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CROSSLINKING

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9.1 INTRODUCTION

The concept of crosslinked polymers has already been introduced in Sections 1.1.7 and 1.2.3 of Chapter 1, as well as in Sections 3.8.1, 3.8.2, 3.8.3, 3.8.4, and 3.9.2 of Chapter 3. Brief mentions to crosslinking reactions or crosslinked polymers are also offered in other chapters of this handbook (e.g., Chapters 6 and 8). Some examples related to the modeling of network formation by free radical copolymerization (FRC) are briefly outlined in Chapters 12, 14, and 15. In Chapter 28, the chemistry of epoxy polymers and other thermosets synthesized by step-growth or chain-growth polymerizations, aimed at producing polymer networks, is described; structural transformations (gelation and vitrification) taking place during network formation are analyzed using a conversion-temperature transformation (CTT) diagram; general criteria and rules for processing the initial formulation are discussed for applications such as coatings and composites; and processing techniques are described for the production of filled or unfilled parts, and small, medium, and large series of composite materials. In this chapter, we define several terms related to polymer network formation; we also examine general aspects of some of the existing gelation theories and describe some aspects related to polymer network formation by copolymerization with crosslinking of vinyl/divinyl monomers.

A polymer network can be envisioned as a polymer molecule with an infinite molecular weight [1]. Crosslinking is a physical or chemical route by which polymers with branched or crosslinked structures are produced. The chemical route may imply a polymerization or postpolymerization stage [2–4]. Crosslinking is especially important from the commercial point of view. Polymer networks may

be undesirable for some applications; in such cases, chain transfer agents can be used to prevent or delay gelation. On the other hand, many commercial polymers owe their value to their crosslinked structures, which can range from only slightly to highly crosslinked materials. Crosslinked polymers exhibit completely different properties when compared to linear polymers with identical chemical compositions. The degree of branching/crosslinking influences polymer properties such as density, melt viscosity, and crystallinity; it also determines the flow behavior of the material. While noncrosslinked polymers are in general thermoplastic, and they can be melted and casted, extruded, or (injection) molded, highly crosslinked polymers become thermoset, and they do not flow when heated. However, polymer properties can also depend on network topology (see Fig. 9.1 for a schematic representation of two possible topologies).

9.2 BACKGROUND ON POLYMER NETWORKS

9.2.1 Types of Polymer Networks Based on Structure

9.2.1.1 Definition and Structure of Polymer Networks

A polymer network can be defined as a highly crosslinked macromolecule in which essentially all units are connected to each other in some way, either via chemical bonds or physical associations.

The structure of a polymer network can be simply depicted as a three-dimensional “mesh” formed by polymer chains interconnected by crosslink points. However, the actual structure of this “mesh” is not regular and the distribution of polymer chain length between joining points is unequal throughout the whole network. Hence, a polymer

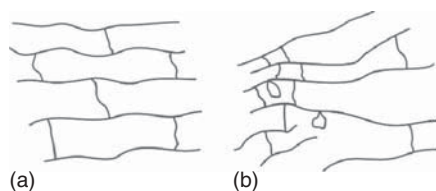


Figure 9.1 Two different topologies for a polymer network.

network represents an ensemble of regions (domains) of different structures with different crosslink densities, resulting in a heterogeneous structure. A homogeneous polymer network would be obtained if a uniform distribution of functional groups took place with the absence of structural defects. Four main types of inhomogeneities are commonly recognized in a polymer network structure: (i) chains attached to the network by only one end, yielding loose, dangling polymer chains; (ii) rings, loops, or cycles produced if a chain is joined by its two ends to the same crosslink point; (iii) permanent chain entanglements between two adjacent crosslinks; and (iv) multiple connection between two crosslink points, as shown in Figure 9.2 [5]. Inhomogeneities can be formed during both physical and chemical crosslinking. Physical networks can possess clusters of molecular entanglements, or domains of highly hydrophobic or ionic association, leading to an unequal distribution of joining points. Polymer networks formed by chemical bonding can contain regions of high crosslink density and low solvent swelling (clusters), immersed in regions of low crosslink density and high swelling index. For the case of hydrogels synthesis, for example, this may be due to hydrophobic aggregation of crosslinking agents, resulting in the formation of high crosslinked clusters [6]. The presence of unequal reactivity of the functional groups involved during network synthesis and the formation of cycles can also result in these types of clusters. According to the topology and structural level of perfection, several type of polymer network can be recognized: ideal (or perfect), model, and imperfect networks.

