polymer reports

A simplified apparatus for the preparation of block copolymers with low polydispersity ratios

R. W. Richards and J. L. Thomason†
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK
(Received 2 *June* 1982; *revised* 27 *July* 1982*)*

A simplified apparatus for the preparation of block copolymers by anionic polymerization is described. Low polydispersity can be obtained without the need for a high degree of manipulative skill.

Keywords Block copolymers; anionic polymerization; low polydispersity

In the preparation of block copolymers with a defined composition and molecular weight, anionic polymerization is a commonly utilized technique[1]. To be successful, it is necessary that polar impurities and air be rigorously excluded from the polymerization and this is usually accomplished using special reaction flasks under high vacuum. Anionic polymerization has been reviewed periodically[2,3] and reaction flasks of varying complexity are described[4]. These commonly have a number of subsidiary flasks flame sealed onto them with glass break seals employed throughout[5]. The successful use of these flasks requires considerable manipulative skill and practice. In this report we describe a simplified apparatus which has been successfully used to prepare block copolymers of styrene and isoprene as well as styrene and methyl methacrylate. A feature of the apparatus is the replacement of break seals with reusable PTFE high vacuum taps and joints. The apparatus has been of particular use in the preparation of copolymers with deuterated styrene blocks where the quantity of monomer used has been necessarily small in view of its high cost.

All solvents and monomers were purified by distillation on to calcium hydride, the monomers being washed to remove inhibitor beforehand, followed by degassing and stirring on a high vacuum line. For styrene–isoprene copolymers the solvent, benzene, was then trap-to-trap distilled into a flask containing a solution of polystyryl lithium, to remove last traces of impurities. The purification of deuterated styrene required a modification of this procedure, and the apparatus shown in *Figure 1*. Deuterated styrene had been previously distilled (on the

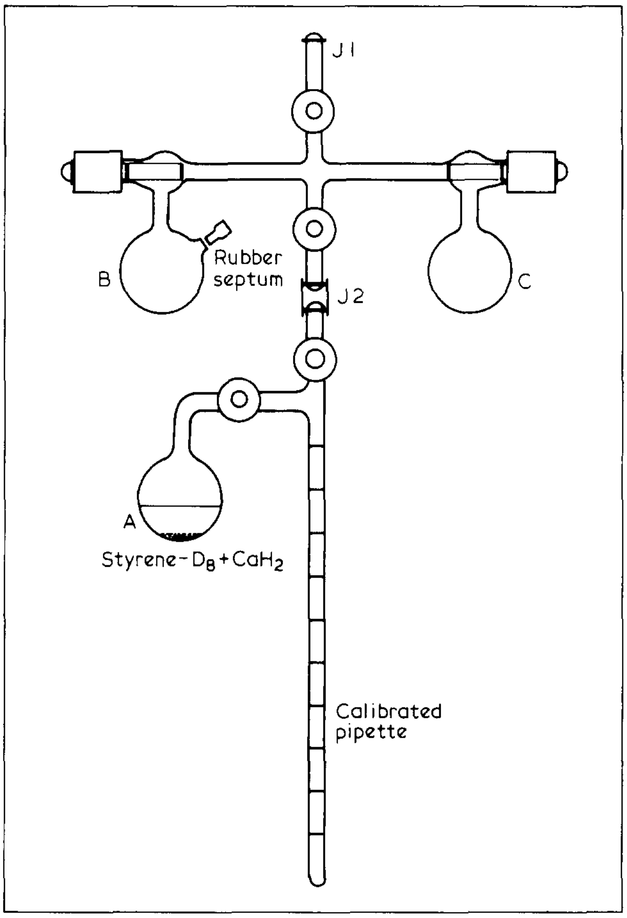

Figure 1 Apparatus for pre-polymerization of deuterated styrene monomer

---

† Present address: Institut für Physikalische Chemie, Johannes Gutenberg Universität, D6500 Mainz, West Germany.

0032-3861/82/131988-02$03.00

vacuum line) into bulb A, which contained calcium hydride and a small stirrer, where it was degassed and dried for a period of 24–48 h. It was then distilled into bulb B and small portions of n-butyl lithium solution added through the septum until a permanent yellow colour appeared. At this point the deuterated styrene was flash distilled into bulb C. For preparation of block copolymer, the deuterated styrene was distilled into the graduated pipette, which was then detached at joint J2 after isolation by closing all taps.

This pipette is then attached to joint J4 of the actual reaction flask shown in *Figure 2*. It consists of a 100 ml flask with a septum inlet and an extended neck to which small side flasks are appended, where all taps and joints are the high vacuum PTFE type. The flask is first evacuated and purged with the polystyryl lithium solution* held in bulb F before being rinsed with benzene distilled from F to remove traces of the polystyryl lithium solution. Following this the pipette is attached and the whole apparatus pumped down. The solvent, benzene, is then distilled into flask D followed by the distillation of the deuterated styrene monomer into the same flask, which is then isolated by closing the tap. After thawing, polymerization is initiated by injecting the desired amount of initiator through the septum. While the styrene polymerization proceeds, the second monomer, isoprene, can be prepared. The final stage of the isoprene purification being prepolymerization by injecting excess n-butyl lithium and stirring for approximately 15 min at 273K. The required volume is then distilled into a flask or pipette which is then attached at J4 and the isoprene distilled into side arm E. Subsequently, the isoprene is poured from E into F to continue the copolymerization. Additional monomer can now be distilled into E and this sequential monomer addition can be continued at will. Finally polymerization is terminated by injecting degassed methanol through the septum after which time the copolymer can be isolated by the usual techniques.

