Block copolymers prepared by an anion to free radical transformation process: 2. Homolytic scission of the C–Pb bond of lead trialkyl-terminated polymers both thermally and by transition metal salts

M. J. M. Abadie, F. Schué and T. Souel
Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques du Languedoc, 34060 *Montpellier Cédex, France*

and D. H. Richards
*Propellants, Explosives and Rocket Motor Establishment, Ministry of Defence, Waltham Abbey, Essex EN*9 1*BP, UK*
(*Received* 12 *November* 1980)

It is proposed that the main competing reaction to the thermally-induced homolytic scission of the polystyrene–lead triethyl bond in the adduct to form polystyryl radicals is that of β-hydrogen abstraction to yield inactive products. Methods are suggested for minimizing this process. The reaction of silver salts with polystyrene–lead triethyl in the presence of methyl methacrylate has been examined, and the prior use of cation complexing agents such as crown ethers shown to enhance the transformation into active polystyryl radicals and to increase the formation of block copolymer. Other transition metal salts have also been shown to be efficient in this transformation process.

INTRODUCTION

In order to synthesize block copolymers efficiently it is necessary that the polymerization mechanisms employed are effective toward each of the monomeric components of the chain. In practice, the monomers selected are those capable of being polymerized by a given mechanism (e.g. styrene and butadiene by an anionic process) but such a requirement can be restrictive. A more general approach is to transform the propagating end from that employed with the first monomer to that best suited to propagate the second monomer, and so on. This requires the development of a series of transformation reactions to interrelate the basic polymerization mechanisms, and we have been active in this area with varied success.

We have fully reported methods by which block copolymers may be efficiently prepared by an anion to cation transformation[1–4], and accounts have been briefly given of two methods by which polymeric anions may be transformed into free radicals[5–7], although no systematic effort was made in these processes to maximize the yield. This paper reports a more detailed study of some of the reaction variables in one of these anion to free radical techniques, and their effect on the efficiency of block copolymer formation.

The basic approach is to polymerize the first monomer (styrene butadiene, etc.) by an anionic living process and to react the resulting polymer with a trialkyl lead halide to yield the polymeric lead adduct (equation 1).

$$\sim\!\sim\! M^- Li^+ + R_3PbX \longrightarrow \sim\!\sim\! M\,PbR_3 + LiX \qquad (1)$$

This reaction has been shown to proceed virtually quantitatively. The material can be isolated, purified, redissolved in an appropriate solvent and a second monomer added before decomposing the polymer either by thermal or chemical means to yield polymeric radicals.

$$\sim\!\sim\! M\,PbR_3 \xrightarrow{\Delta} \sim\!\sim\! M\cdot + \cdot PbR_3 \qquad (2)$$

The former process, shown in equation (2), when applied to isoprene oligomers ($DP \sim 1.5$) has been shown to initiate the block copolymerization of styrene with an efficiency of 0.43 if both radical species in equation (2) initiate, or with an efficiency of 0.86 if the organolead radical disproportionates and the polyisoprenyl radical is the sole initiator[6].

The chemical process examined has involved reaction with silver salts, and involves the transient formation of a silver–polymer adduct which immediately decomposes to yield the polymer radical and silver metal (equation 3), the radical

$$\sim\!\sim\! M\,PbR_3 + AgX \longrightarrow R_3PbX + [\sim\!\sim\! MAg]$$
$$[\sim\!\sim\! MAg] \longrightarrow \sim\!\sim\! M\cdot + Ag\downarrow \qquad (3)$$

then copolymerizing the second monomer also present in the system[5]. This approach was shown to yield block copolymer but its efficiency was not quantified although it was apparent that it was subject to side reactions which left a significant quantity of the starting polymeric material as homopolymer.

0032–3861/81/081076–05$02.00

Both methods of using these polymer–lead salts as initiators have now been re-examined and the effect on the reaction efficiency of using crown ethers to complex the silver salts has been studied. The equivalent redox reactions of polymer–lead salts with the salts of other transition metals have also been evaluated, and the results of these examinations are reported in the present communication.

