as the homopolymer, although some block copolymer has been formed as evinced by the u.v. absorption peak appearing at 10 000 molecular weight. There is little evidence of any broadening of the curves toward higher molecular weight owing to the presence of 15 000 molecular weight block copolymer, but the logarithmic relationship of the baseline with molecular weight makes this a very insensitive diagnostic tool.

It may be roughly estimated from the shape of the u.v. trace of the product that about 20–30% of the reaction only is additive. The fact that the specific u.v. signal strength of the residual homopoly(α-methylstyrene) approximates to that of the protonated sample strongly indicates that the reaction causing homopolymer is β-proton transfer (equation 2) rather than hydride transfer (equation 3), since the terminal substituted styryl unit resulting from the latter reaction has been shown to have a very high extinction coefficient at 254 nm and consequently confers an enhanced absorption on the polymeric product[8].

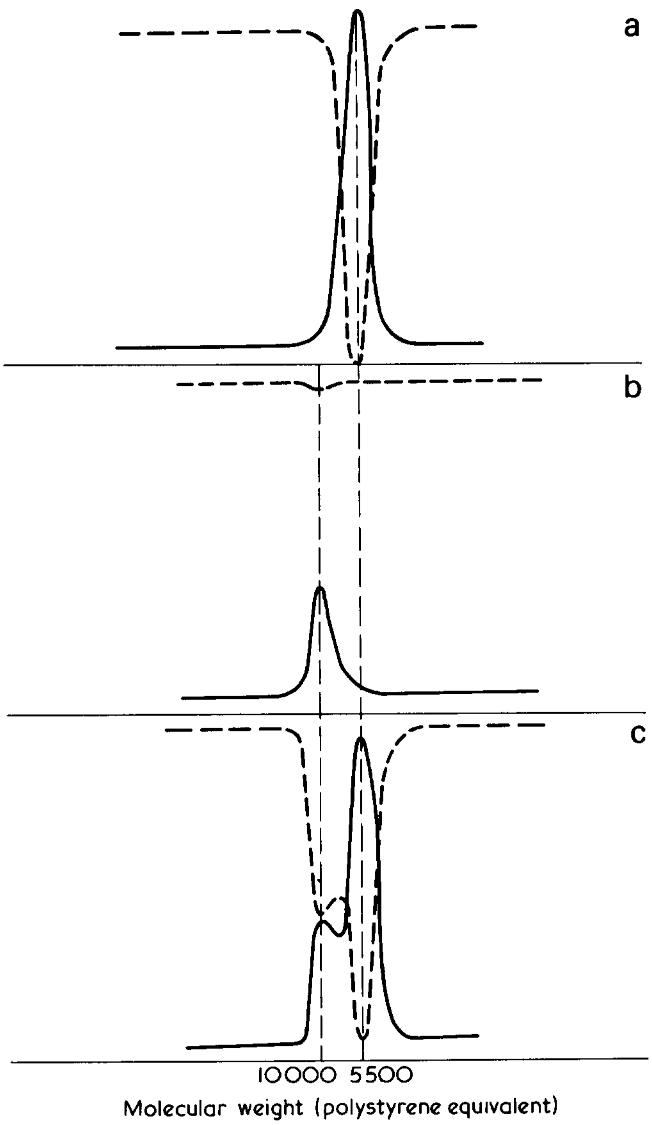


*Figure 1* G.p.c. traces of (a) methanol-terminated poly(α-methylstyrene); (b) methanol-terminated polyTHF and (c) the products of the reaction of living poly(α-methylstyrene) and living polyTHF at −78°C. (— — —), UV 32X; (——), DR8X

Similar results are obtained from the experiment recorded in *Figure 2*. In this instance the molecular weight of the polyTHF is less than that of the poly(α-methylstyrene) so that block copolymer formation is only shown by a drop in the u.v. to d.r. ratio at 12000 molecular weight for the product relative to the homopoly(α-methylstyrene). Residual polyTHF is shown as a low molecular weight shoulder by the d.r. detector and is unobserved by the u.v. detector. This product trace is also consistent with an estimate of the addition process being about 20–30% efficient.

The fourth trace (*Figure 2d*) shows the product resulting from the reaction of living polyTHF with poly(α-methylstyrene) after the latter had been converted into a polymeric Grignard. It was felt that a reduction in the basicity of this component polymer could influence the relative probabilities of the addition and metathetical reaction processes. Comparison of *Figures 3c* and *3d* indicates, however, that although the probability of addition has increased, the extent is small and the reaction is still predominantly one of elimination.

