3 Porous Polymer Structures by Synthesis from Liquid Two-Phase Systems

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3.1 INTRODUCTION

There are a large number of materials that include polymeric multiphase systems. These refer to structured copolymers, various types of blends with flexible linear chains, weakly crosslinked linear chains (elastomers), interpenetrating polymer networks, composites, three-dimensional crosslinked networks, high thermoresistant materials, and so on. Among the polymer structures obtained from liquid–liquid
two-phase systems, porous crosslinked polymers occupy an important position due to their special properties (high chemical and mechanical stability) and structural variety, both of which generate a large number of usage possibilities. Particle morphology is an important characteristic of porous polymers, with pore size a fundamental factor in specific high tech applications.

The term crosslinked refers to a small region in a macromolecule (from a polymer chain) where there at least one point is tetra-connected. Covalent polymer networks can be considered among the largest known molecules. Such networks usually are referred to as macronetworks. Conversely, the dimensions of micronetworks range from only a few nanometers to several millimeters (Mester et al. 2011).

The terminology and classification of porous polymers have been extensively discussed by specialists. Different classifications—based on pore size (Becher and Birkmeier 1964), level of particle agglomeration (Jacobeli et al. 1979), crosslinker content, solvent retention (Rabelo and Coutinho 1994), or porosity type (Sederel and De Jong 1973)—have been made. But the existence of distinct high and low crosslinking regions within the same polymer, as a consequence of the specific polymerization mechanisms, has not been taken into consideration in these classifications.

Macroporosity, usually related to the permanent porosity in a dry polymer, signifies the network density due to voids from the polymer matrix. Gel porosity refers to the materials that have no pores in a dry state (Kun and Kunin 1964, 1968). At present, we refer to the classification made by the International Union of Pure and Applied Chemistry (IUPAC) in Table 3.1 (Rouquerol et al. 1994).

The internal structure of porous beads consists of many interconnected cavities (pores) of different sizes, the beads’ rigidity being due to the extensive crosslinks. These structures are obtained in presence of porogen which is a substance inert to monomers and is included within beads. Finally, the pore-forming is removed in order to create the granule pores.

### 3.2 CROSSLINKED (CO)POLYMERS

Network formation is possible if at least one of the initial components has a functionality greater than two. There are many synthetic methodologies that allow the preparation of porous polymeric materials (Barbetta et al. 2009; Weigang et al. 2010).

<table>
<thead>
<tr>
<th>Name</th>
<th>Width (nm)</th>
<th>Notes</th>
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<tr>
<td>Micropores</td>
<td>&lt;2</td>
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<td>Mesopores</td>
<td>2–50</td>
<td>• Ultramicropores below 0.7 nm</td>
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<td>Macropores</td>
<td>&gt;50</td>
<td>• Supramicropores 0.7–2 nm</td>
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TABLE 3.1

Pore Classification by the International Union of Pure and Applied Chemistry
Taking into account the chemical formation mechanism, networks can be obtained by polyaddition, polycondensation, or by crosslinking (co)polymerization of polyunsaturated monomers or of existing primary chains. When written without the parentheses, this term refers exclusively to copolymerization (Dusek 1993).

Porous crosslinked (co)polymers in a bead shape can be prepared by using a mixture of two or more liquids and various polymerization techniques such as suspension, dispersion, emulsification, precipitation, seeded polymerization, and so on (Dragan and Vlad 2006; Mohamed and Wilson 2012).

Considering the large range of porous polymer structures that are synthesized in heterogeneous systems, this chapter presents some aspects of the suspension polymerization technique that is performed by a radical polymerization mechanism (Gokmen et al. 2012; Falk et al. 2004). Radical crosslinking (co)polymerization (Degirmenci et al. 2007) is a more complex method of polymer network preparation. This is due to the kinetic reaction mechanism and the strong spatial correlations that cause big differences in a polymer chain’s branching mode (Dusek and MacKnight 1988; Gridnev et al. 2001).

### 3.2.1 Suspension Polymerization Technique

Suspension polymerization (SpP) can be considered the least complicated heterogeneous polymerization technique in terms of its mechanism.