EXPERIMENTAL

Solvents

Tetrahydrofuran (THF) was first dried with potassium hydroxide and calcium chloride before distilling on to potassium. It was stored under vacuum over a 1:3 sodium–potassium alloy which yielded a blue solution. Samples were then removed by vacuum distillation.

Benzene and toluene were treated with concentrated sulphuric acid, then distilled on to potassium and finally stored under vacuum with added n-butyl lithium.

Complexing agents

The crown ethers were distilled under high vacuum prior to use. Cryptate [222] was recrystallized from n-hexane and dried under vacuum.

Salts

Triethyl lead chloride was crystallized from n-hexane/chloroform, and copper (I) trifluoromethane sulphonate was prepared from the copper (II) salt by a published method[8]. All other salts were used as received.

Polymerization

The purification, oligomerization and/or polymerization of the monomers have been previously published[5–7].

Thermal initiation

Experiments were conducted according to the following procedure: 1 g polystyrene–lead triethyl of molecular weight 2000 in solution in a mixture of 60 ml benzene and 10 ml methyl methacrylate (MMA) was decomposed under nitrogen at 80°C. Samples were removed at set time intervals and the polymeric product isolated by precipitation from 50/50 v/v methanol/water mixtures, dried and weighed.

Reactions with silver salts

Experiments were carried out in which uncomplexed silver salts (10^{-3} mol) in toluene were added to solutions of polystyrene–lead triethyl (0.5×10^{-3} mol, *MW* 2000) and MMA (10 ml) in toluene (100 ml) over an hour at room temperature. Other tests were conducted in which the two solutions were mixed rapidly at −78°C and brought slowly up to room temperature (silver precipitation occurs between −50 and −30°C).

In experiments involving complexation with crown ethers, silver perchlorate (10^{-3} mol) was introduced to equimolar 12C4, 15C5 or 18C6 in solution in a 50/50 v/v toluene/methanol mixture. This was then added to solutions of polystyrene–lead triethyl (0.5×10^{-3} mol, *MW* 2000) and MMA (10 ml) in toluene (100 ml) over an hour at room temperature. The solutions were stirred over 20 h and the polymeric product isolated by precipitation from methanol, dried and weighed. The same procedure was used in experiments with other transition metal salts.

Gel permeation chromatography (g.p.c.)

G.p.c. analyses were carried out on a Waters Associates ALC/GPC 301 equipped with a differential refractometer detector thermostatted at 25°C and a u.v. detector monitored at 254 nm. Four styragel columns (10^2 to 10^5 Å) were used.

RESULTS AND DISCUSSION

Thermal initiation

Experiments were initially carried out to determine whether the $\cdot PbR_3$ radical generated by thermal decomposition was an effective initiator of polymerization. Polystyrene–lead triethyl in benzene solution and in the presence of methyl methacrylate (MMA) was quantitatively thermally decomposed and the polymeric product carefully isolated, purified and redissolved in tetrahydrofuran (THF). A solution of $AgClO_4$ was then added, but no precipitate of silver was observed. This is a very strong indication that the $\cdot PbR_3$ species does not directly initiate polymerization since any polymer thus produced would possess an alkyl lead terminal group which should react with a silver salt in the manner shown in equation 3 to yield a silver metal precipitate. There still, however, remains the possibility of indirect initiation by this species if a decomposition step of the type shown in equation 4 were a stage in the disproportionation process normally represented by the overall equations 5 and 6.

$$\cdot PbR_3 \longrightarrow PbR_2 + R\cdot \qquad (4)$$

$$2\cdot PbR_3 \longrightarrow R_3Pb\,Pb\,R_3 \qquad (5)$$

$$2R_3Pb\,PbR_3 \longrightarrow 3\,PbR_4 + Pb \qquad (6)$$

In other thermal initiation experiments involving MMA as a second monomer the isolated dried products from samples taken at set intervals of time were weighed and the systematic increase observed indicated progressive polymerization of MMA until, after 10 h, about 50% conversion had been achieved. G.p.c. traces of the products (*Figure 1*), however, showed two distinct peaks, one at the retention time corresponding to starting material and the other at a molecular weight (polystyrene equivalent) of 230 000. The latter peak increased in relative size with MMA conversion and is almost certainly a block copolymer of this monomer with the polystyrene initiator because of the small but significant u.v. absorbance it exhibits, although this could include a small contribution from the terminal unsaturation resulting from disproportionation of the PMMA radicals.

