

respectively, resulting in a wide range of functionalized polymers. For various modification reactions of polystyrene, see Chap. 9.

Two types of cross-linked polystyrene are often favored. One is a polymer that is cross-linked by only 1–2% of divinyl benzene. The material, though fairly strong mechanically, swells and expands significantly in volume when dispersed in proper solvents. It is called *micro porous*. A copolymer with up to 20% divinyl benzene is the second type. It is prepared in the presence of large quantities of diluents to retain the products in expanded form. As a result, the structures are *macro porous* or *macro reticular*. The advantages of micro porous over macro porous structures are faster reactions, less fragility, and easier handling. Although, macro reticular supports are less often used, they have the advantage of being useful in almost any solvent.

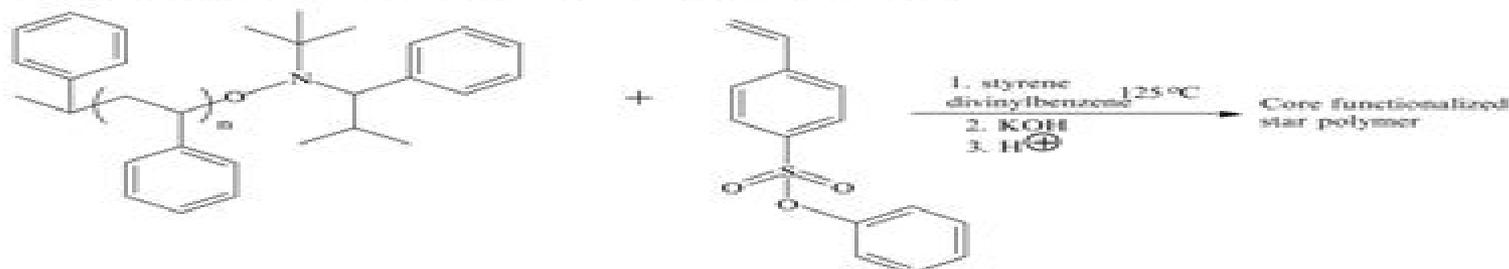
As a variation of the process, Fréchet and coworkers introduced *reactive filtration* [6]. In place of beads, they used discs of cross-linked polystyrene that were cut from a rod of the material. On the surface of these discs, they grafted 2,2-dimethylazlactone. These discs were then used in a filtration to efficiently scavenge excess amines from a reaction mixture. Subsequently, Fréchet and coworkers also used such discs in a flow through acylation reaction [7].

To improve the access to the functional groups, Lee and coworkers developed a process of placing most of the functional groups on the outer surface of the polystyrene beads [7]. This was done by surface aminomethylation of preformed cross-linked commercially available polystyrene beads. Such bead usually range in size from 100 to 400 mesh (in.) in diameter and can be functionalized by surface reactions or by surface grafts. This yielded materials with a lower number of functional groups, but with the majority of them being accessible. Lee and coworkers then utilized the beads in a solid peptide synthesis [7].

Lee and coworkers also prepared beads with *N*-heterocyclic carbene ligands located on the outer shell. In this preparation, they used beads formed in a suspension polymerization [8, 9].

Fréchet and coworkers [7] reported a variation of the strategy by attaching functional groups to cross-linked polystyrene in the interior of a soluble star polymer matrix. In this process, the catalytic groups are core-confined through the use of low molecular weight macroinitiators that form the surface of the final polymer. Presumably, this allows using simultaneous incompatible reagents, like acids and bases, because they are physically isolated from one another.

Lu and Toy [10] illustrated a similar approach: by showing how core-functionalized star polymers are prepared to form sulfonic acid-functionalized core material:



There is a drawback, however, of using the polymer described above, because many functional groups end up imbedded inside the resin and access to them requires the type of solvents that can thoroughly swell the resin. Many polar solvents, however, fail to swell cross-linked polystyrene adequately, yet may be required for specific reactions. That led to modifications, such as, the use

Chemistry Of Polymeric Resins Principles And Recent Developments

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