9.2.1.2 Ideal or Perfect Networks¹ The IUPAC Commission on macromolecular nomenclature defines a perfect network as a network composed of chains all of which are connected at both of their ends to different junction points [7]. If a perfect network is in the rubbery state, then, on macroscopic deformation of the network, all of its chains are elastically active and display rubber elasticity. An ideal or perfect network can also be defined as a collection of individual Gaussian elastic chains (linear

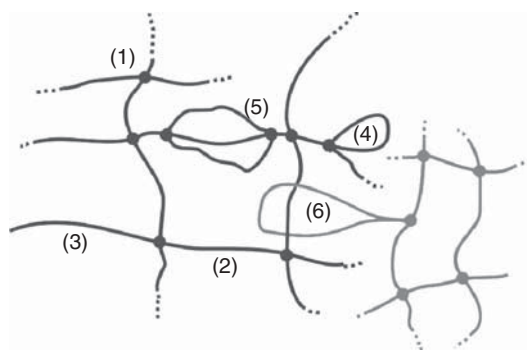


Figure 9.2 Main elements constituting the structure of a polymer network: (1) crosslink point, (2) elastically active chain, (3) dangling chain, (4) loop or cycle, (5) multiple connection between two crosslink points, and (6) permanent chain entanglements between two adjacent crosslinks.

chain elements) connecting f -functional crosslinks (junction points or branch points). This definition has several basic requirements [5]: (i) the lengths of all elastic chains of the network should be identical: all of them should be connected by one elastic chain only; (ii) the network should be Gaussian: the dimensions of each effective elastic chain should obey Gaussian statistics; (iii) the network should be macroscopically as well as microscopically homogeneous: no syneresis should have occurred during its formation; segment and crosslink densities should be identical throughout the network; and (d) the functionality f of the crosslinks should be known and constant throughout the entire network.

9.2.1.3 Imperfect Polymer Network In this network, both the elastic chain lengths and the functionality f are broadly distributed throughout the entire network. Moreover, the two major types of network defects are present at a noteworthy extent in this type of network: loose, dangling (singly attached) chains, and inactive rings or loops (cycles). For the case of a polymer network synthesized chemically with a tetrafunctional crosslinker, a junction point would be elastically active if at least three paths leading away from it are independently connected to the network. In addition, a polymer chain segment (strand) in the network would be elastically active if it is connected at each end by elastically active junctions. For a perfect tetrafunctional network, there are twice as many strands as junctions. Thus, besides causing a lack of structural order in the polymer network, free chain ends and loops also represent defects because they are not part of the network, and therefore, they do not contribute to the elasticity of the structure, thus reducing the concentration of elastically active network chains, and as a result, the shear modulus and Young's modulus are less than their respective value expected for an ideal network [8].

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9.2.1.4 Model Polymer Network² Ideal and imperfect polymer networks represent the two extremes in polymer network structures. Model networks are intermediate between these two. A model network can be prepared using a nonlinear polymerization or by crosslinking of existing polymer chains. A model network is not necessarily a perfect network. If a nonlinear polymerization is used to prepare the network, nonstoichiometric amounts of reactants or incomplete reaction can lead to networks containing loose ends. If crosslinking of existing polymer chains is used to prepare the network, then two loose ends per existing polymer chain result [7]. Rings can be present in model networks as well.

A model network should, at least, satisfy the following conditions [5]: (i) the linear chain element of a model network should exhibit known length and, if possible, a narrow molar mass distribution (\mathcal{D}_M): each elastic chain should be connected by its two ends to two different crosslink points; (ii) a model network should be homogeneous: crosslinking density should be constant throughout the gel; and (iii) a model network should exhibit a known and constant functionality of crosslink points.

9.2.1.5 Interpenetrating and Semi-Interpenetrating Polymer Networks The void space in the structure of the polymer network can be occupied by other molecules. When this space is occupied by other polymer network, interpenetrating or semi-interpenetrating polymer networks result.

Interpenetrating Polymer Network (IPN) An interpenetrating polymer network (IPN) is an intimate combination of two or more polymer networks where at least one of which is synthesized and/or crosslinked in the presence of the other. These two polymer networks are partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken. However, phase separation could limit actual interpenetration [8].