What is of more concern is that calculations based on the observed copolymer molecular weight indicate only about 5–10% initiating efficiency, as is confirmed by the substantial residual peak at 2000 *MW* after 10 h decomposition time. This efficiency is substantially lower than the 86% efficiency found with the oligo isoprenyl lead trimethyl/styrene system,[6] and the difference is not easy to explain since the reagents and conditions were the same. It is possible that the inefficiency observed in the present system is due to the participation of some alternative reaction to produce stable products which

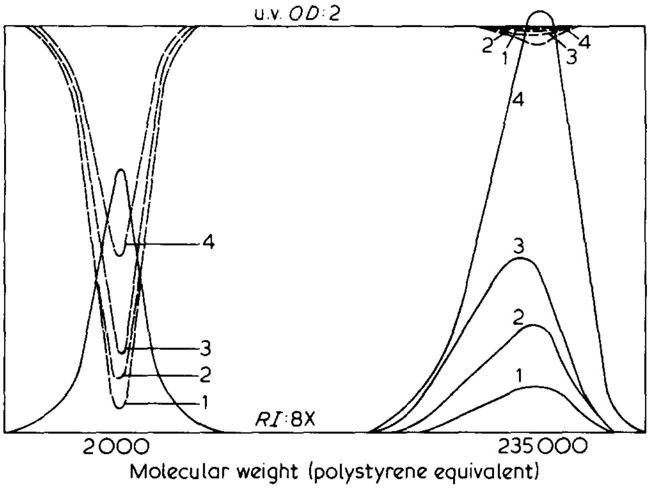
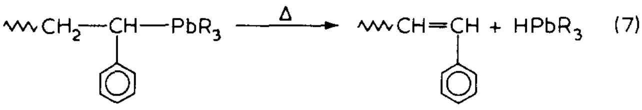


Figure 1 G.p.c. traces of poly(styrene-b-MMA) copolymers prepared by thermal initiation: (1) after 1 h reaction; (2) after 2 h; (3) after 3 h; (4) after 10 h

competes with that which induces polymerization, and it is profitable to speculate on what this might be.

Firstly, it cannot be the rapid termination of polystyrene radicals generated by homolytic scission prior to initiation of MMA since these react primarily by combination and there is no evidence of molecular weight doubling. Although PMMA radicals terminate by disproportionation and the enhanced u.v. absorption could theoretically therefore be caused by termination of polystyrene species possessing a single MMA unit as a terminal radical, this is extremely unlikely since one would expect on this basis a continuity of product up to the observed peak at 200000 *MW* and this is not observed. Indeed, the discontinuity in molecular weight between the residual polystyrene and the copolymer strongly suggests that the competing reaction causes direct deactivation of the reagent and is therefore different in kind from the initiating process.

A clue to the nature of this reaction is given by the observation that the u.v./*RI* ratio of the residual polystyrene is consistently about 65% greater than that of the starting material. Similar observations were made in studies on anion to cation transformations involving a polystyrene initiator[2-4] where it was ascribed to, and subsequently proved to be caused by the production of homopolystyrene with a terminal double bond by a β-proton elimination process (ε_{254} styrene $\gg \varepsilon_{254}$ ethylbenzene), and it seems likely that a similar inactive product could be generated in these thermal experiments by a β-hydrogen elimination reaction (equation 7). The corresponding reaction cannot occur with the polyisoprene adduct since the polyisoprene chain is predominantly 1,4 structured and


$$\sim\!\sim CH_2-CH(C_6H_5)-PbR_3 \xrightarrow{\Delta} \sim\!\sim CH=C(C_6H_5)H + HPbR_3 \quad (7)$$

consequently the bulk of the β carbons of the terminal group possess no hydrogen. Although alternative hydrogen elimination routes might be devised, they are not likely to be as facile as that proposed for the polystyrene adduct, and so the much greater initiating efficiency of the polyisoprene–lead adduct may be explained on this basis.