Generally, we can discuss two types of suspension polymerization, “bead” and “powder” SpP (Kotoulas et al. 2006). In “bead” SpP, the polymer is soluble in its monomers and smooth spherical particles are produced. In the “powder” SpP process, the polymer is insoluble in its monomers; thus, it precipitates out, which leads to the formation of irregular grains of particles.

In “bead” SpP, the monomers are dispersed (as droplets) in the continuous phase (commonly water) by the combined action of surface agents (inorganic and/or organic water soluble polymers) and agitation. All the reactants (monomers, initiators, etc.) reside in the organic or “oil” phase. The droplets adopt a spherical shape for minimum interfacial energy (maximum stability), their average size primarily being controlled by a number of factors. Among these, the stirring speed and the stabilizing agent quality and the quantity are very important. The correct prediction of droplet size, mixing effects, and polymer sedimentation require particular attention (Silva et al. 2004). Polymerization occurs in the monomer droplets that are progressively transformed into sticky, viscoelastic monomer–polymer droplets and, finally, into rigid and spherical polymer particles. Particle size and internal structure affect the use of resins in their applications.

### 3.2.2 Bead Formation Mechanism

The mechanism affecting the appearance and development of crosslinked polymer particles during suspension polymerization may be described usually by different schemes, depending on the monomer systems used. Starting from the suspension of water-insoluble monomers, the formation mechanism of the crosslinked polymers might be schematically depicted such as in Figure 3.1.
Covering the monomer droplets with a stabilizer layer (Figure 3.1a) controls and reduces the coalescence process, helping to stabilize droplet size. Radical crosslinking (co)polymerization (CRR) has some specific behaviors, and the processes of chain initiation and growth are fundamental factors in the morphological differences of the resulting crosslinked structures. When considering the copolymers obtained from mono- and poly-unsaturated monomers by use of the CRR mechanism, we must assume that at the beginning of the (co)polymerization reaction, polyfunctional linear macromolecules—which remain dissolved in monomers (Figure 3.1a)—are formed. As the reaction progresses, the insoluble polymer granules that constitute “centers” or “nuclei” of polymerization appear (Figure 3.1b) and increase in number; the granules become sticky, bind to each other (Figure 3.1c), begin to contract, and polymerization continues according to the mechanism required by the type of monomers. Finally, a solid phase is formed (Figure 3.1d), which—under certain conditions—can contain pores.

As the polymerization progresses, the monomer is consumed, and the pores from the surface clog while the pores from inside close, resulting in a bead-shape polymer (Figure 3.1e). The SpP kinetics and mechanism depend on the nature, structure, and quantity of monomers; the water to monomers ratio; initiators and stabilizers; temperature; the form of reactor and agitator; the hydrodynamic regime; and so on. All these factors are essential for the products’ properties (molecular weight distribution, the amount of the residual monomers, the particle morphology, side reactions, etc.) and their performance.

3.2.3 Factors Influencing the Formation of Crosslinked Beads

Bead formation imposes some conditions that are essential for obtaining uniform suspension of monomer droplets in aqueous phase and for reducing coalescence during polymerization (Hulubei et al. 2014).

3.2.3.1 The Stabilizer

To a great extent, the morphology of the resulting crosslinked (co)polymers is determined by the type of suspending agent used because it protects the droplets from collision during polymerization. Throughout the entire suspension polymerization process, the two phases (organic and water) remain separated (Guerrero et al. 2006). Polymerization takes place in the suspended droplets, which act like isolated microreactors.
In the continuous phase, a stable dispersion of droplets is ensured by stabilizing and stirring. The action mechanism of the stabilizer depends on its nature. Chemical structure is of prime importance. The balance between the polar groups (that ensure the dissolution of the stabilizer in water) and the hydrophobic groups (that physically interact with the monomer droplets’ surface) can help locate efficient stabilizers for each suspension polymerization system.

It is well known that the final particle size and particle size distribution are decisively impacted by the initial drop size distribution of the monomer/water dispersion and the controlled breakage/coalescence processes, even from the earliest stages of polymerization.

Following are the features of a good stabilizer:

- The stabilizer does not inhibit or delay polymerization.
- It has an optimum ratio of hydrophilic/hydrophobic groups (promoting the solubilization in water and physically interacting with the monomer).
- It ensures the formation of a mechanically resistant layer around the protected droplets.
- The stabilizer ensures optimal growth of the environment viscosity to protect against the good monomers dispersing.