Semi-Interpenetrating Polymer Network (SIPN) A semi-interpenetrating polymer network (SPIN) is a combination of two or more crosslinked polymers with two or more linear or branched polymers, at least one of which was synthesized and/or crosslinked in the presence of the others. An SIPN is distinguished from an IPN because the constituent linear or branched macromolecules can, in principle, be separated from the constituent polymer network(s) without breaking chemical bonds; it is a polymer blend [7].

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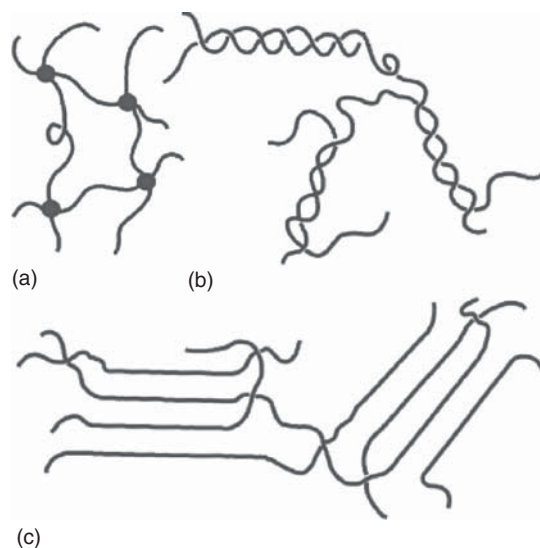


Figure 9.3 Types of links in a thermoreversible gel (a) by junction points, (b) by junction zones, and (c) by fringe micelles. Source: Reprinted with permission from Sperling LH. *Introduction to Physical Polymer Science*. 4th ed. Hoboken, Wiley Interscience; 2006 [8]. Copyright 2006 John Wiley and Sons.

9.2.2 Chemical and Physical Networks

Polymer networks can be classified as physical or chemical depending on the way of interconnection of the polymer chains that constitutes the network.

9.2.2.1 Physical Networks If the polymer chains in a polymer network are bonded via physical association, the networks are called *physical* or *reversible*. Physical interactions need not be permanent over the time scale of the observation or measurement [7]. The interaction can be due to hydrogen bonds, π – π interactions, chain entanglements, etc. A physical network tends to be reversible. Reversible networks are those that form or break up as temperature is changed or under the action of a force. There are three types of links in thermoreversible gels: (i) single point bonds, called *point crosslinks*; (ii) junction zones, where interactions between chains act over a segment of their length, forming ordered secondary structures such as multiple helices; or (iii) fringe micelles, where the chains align in some regions to form small crystallite domains (Fig. 9.3). Some other weak interactions, as ion complexation, can also lead to the formation of physical networks [9].

9.2.2.2 Chemical or Covalent Networks If the interconnections that join the constituting polymer chains in a polymer network are made via chemical bonds, the networks are

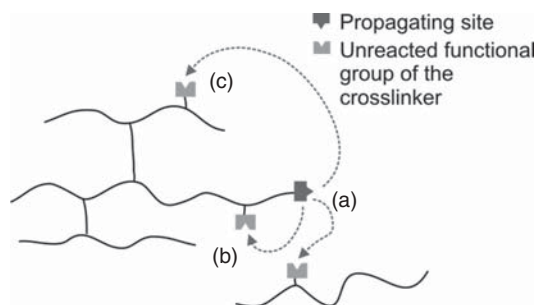


Figure 9.4 Different types of crosslinkages: (a) intermolecular, (b) intramolecular, yielding a primary cycle, and (c) intramolecular, yielding a secondary cycle.

called *chemical* or *covalent*. These polymer networks possess intermolecular or intramolecular interactions that are stable under the conditions of use of the material formed.

9.2.3 Intermolecular and Intramolecular Crosslinking

Intermolecular crosslinking involves the bonding between functional groups present on two different polymer molecules and, as a result, these two molecules link together, forming a single new macromolecule with an increased chain length. Intramolecular crosslinking occurs between two functional groups on the same polymer, causing connective loops or cycles within the macromolecule. Hence, this type of reaction is commonly referred to as *cyclization*. Similar types of intramolecular connections occur in polypeptides [10]. Typically, two different types of cycles can be distinguished. When the cycle is formed by reacting two functional groups attached to the same primary chain, a primary cycle results. On the other hand, when an extra link is formed between two primary chains that have already experienced crosslinking, a secondary cycle is formed (Fig. 9.4).