If this analysis is confirmed experimentally, then the β-hydrogen side reaction may be minimized by physical means through suitable manipulation of the reaction parameters, particularly temperature, to favour homolytic scission, or by chemical means through adding a few isoprene units on to living polystyrene before terminating with the lead halide to ensure that, although the physical characteristics of polystyrene would be maintained, the terminal unit would be isoprenyl–lead trialkyl, the more efficient radical initiator.

Reaction with silver salts

Some experiments were carried out where silver salts in toluene were added to solutions of polystyrene–lead triethyl and MMA in toluene slowly over an hour, and others were conducted where the two solutions were mixed at −78°C and brought slowly up to room temperature (silver precipitation occurring in the temperature range −50 to −30°C). The object of both these sets of experiments was to produce polymeric radicals at a controlled low rate so that the termination reaction was retarded and thus copolymerization maximized. None of these procedures resulted in efficient copolymerization; the g.p.c. traces of the products showed common features illustrated in the typical trace shown in *Figure 2*. The most prominent peak was always at the same retention time as the initiating polymer (2000 *MW*) and this possessed a shoulder of variable relative size at double the molecular weight. Block copolymer formation was indicated by a broad peak at about 30000 *MW* with a weak but significant u.v. absorbance. Estimates from the u.v. absorption of this peak and the total u.v. absorbance (assuming ε_{254} to be a constant) indicated that less than 5% of the polystyrene had been consumed to form block copolymer.

The following comments may be made on these observations. The coupled polystyrene which appears as a shoulder is evidently formed by the recombination of polystyryl radicals generated by homolytic scission, but the high quantity of uncoupled material is less easy to rationalize. The increase in u.v. absorbance of this product again suggests terminal unsaturation, although the mechanism of its production must differ from that proposed for the thermal process. Hydrogen abstraction from the toluene solvent by the polystyryl radical must take place, but this cannot be invoked as the complete answer since this would not account for the enhanced u.v. absorption.

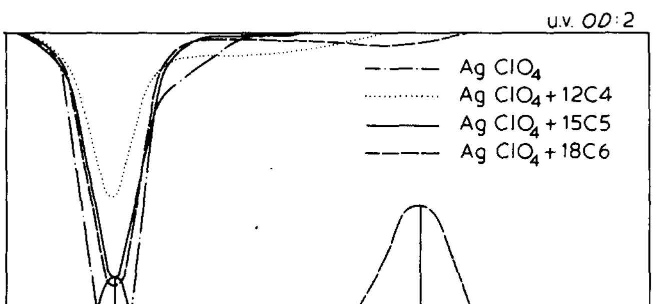


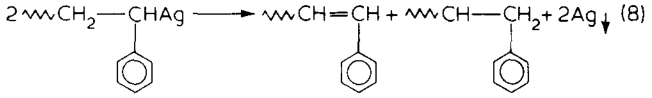
Figure 2 G.p.c. traces of poly(styrene-b-MMA) copolymers prepared with different complexes of silver salts

Table 1 Data on products obtained by chemical reactions of transition metal salts with polystyrene–lead triethyl

Salt	U.v./*RI* residual PS	% Conversion PS	% Conversion MMA
$AgClO_4$	2.36	5	5
" + 12C4	1.03	30	7
" + 15C5	1.74	7	17
" + 18C6	1.75	15	35
Cu OTf	1.28	10	32
$Cu(OTf)_2$	1.86	23	20
$Cu(NO_3)_2$	1.07	15	26
$Fe(NO_3)_2{\cdot}9H_2O$	1.00	15	6
$Cr(NO_3)_3$	1.14	34	33
$NH_2Ce(NO_3)_6$	1.19	25*	28