### 3.2.3.2 Stirring

Nonuniform agitation cannot generate a monodisperse system because there is a direct relationship between the dispersion velocity and the particle average size. Optimal stirring is ensured by the coalescence/dispersion ratio.

Some of the basic aspects for calculating stirring conditions include the ratio between the stirrer and the liquid level, the stirrer type, the viscosity ratio of the initial monomer and of the aqueous phase, the density of the two phases, the fluid flow parameters, and the Reynolds and Weber criteria (Leon et al. 2011; Vivaldo-Lima et al. 1997).

Agitation should be sufficient to prevent particle separation caused by the differences between the specific densities of the two phases. The monomer must be insoluble in water, with a surface tension lower than water. When the stirring is stopped, the system separates into two phases. Coalescence is prevented by a continuous control of the combined effect that is induced by the surfactant/stirring system. If there are no stabilizers in the system, an unstable dispersion occurs because of the breaking/coalescence ratio of the droplets.

### 3.2.3.3 Initiation

The radical initiators (equal to 0.1% of the monomer weight) are organic peroxides (benzoyl or lauroyl peroxide) or azo compounds (AIBN); these agents, insoluble in the aqueous phase, are usually solubilized in an organic solvent or in monomers after their introduction into the reactor (Vlad et al. 1994).

### 3.2.3.4 The Temperature

In the suspension polymerization process, the temperature usually is in the range 40°C–90°C, depending on the specific initiation type, kinetics, and on the system’s
reaction mechanism. The temperature value is selected to ensure that the initiator has a high decomposition rate (resulting in a great number of free radicals and, implicitly more nuclei and microspheres, as well as the diluents having a high solvating power). These factors contribute to smaller pore size because the polymerization rate increases with temperature (Okay 2000; Svec and Frechet 1995).

Polymer solubility in monomers is characterized by the solubility parameter. A slight difference between the solubility parameter of the monomer and the polymer implies that the mixing enthalpy of these two components is small. In such systems, sample agglomeration is avoided and the lack of defects suggests that the union of two particles and their adherence happens for a short period of time. Even though there is a density difference between the monomer and polymer, the droplets do not collapse because crosslinking occurs. The solubility parameter is a convenient measure that estimates polymer system solubility and influences bead morphology. The solvent–polymer compatibility can be semiquantitatively approximated using the solubility parameter (Tang et al. 2015; Vlad et al. 1997).

Bulk and suspension polymerization follow the same principles when all the system components are soluble in the monomer phase (initiators, macro radical, chain transfer agents). The rate of polymerization is not influenced by particle size and stabilizer type.

3.2.4 Free-radical Crosslinking (Co)Polymerization Mechanism

In suspension polymerization, the crosslinked polymer formation from mono- and poly-unsaturated monomers takes place by free-radical crosslinking of the chains (Elliott and Bowman 2002). At the beginning of (co)polymerization, only a few linear polyfunctional macromolecules (that remain dissolved in monomers) are formed.

Radical crosslinking (co)polymerization (CRR) has several specific behaviors. The primary feature is the initiation process of the growing chains, a process that causes morphological differences in the resulting crosslinked structures.

From the standpoint of elementary reaction steps, free-radical crosslinking (co)polymerization starts with initiation, proceeds by propagation (in which the monomers are added to the active ends of the growing chains accompanied by chain transfer), and ends with termination reactions (when the active chain ends are deactivated).

Differences arise because of the unsaturated monomers’ presence. This can be incorporated into the growing chain by a single double bond. Others, that remain pendant (free), are able to participate in (co)polymerization so that, gradually, the chains are united by the pendant double bonds, and thus forming crosslinks.

It often happens that chemical reactivity of the pendant bonds is equal to that of the polyunsaturated monomer; in this case, the copolymerization scheme is identical to that of the linear binary copolymerization.

The macroradical has different possibilities for growth by reacting with the following to form covalent bonds:

- A double bond of the polyunsaturated monomer
- The other pendant bonds
Porous Polymer Structures by Synthesis from Liquid Two-Phase Systems

- An active end of the same chain (intramolecular cyclization crosslinked)
- An active end of a growing free chain (intermolecular crosslinking)

During the crosslinking process, two types of cyclization reactions take place: (1) cyclization with a pendant double bond from the same molecule and (2) cyclization with a double bond from another existing chain in the same molecule, the so-called “multiple cyclization.”

