Polymer beads should be porous enough to allow the transport of substrates and products in and out of the bead. They are usually formed in the presence of cells and can be prepared by one of the following methods:

1. *Gelation of polymers:* Gelatin and agar beads may be prepared by mixing the liquid form of these polymers with cell suspensions and using a template to form beads. Reduction of temperature in the templates causes solidification of the polymers with the cells entrapped. Gel beads are usually soft and mechanically fragile. However, we can use a hard core (glass, plastic) and a soft gelatin shell with entrapped cells to overcome some mechanical problems associated with polymer beads. Because of diffusional limitations, the inner core of such beads is often not active, so this approach does not necessarily decrease the amount of product made per bead.

2. *Precipitation of polymers:* Cells are dispersed in a polymer solution, and by changing the pH or the solvent, the polymer can be precipitated. The starting solution of the polymer has to be prepared with an organic solvent or a water-solvent mixture. Ethanol and acetone are examples of water-miscible solvents. Polymers used for this purpose are polystyrene, cellulose triacetate, and collagen. The direct contact of cells with solvents may cause inactivation and even the death of cells.

3. *Ion-exchange gelation:* Ion-exchange gelation takes place when a water-soluble polyelectrolyte is mixed with a salt solution. Solidification occurs when the polyelectrolyte reacts with the salt solution to form a solid gel. The most popular example of this kind of gelation is the formation of Ca-alginate gel by mixing Na-alginate solution with a $CaCl_2$ solution. Some other polymers obtained by ion-exchange gelation are Al-alginate, Ca/Al carboxymethyl cellulose, Mg pectinate, κ-carrageenan, and chitosan polyphosphate. Alginate and κ-carrageenan are the most widely used polymers for cell-immobilization purposes. Ionic gels can be further stabilized by covalent cross-linking.

4. *Polycondensation:* Epoxy resins are prepared by polycondensation and can be used for cell immobilization. Polycondensation produces covalent networks with high chemical and mechanical stability. Usually, liquid precursors are cured with a multifunctional component. Functional groups usually are hydroxy, amino, epoxy, and isocyanate groups. Some examples of polymer networks obtained by polycondensation are epoxy, polyurethane, silica gel, gelatin–glutaraldehyde, albumin–glutaraldehyde, and collagen–glutaraldehyde. Severe reaction conditions (high temperature, low or high pH values) and toxic functional groups may adversely affect the activity of cells.

5. *Polymerization:* Polymeric networks can be prepared by cross-linking copolymers of a vinyl group containing monomers. Polyacrylamide beads are the most widely used polymer beads, prepared by copolymerization of acrylamide and bisacrylamide. Several different monomers can be used for polymer formation; acrylamide, methacrylamide, and 2-hydroxyethyl methacrylate are the most widely used. Cross-linking is usually initiated by copolymerization with a divinyl compound, such as methylenebis-acrylamide.

Immobilization by polymerization is a simple method. The polymerizing solution is mixed with the cell suspension, and polymerization takes place to form a polymeric block, which is pressed through a sieve plate to obtain regular-shaped particles. Suspension or emulsion polymerization can also be used to form polymeric beads for cell entrapment.