* Estimate includes polystyrene at double initial molecular weight

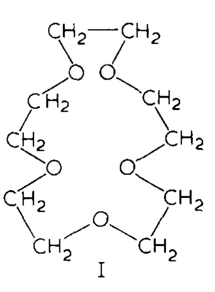
It is, however, conceivable that the cause could be disproportionation of polystyrene possessing terminal MMA radicals since in this case, unlike the thermal experiments, there is a continuity in the u.v. absorbance up to high molecular weight. Alternatively the reaction could possibly involve disproportionation between two molecules of the transient silver adduct (equation 8) in competition with the unimolecular decomposition into radicals shown in equation 3. It is difficult to distinguish between the last two alternatives kinetically since both are bimolecular, but both would be reduced if the rate of reaction between the silver salt and the polystyrene–lead adduct were retarded, with a consequent increase in copolymerization efficiency.



$$2\sim\!\!\sim CH_2{-}\underset{C_6H_5}{CHAg} \longrightarrow \sim\!\!\sim CH{=}\underset{C_6H_5}{CH} + \sim\!\!\sim CH{-}\underset{C_6H_5}{CH_2} + 2Ag\downarrow \quad (8)$$

One approach to achieve this slower reaction is to complex the silver ion with an appropriate reagent such that the rate of silver–polymer formation should be retarded, and its desired unimolecular decomposition consequently better controlled.

Species capable of such complexation are the crown ethers, a typical example of which is shown in structure I. They are designated by the general formula *n*C*m*, when *n* = number of skeletal atoms (C + O), and , = number of oxygen atoms in the ring; thus structure I is designated 15C5. The strength of complexation of a crown ether with a cation is maximized when the size of the ring matches that of the ion, and the logarithms of the association constants of silver ions in aqueous solutions with 18C6 and 15C5 have been shown to be 1.6 and 0.96 respectively[9].



I

Polystyrene–lead triethyl was reacted in toluene at room temperature with silver perchlorate, uncomplexed or complexed with 12C4, 15C5, or 18C6 respectively. The rate of appearance of silver metal was an inverse function of the stability of the silver–crown ether complex; the precipitate began to form almost immediately with the loosely complexed 12C4 adduct whereas it took several hours to develop with the tightly bound 18C6 complex. This difference in reaction rates is reflected in the product obtained, as shown in *Table 1* and by their g.p.c. traces (*Figure 2*) from which the following points may be made.

The efficiency of the process is best estimated by the percentage conversion of polystyrene chains into block copolymers (estimated from the u.v. responses on the g.p.c. traces), although a further important parameter is the MMA converted to polymer (estimated by the weight increase of polymer). Both yields are given in *Table 1*. It can be seen that the percentage conversion by either criterion is increased by the use of crown ethers. Inexplicably, the 12C4 complex gives a much higher conversion of polystyrene than the other two crown ethers, although the MMA conversion is lower owing to the lower molecular weight of the polymer formed. The MMA conversion increases as a direct function of the stability of the silver complex, i.e. 18C6 > 15C5 > 12C4. Secondly, complexation results in the virtual disappearance of the shoulder at 4000 *MW*, indicating that the first order initiation of MMA by polystyryl radicals is favoured over the bimolecular termination reaction at these low free silver ion concentrations. Lastly, the u.v./*RI* ratio of residual polystyrene is lower for the products of the complexed systems than that obtained without complexation, the value with 12C4 being close to that of normal polystyrene and the other two ethers have values somewhat higher. This suggests that the low steady state concentration of silver polystyrene minimizes its destruction by reaction 8, and the residual peak at 2000 *MW* can then only be explained by hydrogen abstraction from solvent.

There are still many features of this reaction which have to be elucidated, but these experiments support the view that copolymerization can be increased by a slow controlled release of silver ions. In this regard even stronger complexing agents such as cryptates could be used, and initial experiments with cryptate 222 (log $K = 10.6$ with Ag^+)[10] have shown that precipitation of silver at room temperature is only observed after a period of about 20 h.