At the beginning of the polymerization process, there are only a few pendant double bonds in the reaction system that can participate in the intermolecular crosslinking. The intramolecular cyclization reaction can occur if the cycle closing is supported by the chain flexibility.

For unequal reactivity of the vinyl groups, the scheme corresponds to that of ternary copolymerization. Therefore, there is exclusively intramolecular crosslinking at the beginning of process. Cycles of various sizes are formed, with the smallest cycles having the highest probability of formation. A very important cyclization can be observed when the reaction system contains a large amount of divinyl monomer (Vlad and Vasiliu 2010). However, a sharp decline in the pendant double bonds’ reactivity appears. This feature of crosslinking (co)polymerization is explainable because many of these links are trapped inside cycles. For a complete conversion of monomers, the presence of double bonds in the reaction system supports the inaccessibility of these links.

Internal crosslinking leads to a very compact microgel structure. The insides of the pendant groups are extremely immobile and, although they are reactive, they do not react with monomers because the monomers cannot diffuse them.

Only the mobile pendant bonds from the periphery of this species (microgel) can react with macro radicals. Therefore, the trend of microgel formation depends on the length and flexibility of the primary chain; the possibility for accessing the unreacted double bonds from inside (their “apparent reactivity”) depends on the microgel size, a fact reflected in the molecular weight value of the polymer chain. The decrease in the apparent reactivity of the pendant double bonds that produces crosslinking is due to the steric factors leading to the formation of inter- and intramolecular crosslinks. These factors strongly control diffusion in the polymerization reaction.

The specific behavior of the formation of a crosslinked (co)polymer structure by radical mechanism for a high crosslinker concentration is determined by: (1) an increase in the unreacted double bonds’ concentration from the unsaturated monomer units (at low conversion) and (2) an increase in the number of pendant double bonds in the newly formed structure.

In the reaction system, a high concentration of polyunsaturated monomer involves a large number of double bonds. At low conversions, crosslinked (co)polymer structures with many unreacted double bonds are formed. When the conversion increases, the crosslinking efficiency decreases (the reaction is very difficult for both double bonds). Even at a low conversion, a decrease in the mobility of the formed structures takes place.

From the perspective of tridimensional structure evolution in crosslinking polymerization, the pendant double bonds’ reactivity is strongly affected by the spatial correlations, resulting in an increase in the forming probability for cycles of different
sizes and a decrease in double bonds’ reactivity due to steric effects induced by the newly formed structure.

An increase in crosslinker concentration leads to the formation of compact macromolecules by internal crosslinking (the particles of the formed microgel bind together via the peripheral vinyl groups’ participation during the growth of the macroradical in the liquid phase).

The pendant double bonds’ reactivity is strongly affected by the spatial correlations induced by steric effects and, as consequence, the probability of cycle formation increases.

Possible reactions in the free radical crosslinking (co)polymerization of monomeric divinyl monomers are shown in the work of Vlad (2008).

Dilution favors contact among particles, and the macroradical is more likely to attack a peripheral vinyl link in the same particle. Paradoxically, the conversion increase does not increase the system heterogeneity. The spaces between the particles are gradually filled with the new polymer formed from monomers (by the peripheral vinyl groups participating from the all existing particles) so that the density fluctuation flattens (heterogeneity fades).

### 3.3 POROUS CROSSLINKED STRUCTURES BY SUSPENSION POLYMERIZATION

Adding a diluent in the polymerization system leads to the formation of heterogeneous permanent structures (with pores, after drying). To obtain rigid porous material, the dispersed liquid of the polymerizable mixture must contain not only monomers but also a diluent medium. The diluent medium is called “porogen” and must not react during the polymerization; it must remain within the newly formed beads, surrounded by the polymerized material. Finally, the porogen is removed and the places it occupied become the pores of the respective structure. Several special features of free-radical crosslinking (co)polymerization make the modeling of the network formation very difficult.