Using this technique it has been possible to quantitatively initiate the polymerization of 0.5 g of deuterated styrene monomer and produce copolymers with low dispersity ratios[6]. Furthermore, a larger scale version of this apparatus has been used to prepare hydrogenous copolymers, in this case the flask D has a capacity of 500 ml. Typical g.p.c. chromatograms of a diblock and triblock styrene–isoprene copolymer are shown in *Figure 3*, which also shows the g.p.c. molecular weights and the polydispersities. The copolymers produced have been subsequently used by us in a small angle neutron scattering study of their solid state structure[6,7].

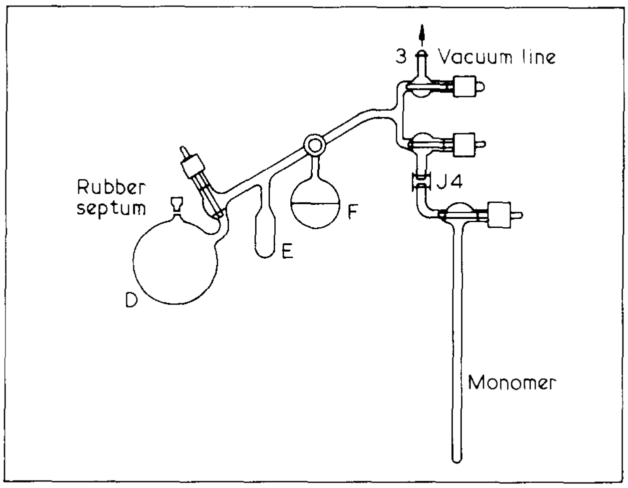

Figure 2 Schematic diagram of reaction flask for preparation of block copolymers

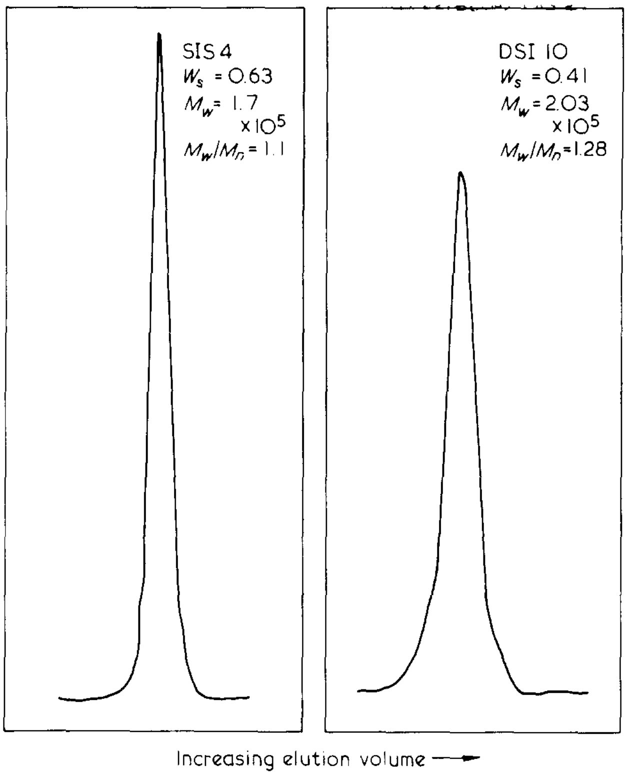

Figure 3 Typical gel permeation chromatograms. W = weight fraction of styrene in copolymers

Apart from styrene–isoprene copolymers, styrene–methyl methacrylate copolymers have also been prepared using this apparatus. For this purpose tetrahydrofuran was used as the solvent with styrene being first polymerized, diphenyl ethylene is then added followed by the methyl methacrylate, all reactions taking place at 195K. Since the amount of diphenyl ethylene added is an equivalent molar amount to the number of living ends, this is added from a syringe through the septum. The polydispersity is somewhat increased but not markedly so, with values of 1.15 being typical[8].

---

* The advantages of polystyryl lithium as a purge solution accrues from its deep colour. Excessive amounts of impurities which would kill the reaction are instantly monitored by the fading of the deep orange of this solution which is very rapid.

REFERENCES

1 Fetters, L. J. in 'Block and Graft Copolymerisation' (Ed. R. J. Ceresa) Vol. 1, Wiley, New York, 1973
2 Fetters, L. J. *J. Res. Natl. Bur. Stand. Sect. A* 1966, **70**, 421
3 Morton, M. and Fetters, L. J. *J. Polym. Sci. D Macromol. Rev.* 1967, **2**, 71
4 Morton, M. and Fetters, L. J. *Rubber. Chem. Tech.* 1975, **48**, 359
5 Urwin, J. R. and Stearne, J. M. *Makromol. Chem.* 1964, **78**, 194
6 Thomason, J. L. *Ph.D. Thesis*, University of Strathclyde, 1981
7 Richards, R. W. and Thomason, J. L. *Polymer* 1981, **22**, 581
8 Edwards, C. J. C., Richards, R. W. and Stepto, R. F. T. unpublished results