The inferences drawn about the efficiency of the linking process depend entirely on the assumption that all the chains possess active ends, and that there is no significant terminal deactivation by spurious impurities or by chain transfer. Living carbanions are particularly susceptible to the former hazard whilst living cations are prone to the latter. The living polyTHF generated for this study was prepared in a manner identical with that used in the study of its reaction with living polystyrene[1]. In this circumstance it was shown that the g.p.c. peak associated with the homopolymer was totally removed by the addition reaction so that a chain transfer process had not occurred. It is therefore very unlikely that the residual peak observed in the present investigation can be attributed to this process inadvertently occurring due to experimental faults and must be ascribed to the product of a metathetical reaction. Similarly, in the former work all the living polystyrene chains were seen to react additively and, as the living poly(α-methylstyrene) was prepared in a comparable if not identical way, it also seems unlikely that the residual poly(α-methylstyrene) observed was caused by termination by impurities. Since a termination reaction would

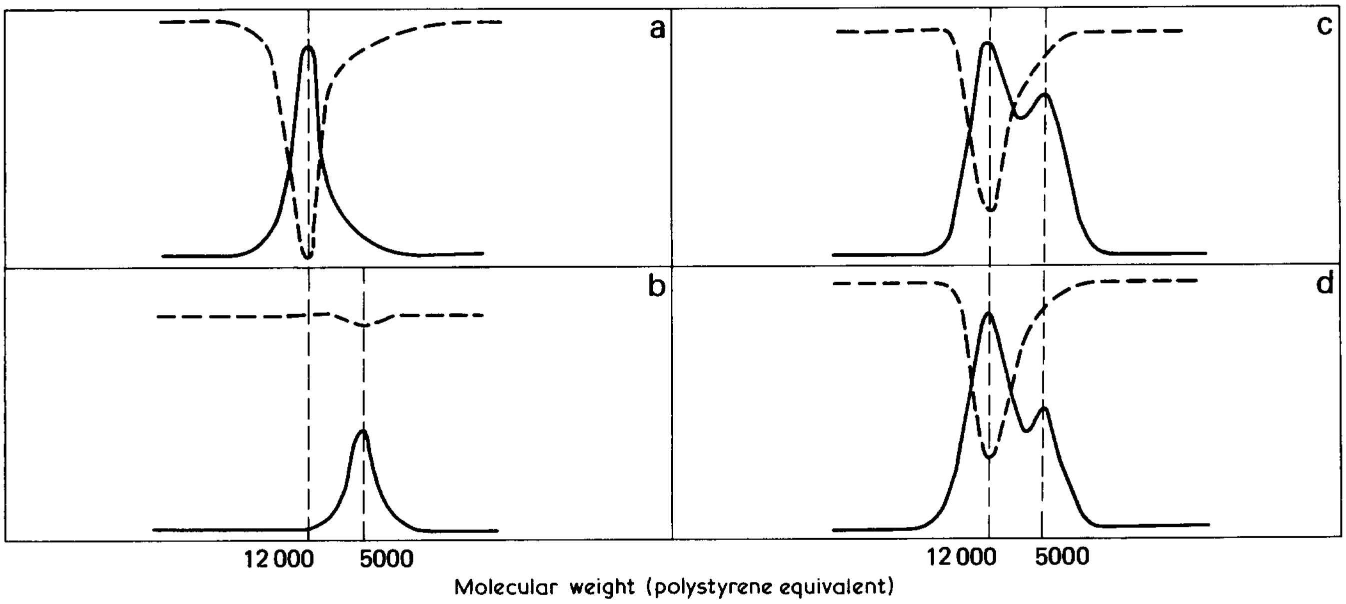


*Figure 2* G.p.c. traces of (a) methanol-terminated poly(α-methylstyrene); (b) methanol-terminated polyTHF; (c) the products of the reaction of living poly(α-methylstyrene) and living polyTHF at −78° and (d) the products of the reaction of poly(α-methylstyrene) Grignard and living polyTHF at −78°C. (— — —), UV 32X, (———), DR 8X

