volume decreases with increasing temperature. Since *trans*-decalin is a θ-solvent at about 20°C and could be considered as a thermodynamically good solvent at 40°C, this decrease could qualitatively be explained in the following way. The partial specific volume of the solute depends on both intra- and intermolecular segment–segment interactions and since these interactions are more pronounced in θ-solvents than in good solvents it is not unlikely that the concentration dependence of $\bar{v}_2$ should be stronger at θ-solvent conditions. For a more detailed analysis the nature of the solvent must also be taken into account.

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Apparatus for the manipulation of polymer-supported reagents

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There is now a considerable literature describing the preparation, purification and reactions of a wide variety of polymer-supported reagents[1]. The majority of these employ a bead form of polystyrene with a low crosslink ratio (1–2%) or of a macroporous nature, in order to minimize diffusional problems. Unfortunately such supports, particularly the latter type, can be somewhat mechanically unstable, and rapid magnetic stirring using a follower, or overhead stirring using a shafted impeller, can cause fragmentation of the spherical particles.

In order to overcome this problem we have produced two very simple devices for the rotation of flanged round-bottomed flasks, which produce highly efficient agitation, without mechanical damage. The first, *Figure 1*, is useful for reactions carried out at room temperature, and consists of a brass cage which can be mounted directly in the chuck of a standard geared-down laboratory stirrer motor. Two round brass plates, P, one having a central orifice, are connected by three long bolts, B, such that a flanged flask can be clamped firmly between them, within sections of a cork ring, R. The axis of rotation is adjusted to be ~25° to the vertical and a steady speed of ~50 rev/min maintained. The present device is suitable for 100 and 250 ml flasks, in which reactions involving up to ~30 g of polymer beads can be performed.

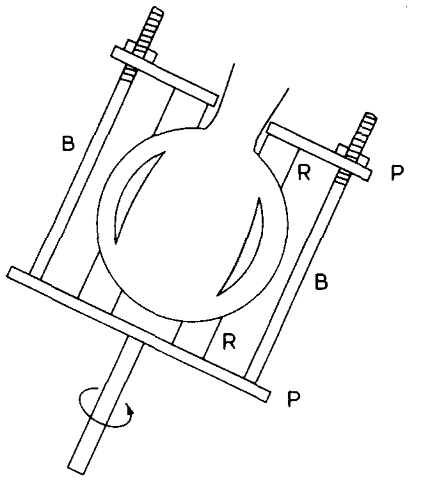

Figure 1 Rotating flask holder

The second apparatus, *Figure 2*, consists of an early pulley-driven, P, rotary evaporator, adapted for a new role. Rotation takes place within concentric ground glass tubes, T, clamped at ~20° to the horizontal. Flanged flasks up to 1 litre can be employed, and heat applied using conventional baths if necessary. The reflux condenser is connected via an adaptor, A, which allows additions to be made to the flask while it is in motion.

Both devices can readily be used for air/moisture sensitive reactions.

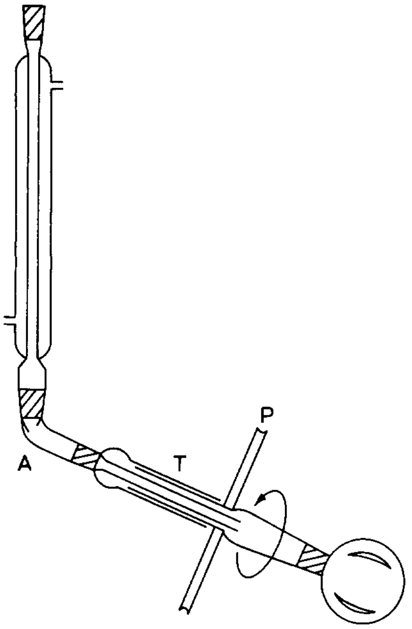

Figure 2 Rotary reaction

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.

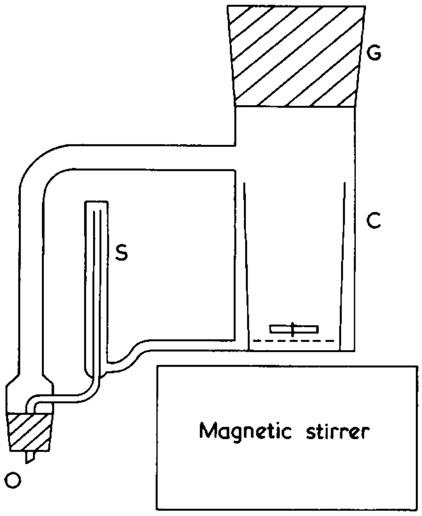

Figure 3 Stirrer/Soxhlet extractor

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

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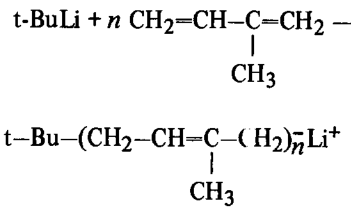
This study is a facet of a general investigation into techniques of preparing novel block copolymers by transforming the initial propagating species via a metastable intermediate into another better able to polymerize the second monomer. Thus methods have been fully reported whereby the anion to cation 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):



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