Intramolecular reactions (cyclization), in contrast to intermolecular ones, do not contribute to the growth of the molecular structure during polymerization and, therefore, they do not affect the molar mass distribution of the polymer population. However, the cyclization reaction manifests itself by a shift to a higher value of the critical conversion for onset of gelation and by a reduced amount of gel content during the formation of the polymer network. In addition, as more compact structures are produced by intramolecular crosslinking, it is also expected that some hydrodynamic volume dependant properties are affected, for instance, intrinsic viscosity [11]. Intermolecular and intramolecular crosslinking tend to occur simultaneously because both reactions involve the same functional groups. The relative reaction rates are determined by polymer concentration and chain length. Thus, at very low polymer concentrations, intramolecular crosslinking dominates, yielding

highly crosslinked particles (usually referred to as microgels) as product, whereas at higher polymer concentrations, intermolecular crosslinking is the dominant route, leading to a polymer network [12]. The presence of microgels in the network structure brings about an extremely restricted segmental mobility, while other regions of the polymer network experience a more mobile local environment, resulting in an inhomogeneous distribution of segmental mobilities and broader relaxation time distributions.

The experimental evidence reveals that the main parameters affecting the ratio intramolecular/intermolecular crosslink reaction rates are polymer concentration (degree of dilution), crosslinker content, and crosslinker structure.

9.2.4 Monomer Functionality (f)

The key parameter during the synthesis of polymer networks is the functionality f of the monomer, which is defined as the number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants [7]. Note that there are no monofunctional monomers, as the minimum required functionality for the backbone formation is two. When $f = 2$, only a linear chain macromolecule or a macrocycle can be formed.

9.2.5 Crosslink Density

According to the IUPAC Commission on macromolecular nomenclature, crosslink density is defined as the number of crosslinks per unit volume in a polymer network [7]. The degree of crosslinking is a fundamental property for polymer networks. A change in the level of crosslinking causes remarkable changes in the properties of the polymeric material. Crosslinking improves resistance to thermal degradation and resistance to cracking effects by liquids and other harsh environments, as well as resistance to creep, among other effects. Slight crosslink densities impart good recovery properties to polymers used as elastomers. On the other hand, high crosslink densities impart high rigidity and stability under heat and stress to polymers such as phenol–formaldehyde and urea–formaldehyde polymers.

9.2.6 Gelation and Swelling Index

During the formation of polymer networks, consecutive crosslinking brings about insolubility as a result of the remarkable increase in molecular weight. A polymer network will not dissolve in any solvent at any temperature before degradation, and it will only swell, reaching an equilibrium degree of swelling as solvent molecules diffuse into the polymer network. The formation of gel at some point of the network-forming process is characteristic when synthesizing polymer networks. A polymer gel is formed by

a polymer network expanded throughout its whole volume by its own monomer or the solvent employed during the synthesis of the network. The time of incipient network formation is referred to as *gelation point*. The mass fraction of the polymer that still remains soluble is referred to as *sol fraction*, whereas the insoluble fraction is known as *gel fraction*. Before the gelation point, the entire polymer is sol, but beyond this point, soluble polymer incorporates into the network and the amount of gel increases. The gelation point is characterized by a significant increase in the value of several properties, such as viscosity, which quickly diverges at this point, or the case of equilibrium shear modulus, which rises from zero to eventually reaching a plateau [8].

9.2.6.1 Swelling Index Swelling is defined as the increase in volume of a gel or solid associated with the uptake of a liquid or gas [7]. In fact, swelling represents the first stage in every polymer solution process, in which the solvent molecules diffuse through the polymer matrix to form a swollen, solvated mass, known as *polymer gel*. However, the gel formed after swelling polymer networks does not break up and the polymer molecules do not diffuse out of the swollen mass, and therefore, no real solution can be formed.