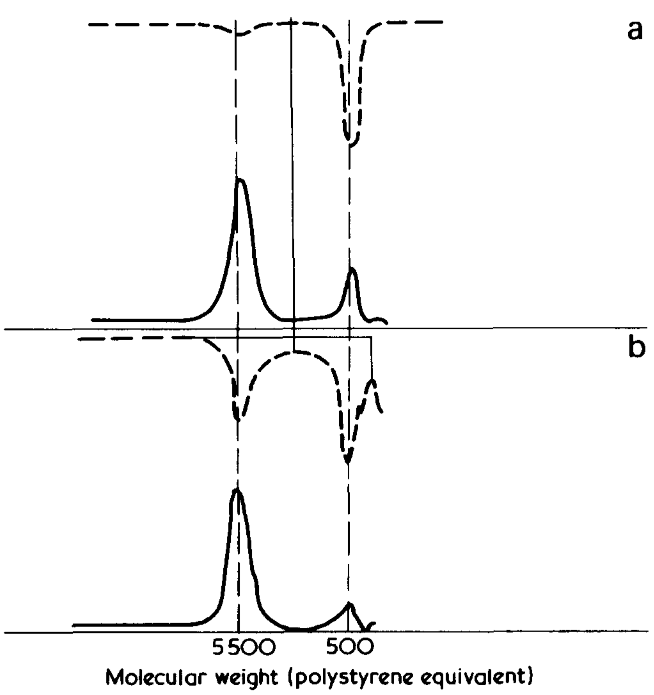
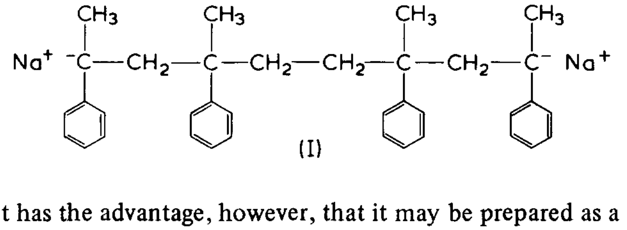


*Figure 3* G.p.c. traces of (a) methanol-terminated α-methylstyrene tetramer and methanol-terminated polyTHF (combined trace from two separate traces), and (b) the products of the reaction of living α-methylstyrene tetramer and living polyTHF at –50°C. (— — —) UV 32X; (———), DR8X

reduce the number of active ends, the latter conclusion is reinforced by the fact that the observed titration figures were within ±3% of those calculated from the amounts of catalysts used in the generation of the homopolymer. The interpretation of the results as indicating the presence of a pronounced metathetical reaction in the system must therefore be valid.

Although the study of the poly(α-methylstyrene)–polyTHF reaction could have been made more quantitative by choosing molecular weights for the component polymers sufficiently far apart for there to be no significant overlap in the g.p.c. traces of the products, this method suffers from the overall limitation that the reaction is carried out at low temperatures to avoid depropagation of the anionic reagent, and so it is difficult to obtain a temperature profile of the process. This problem can be avoided if the reaction between living polyTHF and the difunctional living tetramer of α-methylstyrene ($\alpha_4^{=}$) is examined.

The tetramer is of structure I and therefore should be a good model for the reaction with the polymer since the terminal units are linked in the head–tail manner characteristic of the polymer.



$$Na^+\,{}^-C(CH_3)(C_6H_5)-CH_2-C(CH_3)(C_6H_5)-CH_2-CH_2-C(CH_3)(C_6H_5)-CH_2-C^-(CH_3)(C_6H_5)\;Na^+$$

(I)

It has the advantage, however, that it may be prepared as a unique species by reacting the monomer in THF directly with sodium metal at a concentration of the former just below that characteristic of the monomer in equilibrium with its own living polymer at the chosen reaction temperature. Once prepared (at 0°C, say) it may then be used as a stable reagent over a range of temperatures without introducing difficulties due to its depropagation.

The fact that the tetramer possesses a sodium Gegen ion rather than the lithium associated with the living poly(α-methylstyrene) should not significantly affect its use as a model for this system, since replacement of the lithium Gegen ion by $MgBr^+$ showed only a second order effect on the product ratio (*Figure 2*). The tetramer is, however, difunctional and this does add a minor complication to the interpretation of the g.p.c. traces which can now be analysed in the following way. If the probability of one end of the tetramer species reacting metathetically is $p$, independent of the mode of reaction of the other end, then the probabilities of forming ABA copolymer, AB copolymer, homopolyTHF and tetramer are $(1\text{-}p)^2$, $2p(1\text{-}p)$, $p$ and $p^2$, respectively. It will be seen later (*Figure 3*) that this probability $p$ is most conveniently measured from the u.v. signals on the g p.c. trace. This allows a determination of the ratio between those tetramer units residing in the copolymer envelope (as AB and ABA copolymers) and those remaining as distinct tetrameric species, and thus yields $p^2$ directly.

Initially, however, the reaction with the tetramer was used to confirm that the metathetical reaction was one of proton rather than hydride transfer. The former reaction requires that the α-methylstyrene product should be the diprotonated adduct, $H\alpha_4H$, whereas the latter would yield a tetramer with double terminal unsaturation. The diprotonated material had been prepared on previous occasions[10,11] and so authentic samples were available for comparison purposes. The product of the reaction between the tetramer and low molecular weight polyTHF was therefore isolated and subjected to g.l.c. analysis and separation for $^1H$ n.m.r. identification. The solitary volatile peak was shown to have a retention time identical with that of the authentic sample, and its structure was confirmed as being $H\alpha_4H$ by $^1H$ n.m.r. spectroscopy. Thus the predominating reaction is one of β-hydrogen transfer.

