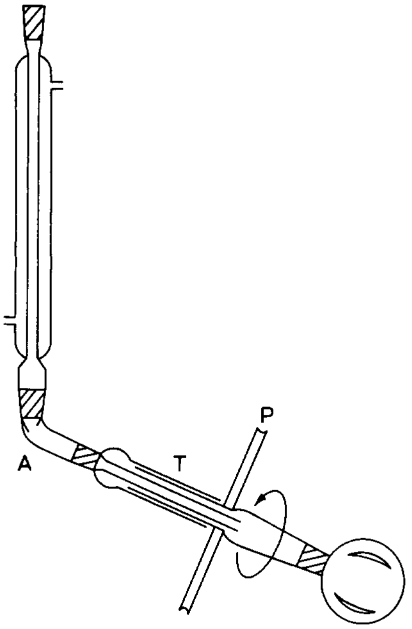


Figure 2 Rotary reaction

Another problem which arises with polymer-supported species is their efficient purification from contaminant reagents used in their syntheses. More often than not a washing procedure is terminated by a Soxhlet extraction with a suitable solvent, prior to drying. We have also found this process to be enhanced in some instances, by stirring in an appropriate solvent, and we have now produced a modified Soxhlet extraction vessel which allows simultaneous magnetic stirring, *Figure 3*. We have still to produce an extraction device with stirring by rotation!

The Soxhlet chamber, C, consists of a flat bottomed glass tube, 7 cm in diameter and 12 cm in length, and carries a B60 ground glass socket, G. This allows the introduction of large glass sinter crucibles (pore size 1), capable of holding up to ~50 g of polymer beads in one operation. When the polymer particles are less dense than the extracting solvent, crucibles must be covered with filter papers tied in place. The off-set syphon, S, allows a magnetic stirrer to be placed below the Soxhlet chamber, and agitation achieved in the normal way with a small follower. The flask of boiling solvent is attached at cone, C, and an appropriate adaptor and reflux condenser at socket, G.

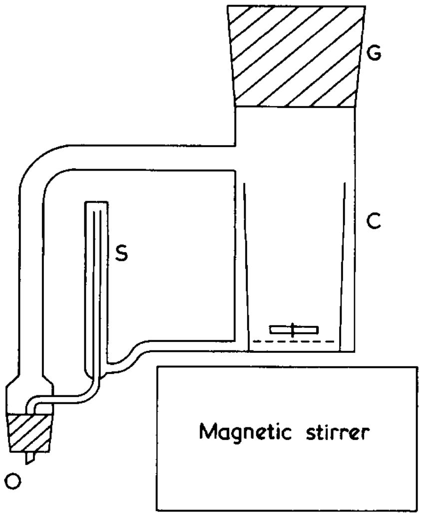


Figure 3 Stirrer/Soxhlet extractor

ACKNOWLEDGEMENTS

We thank the Science Research Council for studentships for J. A. G. and W. M. M. and the staff of our workshops for their technical assistance.

REFERENCE

1 Heitz, W. *Adv. Polym. Sci.* 1977, **23**, 1

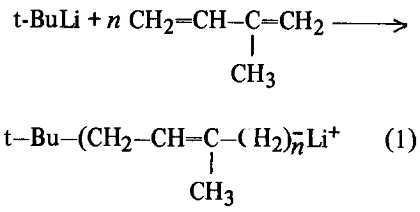
Block copolymers prepared by an anion to free radical transformation process. 1. Kinetics and efficiency of initiation by polyisoprene–lead trimethyl

T. Souel and F. Schué
Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex, France
and M. Abadie
Laboratoire de Chimie Macromoléculaire, Université des Sciences et de la Technologie d'Alger, Bab Ezzouar, Alger, Algerie
and D. H. Richards
Explosives Research and Development Establishment, Ministry of Defence, Waltham Abbey, Essex EN9 1BP, UK

(Received 27 June 1977)

This study is a facet of a general investigation into techniques of preparing novel block copolymers by transforming the initial propagating species via a metastable intermediate into another better able to polymerize the second monomer. Thus methods have been fully reported whereby the anion to cation transformation may be efficiently carried out[1–4], and preliminary accounts have been given of two methods which enable the anion to free radical transformation to be achieved[5,6]. This is a report on further developments in one of the latter systems[5] in which the anionic component is oligomeric polyisoprene, and its adduct with trimethyllead is the free radical precursor.