The swelling coefficient, Q , is defined by

$$Q = \frac{m - m_0}{m_0} \frac{1}{\rho_s} \quad (9.1)$$

where m is the weight of the swollen sample, m_0 is the dry weight, and ρ_s is the density of the swelling agent [8]. Equilibrium swelling index is determined by crosslink density and the attractive forces between solvent and polymer. The theoretical extent of swelling is predicted by the Flory–Rehner equation [13] (Eq. 9.2):

$$\ln(1 - v_2) + v_2 + \chi_1 v_2^2 = -\frac{V_1}{\bar{v}_2 M_c} \left(v_2^{1/3} - \frac{2v_2}{f} \right) \quad (9.2)$$

where v_2 is the volume fraction of polymer in the swollen mass, χ_1 is the Flory–Huggins solvent–polymer dimensionless interaction parameter, \bar{v}_2 is polymer specific volume, M_c is the average molecular weight between crosslinks, V_1 is solvent molar volume, and f the functionality of the crosslinks. The relationship between swelling index, Q , and volume fraction, v_2 , is given by

$$Q = \frac{V_H}{V_0} = \frac{1}{v_2} \quad (9.3)$$

where V_H is the volume of the swollen gel at equilibrium and V_0 the volume of the dry polymer network.

9.3 MAIN CHEMICAL ROUTES FOR SYNTHESIS OF POLYMER NETWORKS

From a general point of view, chemical crosslinking processes can be classified into four major types of reactions: step-growth polymerization, free radical polymerization, vulcanization, and end-linking of prepolymers.

9.3.1 Step-Growth Polymerization

Chapter 3 is devoted to step-growth polymerization. Here, some aspects related to crosslinking and gelation are highlighted. Nonlinear polymer molecules are obtained by step-growth polymerization when the functionality of one of the monomers is greater than two. The simplest example of such a reaction is the step-growth copolymerization of an AB monomer with a small amount of a f -functional monomer A_f (with $f > 2$). The resultant polymer has a branched structure in which f chains emanate from a branching point induced by the presence of the multifunctional monomer. However, since the reactive groups type A do not react with themselves, a crosslinked polymer will not be formed, as all growing chains coming from the branching point have functional groups type A at their ends. However, the copolymerization of AB with A_f in the presence of B_2 will lead to the formation of a crosslinked polymer. Other reacting systems that can lead to a crosslinked polymer, and eventually to gelation, are the polymerization of $A_2 + B_f$, $A_2 + B_2 + B_f$, and $A_f + B_f$, (all with $f > 2$). Many thermoset polymers of major commercial importance are synthesized by step-growth polymerization, as the case of unsaturated polyester, polyurethanes, melamines, phenolic and urea formaldehyde resins, epoxy resins, silicones, etc. In these systems, the crosslinking process, which leads to a polymer network formation, is usually referred to as *curing*.

9.3.2 Vulcanization

Vulcanization is a chemical process where linear polymer chains become crosslinked by the action of certain agents that attack some active functional groups present in the polymer backbone, thus improving the mechanical properties of the resultant polymer structure. Vulcanization by sulfur bonding is one of the main employed techniques for crosslinking of elastomers (Fig. 9.5). In vulcanization by sulfur, allylic hydrogen atoms represent the active sites. Rhombic sulfur is the most widely vulcanizing agent used for crosslinking of polymer chains with diene groups, such as natural rubber, styrene–butadiene rubber, and polybutadiene, although other chemical compounds can also be used as sulfur source, such as tetramethylthiuram disulfide (TMTD), which is also employed as an accelerator agent to speed up vulcanization rate. Some other accelerators are thiazoles, sulfenamides, guanidines, carbamates, thiurams,

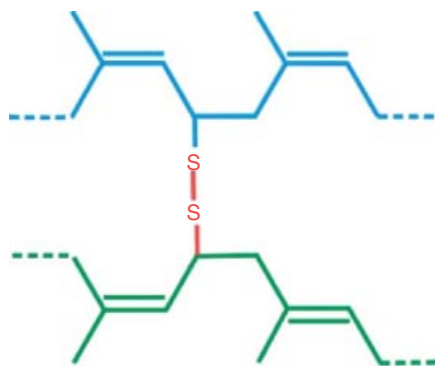


Figure 9.5 Representation of two primary chains of natural rubber (*cis*-1,4 polyisoprene) linked by vulcanization with sulfur.

xanthates, and phosphates [14]. Activators such as a zinc salt of a fatty acid or a combination of zinc oxide and a fatty acid are also used to increase the solubility in rubber of accelerators. Other broadly used vulcanizing agents are peroxides, which crosslink the polymer chains by the formation of stronger carbon–carbon bonds, instead of carbon–sulfur bonds. In fact, vulcanization by peroxides represents the route of choice for crosslinking of saturated elastomers, such as ethylene–propylene rubber (EPM), since sulfur cannot be employed for the curing of these materials because of the absence of double bonds in the polymer backbone [15]. Some metal oxides are employed as vulcanizing agents for the case of halogenated elastomers. High energy irradiation is also used [16, 17].