Reactions were therefore carried out between the tetramer dianion and monofunctional living polyTHF over a temperature range of – 10° to –78°C. The g.p.c. traces of the methanol-terminated reactants and of the products of the reaction at one of the selected temperatures are shown in *Figure 3*. The probabilities of metathetical reaction, $p$, were calculated from the relative areas of the two u.v. peaks (*Figure 3b*), but since the trace did not return to the baseline between the peaks or at the low molecular weight end, verticals were dropped at the absorption minima as shown, and the areas thus confined were taken as representative of the relative proportions. Clearly this procedure introduces some inaccuracy into the absolute values of the probabilities derived from these measurements, but as similar traces were obtained for, and similar procedures were applied to the products of the reaction at other temperatures internal consistency was probably achieved.

Before considering the temperature profile of this reaction, it is relevant to confirm the simple reaction pictures inferred from equations (1) and (2). It is implied in these equations that the two competing reactions proceed *via* similar paths in which the order of reaction with respect to the components is the same in both cases. If this be so, then the value of $p$ should be independent of the relative concentrations of the reagents, and this was checked by deriving the values from samples where only 50% of the calculated amount of tetramer had been added to the living polyTHF, the remaining ends being terminated with methanol. Although the g.p.c. traces are not shown, the $p$ values obtained are listed in

*Table 1* Probability ($p$) of occurrence of a metathetical reaction between living poly(α-methylstyrene) and living poly THF as a function of temperature

| | $p$ | | |
|---|---|---|---|
| $T$(°C) | $\alpha_4^{=}$ (100% reaction) | $\alpha_4^{=}$ (50% reaction) | $\alpha_4(MgBr)_2$ (100% reaction) |
| –10 | 0.78 | 0.76 | 0.63 |
| –20 | 0.78 | 0.80 | 0.68 |
| –50 | 0.79 | 0.81 | – |
| –78 | 0.80 | 0.81 | 0.74 |

*Table 1*, where, within experimental error, they are seen to agree closely with those obtained from the stoichiometric reaction.

Similar experiments were carried out over the same temperature range with tetramer which had been transformed into the diGrignard derivative before the stoichiometric reaction with polyTHF was carried out. Again, the $p$ values were calculated and are recorded in *Table 1*. In this instance the values are significantly lower than those obtained from the direct reaction with the dianion, in confirmation of the comparative observations recorded in *Figures 2c* and *2d*, that the degree of linking with the polymeric Grignard reagents is higher.

The temperature coefficient for the relative reaction rates involving the Grignard derivative seems to be greater than that involving the direct reaction, although neither is large. The activation energy difference [$E$(addition)-$E$(methathetical) = $\Delta E$] may be evaluated by application of the readily derived equation (4), where $rA$ is the ratio of the pre-exponential factors of the two reactions.

$$\log\left(\frac{1}{p} - 1\right) = \log rA - \Delta E/2.303RT \qquad (4)$$

The inaccuracies inherent in the area measurements allow an assessment of $\Delta E$ only within wide limits, but figures of 0.5 ± 0.3 kcal/mol$^{-1}$ and 0.7 ± 0.3 kcal/mol$^{-1}$ were obtained for the reactions involving the tetramer dianion and diGrignard, respectively. These low values are to be expected from competitive reactions which individually have low activation energies. Perhaps the only safe conclusion to arrive at, based on these results, is that the addition reaction has a marginally higher activation energy than the metathetical reaction. This seems reasonable when it is realized that the former process requires replacement of a tightly coordinated THF molecule (equation 1) whereas the latter involves the elimination of a proton bound to the $\beta$ carbon atom by a bond weakened by the proximity of the carbenium ion (equation 2).

Lastly, the marked difference in behaviour between living polystyrene and living poly(α-methylstyrene) in their reactions with living polyTHF must be commented upon. It is unexpected that the introduction of a methyl group on to the terminal carbanion of the chain should reduce the efficiency of linking from 100 to about 20%. Although the presence of the methyl group increases the nucleophilicity of the carbanion, and the experiments with the Grignard derivatives indicate that a reduction in this property enhances the probability of addition, it seems unlikely that this degree of change in reactivity is sufficient to account for a drop in the linking efficiency of this magnitude. It is perhaps more likely that the increased steric hindrance resulting from the presence of the methyl group renders attack at the oxonium ion more difficult and thereby enhances the probability of reaction at the more accessible $\beta$ carbon atom. This postulate is, however, only partly supported by examination of molecular models.

Further work is continuing on the efficiencies of the linking processes between living polydienes and living polyTHF and will be reported in a later communication

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