Very low molecular weight monofunctional anions may be prepared by established techniques[7,8] and then reacted with trimethyl lead chloride to form the monolead adduct (equations 1 and 2):



$$\text{t-BuLi} + n\,CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \longrightarrow$$

$$\text{t-Bu}{-}(CH_2{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2)_n^{-}Li^{+} \qquad (1)$$

$$\mathrm{RLi + ClPbMe_3 \longrightarrow RPbMe_3 + LiCl} \quad (2)$$

(R = isoprenyl oligomer)

This material may then be isolated, redissolved with a second monomer either in bulk or in a suitable solvent, and homolytic decomposition thermally induced (equation 3):

$$\mathrm{RPbMe_3 + M_2 \xrightarrow{\Delta T} R\cdot + M_2 + \cdot PbMe_3} \quad (3)$$

The efficiency of this method as a means of preparing block copolymer is largely dependent on the activity of the trimethyllead radicals formed; if they initiate polymerization then the block copolymer produced will be contaminated by homopolymer derived from the second monomer. Alternatively, it has been reported[9] that this radical readily dimerizes to form hexamethyldilead which can disproportionate to form inactive products (equations 4 and 5):

$$\mathrm{2\,PbMe_3 \longrightarrow Me_3PbPbMe_3} \quad (4)$$

$$\mathrm{2\,Me_3PbPbMe_3 \longrightarrow 3Me_4Pb + Pb} \quad (5)$$

EXPERIMENTAL

Synthesis

Trimethyl lead chloride was prepared using the method published by Gilman *et al.*[10,11].

Oligoisoprenyllithium was synthesized with $\overline{DP}_n = 2$ by distilling 5×10^{-2} mol isoprene slowly into a solution of 2.5×10^2 mol t-butyllithium in benzene at 10°C[7,8] and the mixture was allowed to stand for 24 h to ensure completion of the reaction. A high vacuum technique involving the use of breakseals was employed.

The trimethyllead adduct of oligopolyisoprene ($\mathrm{RPbMe_3}$) was prepared by adding under high vacuum conditions 5×10^{-3} mol of the 'living' oligomer to a stirred benzene solution containing an equal quantity of trimethyllead chloride at 10°C. ^{1}H n.m.r. analysis indicated a virtually quantitative conversion into $\mathrm{RPbMe_3}$. This material was isolated and stored in the dark at –30°C to await ^{1}H n.m.r. examination and polymerization investigations.

Kinetics

The thermal decomposition of $\mathrm{RPbMe_3}$ (1M in toluene solution) was followed by ^{1}H n.m.r. (100 MHz). The rate of reaction can be determined from the decrease in the singlet signal of the methyl group, $\mathrm{CH_3{-}Pb{<}}$at 0.75 ppm relative to TMS. The tertiary butyl group signal at 0.94 was used as an internal calibrant.

Styrene was chosen as the second monomer, and the rate of its polymerization was determined by dilatometry[13]. A reservoir was filled with monomer under vacuum and the required quantity of catalyst was added. The reaction mixture was then transferred to an attached evacuated dilatometer via a greaseless stopcock which was then closed to seal the dilatometer. The reaction rates were measured at 60°C.

RESULTS AND DISCUSSION

It is well established by studies on unsymmetrical tetra organo lead small molecules that thermal cleavage of allyl–metal bonds occurs in preference to scission of alkyl–, vinyl– or phenyl–metal bonds[14,15]. Since the allyl group may be taken as a good model for the oligoisoprenyl group, it is evident that the adduct $\mathrm{RPbMe_3}$ should behave similarly and thermal decomposition proceed as illustrated in equation (3). Decomposition was shown to be first order and application of equation (6):

$$\ln c_0/c = k_d t \quad (6)$$

where c_0 and c are the initial concentration and the concentration of $\mathrm{RPbMe_3}$ after time t, respectively, enabled the rate constant of decomposition, k_d, to be evaluated at a series of temperatures. These results are recorded in *Table 1*, and a plot of $\ln k_d$ against $1/T$ was linear giving an activation energy of dissociation of 12 kcal/mol which is in agreement with the value found for the model compound[16].

Table 1 k_d as a function of T

Temperature (°C)	$10^6 k_d$ (sec^{-1})
60	3.6
70	6.7
80	10.0
90	15.1

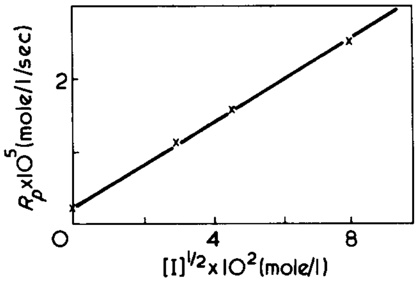


Figure 1 Rate of polymerization (R_p) of bulk styrene as a function of $[I]^{1/2}$

The rate of polymerization (R_p) of styrene by $\mathrm{RPbMe_3}$ is given either by equation (7)

$$R_p = k_p[\mathrm{M}](2k_d f[\mathrm{I}]/k_t)^{1/2} \quad (7)$$

if trimethyllead radicals participate in the polymerization process, or by equation (8) if they do not.

$$R_p = k_p[\mathrm{M}](k_d f[\mathrm{I}]/k_t)^{1/2} \quad (8)$$

In these equations k_p is the rate constant of propagation = 176 l/mol/sec[17]; k_t is the rate constant of termination (by recombination) = 72×10^6 l/mol/sec[18]; and f is the initiation efficiency. Conversions were kept low in these experiments (<5%), and the monomer (M) and the initiator (I) concentrations were assumed to approximate to those obtained initially.