9.3.3 End-Linking

Model networks can be synthesized by end-linking of pre-existent linear polymer chains. In this type of network formation, two f -functional reactive groups are attached to each end of the linear prepolymer (telechelic prepolymers). The crosslinking step is then performed by bonding of the end groups. Anionic polymerization has been used for the synthesis of the well-defined macromolecules by this route. The resulting polymer networks should have crosslink points of functionality equal to that of the crosslinking agent, and the average molecular weight between crosslinks should correspond to that of the prepolymer, before crosslinking. However, this technique does not impart any control over the number of chains attached to one given crosslinking point, and fluctuations of this value can occur along the network. In addition, some network defects can be present, such as dangling ends and cyclization. The incidence of dangling-end network imperfections in model networks is reduced if the end-linking reaction is carried out under stoichiometric conditions and high conversion of

functional groups is reached. A comprehensive review on the end-linking process is available in the literature [5].

9.3.4 Free Radical Copolymerization (FRC)

FRC of a vinyl monomer with a small amount of divinyl monomer represents one of the simplest methods for synthesizing polymer networks. In these systems, the divinyl monomer acts both as a comonomer and as a crosslinker. One of the most common and studied systems of this type is the copolymerization of styrene (STY) and divinylbenzene (DVB). Poly(STY-*co*-DVB) copolymers are widely used as ion-exchange resins and separation media for size-exclusion chromatography, although several other vinyl/divinyl copolymerization systems have also been studied [18].

Polymer networks synthesized by conventional FRC present heterogeneous structures due to the inherent characteristics of this method, such as slow initiation, fast chain propagation, high termination rates, and high molar-mass dispersity (\mathcal{D}_M) of primary chains. In these systems, primary radicals are produced gradually and constantly during the initiation step, allowing polymers of high chain length to be formed from the beginning of the reaction. At this stage, these growing polymer chains are immersed in a highly diluted environment (either by their monomers only, or by their monomers and solvent). Under these diluted conditions, polymer chains hardly ever overlap each other. Consequently, most of the pendant double bonds are consumed through intramolecular crosslinking (cyclization), undergoing gelation at a nanoscale. As the reaction and crosslinking proceeds, new polymer chains are continuously generated, promoting intermolecular crosslinking, which in turn leads to increased chain lengths. Once large polymer chains are produced and polymer concentration increases, they will react with each other through their available pendant double bonds and radical centers, and microgels will be produced. These agglomeration processes will continue until the onset of gelation is eventually reached, when all these microgels are interconnected. Therefore, gel formation by means of conventional FRC is the result of a continuous association of microgels, where each one could experience a different crosslink history, and as a result, these gels are intrinsically heterogeneous.

In the FRC of vinyl and multivinyl monomers, a drift in the instantaneous copolymer composition throughout the reaction will be undergone due to the different reactivities of the vinyl groups. This compositional drift is caused by the fact that the more reactive monomer will be consumed faster than the less reactive ones. In the simplest instance, assuming equal reactivity of the vinyl groups in mono- and divinyl monomers present in the reaction system, the reactivity of the crosslinker would be twice that of the monovinyl monomer, and therefore, the polymer chain

segments formed at early conversions would possess higher content of divinyl monomer than those formed at advanced stages of the reaction. As a consequence, the domains in the polymer network formed at early stages are more crosslinked than the domains formed later, and the resultant polymer network displays a crosslink density distribution. Some of the factors affecting the extent of compositional drift are the ratio of reactivity ratios r_1/r_2 , the initial monomer composition, and monomer conversion [19]. In addition, the pendant double bonds are less reactive, thus making the system more complex, and the polymer network more heterogeneous [20, 21]. The theory and mathematical modeling of polymer network formation by free radical copolymerization of vinyl/divinyl monomers was reviewed and analyzed by the group of Hamielec [22–25].