#### 3.3.1 ROLE OF SOLVENTS

Because the monomers themselves act as diluents in the crosslinking (co)polymerization process and the monomers and (co)polymer concentration depend on the duration of polymerization, the question of how to find the critical conversion at which phase separation takes place (described as function: phase equilibrium versus conversion) becomes very important. Apart from the effect of phase separation, the diluent produces other effects such as lowering the glass transition temperature and the reaction rate, promoting the cyclization reaction, and changing the conformation of chains when it is removed from the network.

There are three types of inert media (and/or mixtures): solvents, nonsolvent, and linear polymers (Krueger et al. 1985).

When inert swelling media (solvents) are used, the macromolecular chains of the crosslinked polymer are completely solvated during all of the synthesis process, and the packing of nuclei becomes more ordered. With increasing dilution, the size of
the chains among the microgel particles (nuclei) increases, and the solvent removal causes the reversible chains to collapse and return to the form that they had during polymerization. Beads with a large specific surface area and small pore diameter may be obtained. The resulting polymers become “porous by solvent.”

An inert, ideal *nonsolvent medium* is difficult to find because, in the liquid phase, the reaction system always contains monomers—the nonsolvent character being exacerbated with an increase in the degree of transformation.

The precipitant character of the inert medium depends on (1) the initial concentration of monomers that are the proper solvent for the (co)polymer and (2) the inert medium/(co)polymer interaction parameter. This, in turn, determines an increase in the degree of permanent packing chains and, hence, an increase in the degree of effective crosslinking, which is manifested by the reduction in the volume. The difference between the volume of the copolymer and the initial monomers will increase as the amount of precipitant increases (resulting in an increase in porosity over the values corresponding to the quantity of inert medium from synthesis) (Bradford et al. 1955).

*Linear polymers* are part of the macromolecular inert media category. They bring a large number of variables to the reaction system because changes in chemical composition as well as in molecular weight and its distribution affect the porosity. When inert polymer media are used, the precipitant character of these macromolecular compounds depends on their degree of incompatibility with the newly formed (co)polymer. This incompatibility is responsible for phase separation at a much lower concentration for this type of inert medium as compared to others.

A mixture of linear polymer and good solvent as an inert medium can be used to obtain copolymers with a porous structure in more advantageous conditions than with the use of a single component as an inert medium. The presence of a solvent in addition to a polymer will contribute to a more uniform distribution of the inert polymer medium in the network, thus increasing the copolymer dispersion degree. The mixture can affect the size and distribution of pores because it acts as a unit of inert medium—the two components are inseparable and unable to react independently of one another.

A mixture of an inert swelling medium together with an inert precipitation medium with small molecules is frequently used to obtain copolymers having specific structures. The ratio of the two inert media depends on the polymer destination. In this case, the softer character of phase separation and the high degree of polymer dispersion lead to appreciable specific surfaces (Cheng et al. 1992).

Mixtures consisting of two inert precipitation media, one with small molecules and the other with a macromolecular structure, were studied theoretically. In that case, the size of the agglomerates greatly increased, resulting in products with very low mechanical strength.

### 3.3.2 Porous Polymers Obtained from Two Liquid Phase Systems

To understand pore formation during suspension polymerization, imagine that every drop is a spherical microreactor, the spherical form being ensured for the final polymer by stirring and interfacial tension. As a result of the crosslinking and solubility
changes associated with increases in polymer chain length, the macromolecules formed inside this “microreactor” precipitate in the environment that surrounds them (porogen/monomer mixture). This phase separation occurs right at the beginning of polymerization, resulting in the formation of microscopic globular entities that begin to grow and are not coalescent because of crosslinking. Eventually, these come in contact with one another and, in an associated form, lead to clusters composed of interconnected cells and voids (pores). In essence, each drop is transformed into a microporous bead, the free volume being well correlated with the used porogen percentage.

The macroporous structure formation is determined exclusively by the behavior of the crosslinked chains obtained in the (co)polymerization reaction. The processes that occur in this stage can be described as follows: the initially formed microgel particles (nuclei) are linked together by chains that contain very few crosslinker molecules. This area of low crosslinking is very swollen in the diluent/monomer mixture. At drying, the new structure does not totally collapse, and the pores formation corresponds to the spaces between particles. The change in diluent thermodynamic quality reflects a different degree of association for the nuclei.