Reaction with other transition metal salts

In principle, other transition metal salts can react with lead compounds according to the general equation 9, and a number of such salts were tested in the system. The compounds used and the conversions obtained are listed in *Table 1*, and some of the g.p.c. traces are shown in *Figure 3*.

$$\sim\!\!\sim M\ PbR_3 + MeX_n \longrightarrow \sim\!\!\sim M\cdot + X\,PbR_3 + MeX_{n-1} \quad (9)$$

All these salts, with the possible exception of Fe (II), were more effective co-initiators than Ag (I) both in initiating the polystyrene chains and in polymerizing MMA. Cr (III) was particularly efficient, initiating a third of the polystyrene chains and consuming a third of the MMA. It must be realised, however, that these results do not represent the maximum efficiency obtainable; the reaction time was arbitrarily selected as 20 h at ambient and it is likely that in some cases reaction was not complete at that time.

There is therefore no correlation between the conversions obtained and the redox potentials of the salts

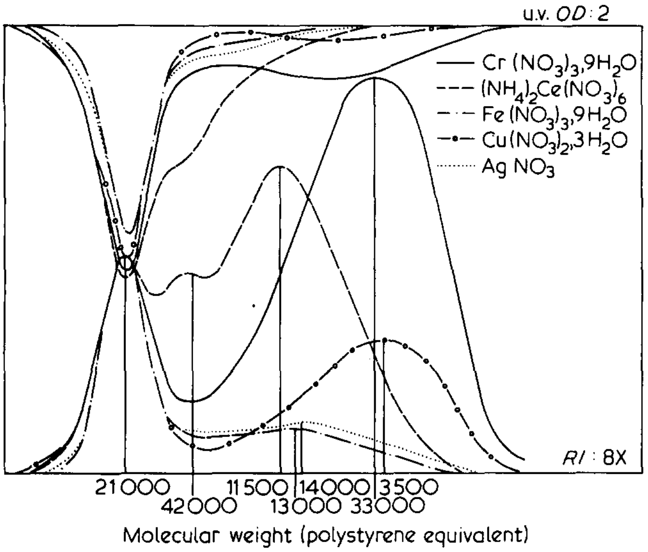


Figure 3 G.p.c. traces of poly(styrene-b-MMA) copolymer prepared with different metal salts

used. However, in preparative terms these results are encouraging and the systems merit further quantitative study in order to optimize block copolymer yield.

REFERENCES

1 Burgess, F. J., Cunliffe, A. V., Richards, D. H. and Sherrington, D. C. *J. Polym. Sci.* (*B*) 1976, **14**, 471
2 Burgess, F. J., Cunliffe, A. V., MacCallum, J. R. and Richards, D. H. *Polymer* 1977, **18**, 719
3 Burgess, F. J., Cunliffe, A. V., MacCallum, J. R. and Richards, D. H. *Polymer* 1977, **18**, 726
4 Burgess, F. J., Cunliffe, A. V., Dawkins, J. V. and Richards, D. H. *Polymer* 1977, **18**, 733
5 Abadie, M. J. M., Burgess, F. J., Cunliffe, A. V. and Richards, D. H. *J. Polym. Sci.* (*B*) 1976, **14**, 477
6 Souel, T., Schué, F. Abadie, M. J. M. and Richards, D. H. *Polymer* 1977, **18**, 1292
7 Cunliffe, A. V., Hayes, G. F. and Richards, D. H. *J. Polym. Sci.* (*B*) 1976, **14**, 483
8 Jenkins, C. L. and Kochi, J. K. *J. Am. Chem. Soc.* 1972, **94**, 843
9 Izatt, R. M., Eatough, D. J. and Christenson, J. J. 'Structure and Bonding', Springer–Verlag, 1973
10 Lehn, J. M. 'Structure and Bonding', Springer–Verlag, 1973