9.4 CHARACTERIZATION OF POLYMER NETWORKS AND GELS

In Section 16.3.9 of Chapter 16, it is mentioned that RT-FTIR is used to follow the polymerization of monomer mixtures leading to either crosslinked copolymers or IPNs. In Section 18.4.3 of Chapter 18, it is mentioned that dynamic light scattering (DLS) has been applied to study the effect of crosslinking on the dynamics of the sol–gel transition. In Section 21.2.1 of Chapter 21, it is recognized that the degree of crosslinking affects the glass transition temperature of a polymer and also affects shear modulus. Other than those just mentioned, there are no other aspects of polymer network characterization covered in other chapters of this handbook. Therefore, some additional aspects of polymer network characterization are summarized here.

9.4.1 Determination of the Gelation Point

At the onset of gelation, some physical properties of polymeric materials suffer significant changes. The change of these physical properties, such as viscosity, modulus, or dielectric properties, is the key in several methods to determine the gelation point. In general, gelation time (t_{gel}) or monomer conversion at the onset of gelation (α_{gel}) are employed to express the occurrence of the gelation point.

Measurement of steady-state viscosity represents one of the simplest methods to estimate the gelation point. According to this technique, the gelation point corresponds to the time t at which the static viscosity “goes to infinity” [26, 27]. However, it possesses some drawbacks, as the gelation point is usually found by extrapolation and the experiments are restricted to the pregel period, usually stopping the measurement before the onset of gelation to avoid overload in the equipments and sample fracture.

The gelation point can also be measured by dynamic mechanical analyses (DMA). Several criteria have been proposed for identifying the onset of gelation. One of these criteria considers the gel point as the point of crossover between the base line and the tangent, drawn from the turning point of a G' curve [28, 29]. Another criterion is to define the gelation time as the point where $\tan \delta$ is independent of frequency [30, 31]. However, the most widely employed criterion for determination the onset of gelation is the point of intersection of the storage $G'(\omega)$ and loss moduli $G''(\omega)$ (ω defined as angular frequency) [32]. It has been pointed out that this condition is only satisfied if stress relaxation at the critical gelation point follows a power law:

$$G(t) = St^{-n} \quad (9.4)$$

where S is a material constant related to the strength of the polymer chains and $n = 1/2$ [33].

As mentioned before, gelation is characterized by a notable increase in viscosity, thus greatly reducing the mobility of polymer chains. This has been employed by some authors to estimate the gelation point by differential scanning calorimetry (DSC), analyzing this phenomenon in a similar way as with polymer vitrification [34]. However, in general, the occurrence of gelation does not provoke a variation in the reaction rate profile, as the case of thermosets, in which the gelation conversion is independent of temperature [35]. Thus, gelation cannot be detected directly by DSC, which is a technique responsive only to the chemical reaction and phase transitions.

Dielectric analysis (DEA) comprises a group of methods that evaluate the response of some properties of polar materials to changes in temperature or frequency. Usually, the evaluated properties are polarization, permittivity, and conductivity. For crosslinked materials, Mangion and Johari [36–38] have demonstrated that the ionic conductivity of a polymer solution decreases at the vicinity of the gelation point, following a power law equation, and they proposed that the relationship between the ionic conductivity (σ) and the kinetics of the reaction during the pregel stage is given by

$$\sigma = \sigma_0 \left(\frac{x_{\text{gel}} - x}{x_{\text{gel}}} \right)^k \quad (9.5)$$

where σ_0 is the conductivity at $x = 0$ and k is a critical exponent that depends on temperature. Equation 9.5 is in agreement with percolation theory. In fact, the form of Equation 9.5 is similar to the one used to estimate the gelation point based on the divergence of viscosity data [39]. A plot of $\log(\sigma)$ as a function of $\log(x_{\text{gel}} - x)$ should yield a straight line with slope k . The functional form of Equation 9.5 suggests that σ approaches zero at the vicinity of gelation. The inflection point of the plot of conductivity

versus time profile has been used as an indication of the onset of gelation [40]. It has been found that the estimates of gelation time using Equation 9.5 are in good agreement with those obtained by DMA [41].

9.4.2 Measurement of Crosslink Density

Usually, crosslink density is expressed in terms of the average molecular weight between crosslinks, M_c . There are several experimental techniques available for measurement of crosslink density, such as DMA, equilibrium swelling, NMR spectroscopy, and dielectric measurements, among other methods. Reviews on these experimental techniques are available in the literature (e.g., Ref. [42]). Some aspects about three of the most important techniques are briefly highlighted here.