The inhomogeneous character of crosslinking polymerization is not a sufficient condition for the formation of the two-phase structure (the second phase refers to diluent or voids after drying). Therefore, the mechanism of phase separation (Hsiao et al. 1995) that appears near the limit of the thermodynamic stability is very important.

The phase separation in the presence of an inert medium occurring during the crosslinked formation was studied using Flory’s thermodynamic theory (Dusek and Duskova-Smrckova 2000). Because the monomers themselves act as diluents, phase separation will be strongly influenced by the polymerization time, the phase equilibrium being described by the conversion function.

The model scheme for the formation of three-dimensional macroporous structures (Scheme 3.1) shows the steps that occur in the suspension polymerization process. Each particle (that can be seen as a “microreactor”) is composed of monomer solution, initiator, and diluent (I). This organic phase is suspended in an aqueous phase containing the suspension stabilizer.

**SCHEME 3.1** Model scheme for the formation of three-dimensional porous structures. (Adapted from Vlad Cristina Doina. Suspension polymerization. In Crosslinking (co)polymers obtained by suspension polymerization, pp. 7–42. Iasi: PIM, 2008.)
The polymerization reaction results in (co)polymer molecules rich in bis- or polyunsaturated components that still contain a large number of unreacted double bonds. The propagation, cyclization, and crosslinking reactions lead to weak intermolecular crosslinked primary nuclei (due to the diluent presence), intramolecular crosslinked microgels, and linear chains soluble in the unreacted monomers.

The presence of a low number of intermolecular bonds among the newly formed nuclei gives rise to a low crosslinking area that swells in the diluent/monomer mixture. The crosslinked polymer formation causes phase separation between the crosslinked polymer and the inert medium, with the monomers being distributed between the two phases (II). Because the weak crosslinked polymer is swollen in the rest of monomers, it behaves like liquids that (due to interfacial tensions) take the most stable form in terms of energy. In this way, mass separation of microspheres takes place (III). During the formation of this microgel, the minimum droplet energy is achieved based on the network deformation (observed as volume change). At a high monomer conversion, the formation of macro gelation and microsphere agglomerates takes place (IV). The first stage of the porous structure formation is the production and aggregation of highly crosslinked microspheres. The second stage is the binding and fixing of the microspheres and of their agglomerates. This is achieved by advancing the crosslinking polymerization reaction when the formation of new nuclei takes place. Based on the monomers’ consumption, these nuclei bind the existing structures in the system (V). The inert medium is now in the spaces between microspheres and their agglomerates. These places occupied by the inert medium, after its removal, become the network pores, and they determine the macroporous structure properties (shape, size distribution, etc.).

3.4 THE MECHANISM OF PHASE SEPARATION

All the porosity formation theories are based primarily on phase separation (PS) and the solvating power of the porogen. A large amount of crosslinker is needed for producing a macroporous resin, to facilitate the phase separation between polymer and porogen during synthesis. A variety of phase morphologies are obtained and decided by the competition between the kinetics of phase separation and the crosslinking chemical reaction. The physical properties of a crosslinked polymer are strongly dependent on its phase-separation morphologies. Among the methods used to investigate phase separation (PS) are as follows:

- Thermally induced phase separation (TIPS): an increased reaction temperature, or a high concentration, produces a high-connectivity phase structure so that the polymerization surpasses the phase separation; using a low-temperature stage, a moderate decrease in phase separation is observed at a lower nucleation temperature (Kim et al. 2016; Padilla et al. 2011; Stieger et al. 2003).
- Nonsolvent-induced phase separation (NIPS).
- Combined NIPS-TIPS (N-TIPS).
- Polymerization-induced phase separation (PIPS) (Yuhong 2013).
The increasing size of the growing polymer molecules and the resulting morphology (stabilized by gelation in crosslinking polymerization) are the main factors affecting PIPS. The PIPS processes are influenced by thermodynamic and kinetic factors that can determine: \textit{stable systems} (where no phase separation is produced), \textit{metastable systems} (when the phase separation may take place), or \textit{unstable systems} (for which the phase separation does not take place).