The plot of R_p *versus* $[\mathrm{I}]^{1/2}$ was found to be linear (*Figure 1*) with an intercept on the ordinate which represents the thermal polymerization of styrene at 60°C. This gave a value of 0.2×10^{-5} mol/l which agrees with that obtained by other workers[19]. More interestingly, the slope of the rectilinear curve gives an initiation efficiency for $\mathrm{RPbMe_3}$ of 0.43 if both radical species initiate and, of course, a value of 0.86 if the isoprenyl radical is the only active species. Thus, as both figures are below unity this method of analysis is unable to distinguish which of the two mechanisms is operative. Nevertheless, since in the former case the value of 'f' is the average between two initiating radicals, it is tempting to speculate that these results are at least consistent with the desired property that the polymeric radical is an efficient initiator whilst the organometallic fragment is catalytically inactive.

More experimentation involving high molecular weight polyisoprene–lead adducts and g.p.c. analysis of the product is necessary, however, before such speculations can be verified, and these experiments are currently being carried out.

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., Burgess, F. J., Cunliffe, A. V. and Richards, D. H. *J. Polym. Sci. (B)* 1976, **14**, 477
6 Cunliffe, A. V., Hayes, G. F. and Richards, D. H. *J. Polym. Sci. (B)* 1976, **14**, 483
7 Schué, F., Worsfold, D. J. and Bywater, S. *J. Polym. Sci. (B)* 1969, **7**, 821
8 Schué, F., Worsfold, D. J. and Bywater, S. *Macromolecules* 1970, **3**, 1970
9 Coates, G. E., Green, M. L. H. and Wade, K. 'Organometallic Compounds', Methuen, London, 1967, Vol 1, p 501
10 Gilman, H. and Jane, R. G. *J. Am. Chem. Soc.* 1950, **72**, 1760
11 Gilman, H. and Robinson, J. D. *J. Am. Chem. Soc.* 1930, **52**, 1975
12 Prud'homme, J., Roovers, J. E. L. and Bywater, S. *Eur. Polym. J.* 1972, **8**, 901
13 Sangster, J. M. and Worsfold, D. J. *Macromolecules* 1972, **5**, 229
14 Gilman, H., Towne, E. B. and Jones, H. L. *J. Am. Chem. Soc.* 1933, **55**, 4689
15 Kreevoy, M. M. *J. Am. Chem. Soc.* 1959, **81**, 1099
16 Neumann, W. P. and Kühlein, K. *Adv. Organometal. Chem.* 1968, **7**, 241
17 Baysal, B. *J. Polym. Sci.* 1958, **33**, 391
18 Matheson, M. S., Auer, E. E., Bevilacqua, E. B. and Hart, E. J. *J. Am. Chem. Soc.* 1951, **73**, 1704
19 Nicolova-Nankova, Z., Palacin, F., Raviola, F. and Riess, G. *Eur. Polym. J.* 1975, **11**, 301

A new quarterly journal

APPLIED MATHEMATICAL MODELLING
environmental, social and engineering systems

APPLIED MATHEMATICAL MODELLING is the new international journal providing a multidisciplinary medium for publishing and discussing recent advances and thinking pertinent to mathematical modelling and practical systems analysis. In addition to methodology – its validation and reliability – emphasis is also given to the practical applications of both novel and successful models.

Some articles published in early issues

Computation of long-term average SO_2 concentration in the Venetian area
E. Runca et al. (IBM Italia, Venice, Italy)

A simple model of economic growth or decline under the influence of resource depletion
Bent Sørensen (Niels Bohr Institute, Copenhagen, Denmark)

Evaluating environmental quality management programmes in which dischargers are grouped
E. Downey Brill Jr. et al. (University of Illinois, USA)

Mathematical modelling of flows in recessed wall flame holder
D. Bhaduri and A.K. Majumdar (CMERI, Durgapur, India)

Arms race and the balance of power
Michael D. Wallace (University of British Columbia, Vancouver, Canada)

Wave forces on vertical cylinders as a basis for the design of offshore structures
L.A. Siegerstetter and A. Kleinschroth (Technical University of Munich, West Germany)

An algorithm for reducing the moment of inertia of a system interaction matrix
A.R. Gourlay (IBM (UK), Peterlee, UK)

Numerical models of wind-driven circulation in lakes
R.T. Cheng et al. (US Geological Survey, Menlo Park, USA)

Manuscripts for publication should be sent to the Editor-in-Chief:
Dr C.A. Brebbia, University of Southampton, Southampton,
England SO9 5NH

ISSN: 0307-904X

One years subscription (four issues) £25.00 ($65.00)

For more details, please write to: IPC Science and Technology Press Limited,
32 High Street, Guildford, Surrey, England GU1 3EW Telephone: 0483-71661 Telex: Scitec Gd 859556