The phase separation mechanism during the porous crosslinked polymer synthesis assumes

1. The sudden appearance of heterogeneity when the threshold concentrations of crosslinker and diluent are achieved
2. The formation of a porous structure with very large sizes compared to that of the primary nuclei
3. Important influences relative to the quantity and quality of diluent

The change in solvent quality from good to poor, from the increase in temperature, eventually leads to phase separation (Stieger et al. 2003).

When reaction takes place in both the dispersed and continuous phases, in spite of the low monomer solubility in water, the thermodynamic equilibrium between the continuous and dispersed phase is established before polymerization starts (Nzihou et al. 1997). A porogen can be used to increase the partition of a water soluble monomer in droplets when the continuous phase is water (Gokmen et al. 2012).

In order to obtain a heterogeneous system, phase separation must take place during the crosslinking process so that the dispersed structure can be fixed through the formation of new crosslinks.

A peculiarity of crosslinked (co)polymerization is the formation of networks at relatively low conversions at the moment when these structures (the networks) are strongly swollen in the mixture diluent-monomer, resulting in the phase separation starting close to the gel point.

The influence of the quantity and inert medium thermodynamic quality in the pore morphology formation depends on the moment in which phase separation takes place. As a function of the (co)polymerization reaction stage, phase separation, can take place at three different times:

- \textit{Before the gel point}, when inferior coarse structures are obtained. This occurs because the difference between the amount of polymer phase and diluent is high (in this case, before the structure to be fixed by crosslinking, the coalescence phenomenon occurs).
- \textit{Long after the gel point} (after the crosslinks formation), when the high crosslinking density from the polymer prevents the liquid microseparation and an exclusion occurs outside of the polymer (macrosinereza). A fine pore structure that determines the high specific surface appearance is created.
- \textit{At the gel point}. The best moment to start phase separation is at the gel point, when the dispersal structure is fixed by the formation of new crosslinks.
During the formation of networks from the unstable systems, when the cross-linking density changes are very fast, the restoring balance takes place due to the crosslinked structure reorganization. Because of the rapid changes in composition, the phase separation is accompanied by a macrogranulation due to the coalescence of the increasing particles. At a high crosslinker concentration and a high dilution, the volume transition phenomenon appears together with the phase separation.

Macrosyneresis occurs after the gel point, when the crosslinks form a coherent network. The beginning of phase separation can be established by combining equilibrium effects that change in the system because of the conversion and the network swelling.

Microsyneresis is a consequence of the polymer–solvent interaction and occurs during the network formation (crosslinking). Microsyneresis is not stable in time; it is a nonequilibrium phase that passes in an equilibrium syneresis (macrosinereza). This transition from micro- to macrosyneresis is due to network deformation, which explains the volume change that takes place in the cross-linked structures.

The porous copolymer volume often is higher than the liquid phase volume (consisting of monomers and inert medium) because the network monomers adsorption on the swollen network determines the network’s volume expansion.

In summary, the mechanism formation of the porous structures is due to the non-homogeneous nature of the crosslinking (co)polymerization as well as to the phase separation process (determined by the thermodynamics of the system).

3.5 THE PARTICLE MORPHOLOGY AND CHARACTERIZATION METHODS

Particle morphology is the factor that determines the commercial applications for these polymers. In a dried state, the (co)polymer beads are characterized by their true (skeletal) and apparent density, total porosity, total volume of pores, pore sizes, distribution of pore size, and their specific surface area.

The shape and structure (morphology) of the beads depend on the polymerization conditions and on the physical properties of the system. Polymerization conditions that particularly influence particle morphology are as follows:

- The coalescing and dispersing drops before and during polymerization
- The density change between monomer phase and polymer phase
- The monomer’s solubility in the polymer

In cases where the monomers are soluble during the copolymerization reaction, they are uniformly distributed in the reaction phase (monomer in the polymer droplet). But, in cases where the copolymer swells in monomers, two different compositions for the polymer droplet are obtained—one that is polymer-rich and another that is monomer-rich. If the compositions are sufficiently different, various structures can be obtained by the polymerization of the two phases.
The swelling capacity of various copolymers is a quantitative method for characterizing the crosslinked beads. The swelling and de-swelling volume depends on crosslinked density (Vlad and Mihailescu 2001).

The coalescence/dispersion factor is responsible for dispersing or particle agglomeration. Changes in the system’s qualitative and quantitative components ratio during the crosslinking reaction can lead to particle collapse (the lower polymer density, when compared with that of the monomer, generates pearls with a lower volume than that of the initial droplet).

Control of the pore size distribution is of great importance in (macro) porous polymer design. For example, small pores and large specific surfaces are typical characteristics of the beads used in column chromatographic fillers, while beads with large pores are used in nucleic acid separation or in enzymes immobilization.

Polydispersity is characterized by the use of specific equipment for high precision optical measurements—atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

### 3.6 ADVANTAGES AND AREAS OF USE

Numerous suspension polymerization experiments have highlighted the technical and economic advantages:

- Low costs compared with the wide variety of particle properties.
- Excellent heat transfer and handling of materials during the monomers’ transformation into the polymer.
- Ability to control the bead size.
- The use and separation of the resulting beads are simple procedures.
- There are a low number of components used in the polymerization system (compared to emulsion techniques).
- The purification procedure for the final product is relatively simple.
- May be stored in silos or tanks according to the manufacturer’s instructions regarding storage temperature and bead shape.

Typical crosslinked polymers do not possess porosity other than when they are swollen in solvents. After solvation, the polymer chains are separated from each other, and they form pores that are places (spaces) filled with solvent. This limited swelling takes place for low crosslinked polymers or macroporous gels (products easily deformable under pressure) and generally precludes their use in bead form (in liquid chromatography, for example).

Macroporous polymer beads, synthesized by suspension polymerization, are a class of polymer beads containing a permanent, well-developed porous structure in a dry state and having a wide range of applications—such as support for catalysts, immobilization of enzymes, HPLC columns, liberation of active substances, or adsorbents.

The beads are obtained in the presence of porogen (inert substance to monomers) that remains embedded inside the polymer bead and, finally, is removed to create
the grain pores. The internal structure of the macroporous beads consists of many interconnected cavities (pores) of different dimensions, with the beads’ stiffness due to extensive crosslinks. Their porous structure improves the diffusion of different solutes through the polymeric network. Because these networks have particular properties, such as a high degree of crosslinking and a rigid structure both in swollen and dry state, the study of their synthesis conditions is very interesting (Gomez et al. 2012).

Macroporous rigid polar organic beads are commonly used for aqueous size exclusion chromatography (SEC), for hydrophobic interaction and affinity chromatography of biopolymers (Svec and Regnier 2002), or to investigate retention properties (Mingcheng et al. 2003).

Significant progress has been made in developing porous polymer designs used in fields that focus on improving life (cosmetics, eye implants, and bone) (Chalasani et al. 2007).

Recent greater interest in porous polymers is due to their controllable porous structure as well as their mass transfer and binding capacity. By using one-step swelling and the polymerization method, the monodispersed macroporous particles are used as a supporting matrix. This novel, macroporous core–shell-imprinted material may become a powerful tool for rapid and efficient enrichment and separation of target compounds from complicated samples (Yongliang et al. 2014).

Two types of morphology in crosslinked polymer resins are commercially available and have been investigated: a gel type and a macroporous resin. The relatively rigid macroporous resin is available as hard opaque beads with permanent pores (Van de Steene et al. 2014). By optimizing the porous polymer synthesis methods through the application of a freeze-drying technique, very efficient adsorbents for removing arsenic have been obtained (Taleb et al. 2015).

Storage is an essential condition in the development of hydrogen-fueled vehicles. In this regard, porous carbon materials have attracted considerable attention as attractive candidates for hydrogen storage due to their good adsorptive capacity, low density, low cost, and high surface area (Jianwei et al. 2012).

### 3.7 REMARKS AND FUTURE DIRECTIONS

This chapter discusses crosslinked polymers with permanent porosity and the factors affecting their synthesis, formation mechanism, and properties. A characterization of these polymers can be made based on network formation theory or on experimental results. Because of differences between experimental results and theoretical predictions, individual methods are used to indicate areas of uncertainty that need further exploration.

Until the last century, crosslinked polymers were studied only for their applicative properties. Today, characterization techniques allow the study of factors affecting the formation mechanism as well as the balance between reaction parameters and properties. Depending on the required properties, this suggests that a porous crosslinked polymer can be prepared for a specific purpose, considering the influences and mechanisms of phase separation that develop during synthesis.
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