When a polymer network is sufficiently crosslinked so that a structure with a reasonable degree of mechanical integrity above its glass transition temperature is obtained, the molecular weight between entanglements or crosslinks can be estimated using DMA, by calculating the storage modulus. The storage modulus, either E' or G' , is a measure of the sample's elastic behavior. An important feature of the storage modulus curve is the plateau in the rubbery region, given that its value is directly related to the crosslink density of the polymer network [43, 44]. The mathematical relationship between elastic (shear) modulus G and molecular weight between crosslinks M_c (and therefore, the crosslinking density), in terms of the elementary Gaussian network theory, is given by Equation 9.6 [43, 44]:

$$G = NkT = \frac{\rho RT}{M_c} \quad (9.6)$$

where N is the number of network chains per unit volume, k represents bulk modulus, ρ is the density of the network, T is absolute temperature, and R the gas constant. Equation 9.6 is valid for polymer networks synthesized with low crosslinker content; a correction is needed for highly crosslinked polymer networks [44]. For a polymer network with loose ends (which make no contribution to the network elasticity), the corresponding shear modulus is given by Equation 9.7 [45]:

$$G = N_e kT = \frac{\rho RT}{M_c} \left(1 - \frac{2M_c}{M}\right) \quad (9.7)$$

where N_e represents the number of effective chains. Additional factors such as a distinction between different types of junction points, according to the functionality of the crosslinker, and the effect of the presence of chains not directly connected to the network (sol) have been considered [46, 47].

The extent of swelling is inversely proportional to network crosslink density and is highly dependent on the

type of solvent and temperature. The thermodynamics of the swelling network process is commonly described by the Flory–Rhener equation [13] (Eq. 9.2, based on the affine deformation model). The crosslink density for $f = 4$ can be determined by using Equation 9.8:

$$\rho = \frac{1}{2\bar{v}_2 M_c} \quad (9.8)$$

When the junctions (crosslinks) are allowed to fluctuate (phantom model), the Flory–Rhener equation takes form shown in Equation 9.9:

$$\ln(1 - v_2) + v_2 + \chi_1 v_2^2 = -\frac{V_1}{\bar{v}_2 M_c} \left(1 - \frac{2}{f}\right) v_2^{1/3} \quad (9.9)$$

The actual swollen behavior of polymer networks lies in between the extremes calculated with the affine deformation and phantom network models [48, 49]. The sources of error/uncertainties during swelling equilibrium measurements, related to the estimation of the volumetric fraction of polymer, the interaction parameter, and the selection of the Flory–Rehner model (affine deformation or phantom network model), have been reviewed recently [50].

Crosslink density can also be measured experimentally by nuclear magnetic resonance (NMR). NMR experiments provide information about the local and long-range mobility of network polymer chains. The spin–lattice relaxation time (T_1) is related to the segmental (short-range) motion in the polymer chains; it provides information regarding the elasticity and flexibility of the material. The transverse magnetization relaxation time, usually referred to as spin–spin relaxation time (T_2), is related to intersegmental (long-range) motions of the polymer chains. These types of motion are highly sensitive to the presence of crosslinks [51] and consider the dynamics of the crosslinked network, as well as of the dangling free chain ends. Therefore, this property has been widely used for the evaluation of crosslink density [52, 53]. Several models have been proposed to relate transverse relaxation time with crosslinking and/or entanglement densities [54–57].

The total transverse relaxation function $M(t)$ for inter-crosslinked chains and dangling chain ends follows an exponential correlation function [58], as shown in Equation 9.10:

$$M(t) = A \exp\left\{-\frac{t}{T_2} - qM_2\tau_s^2 \left[\exp\left(-\frac{t}{\tau_s}\right) + \frac{t}{\tau_s} - 1\right]\right\} + B \exp\left(-\frac{t}{T_2}\right) \quad (9.10)$$

where A and B are the fractions of proton magnetization of the inter-crosslink chains and the dangling chain ends

of the network, respectively; M_2 is the second moment of the dipolar interactions; τ_s is the correlation time for overall isotropic motion; τ_f is the correlation time for segmental motion; q is the remaining fraction of the dipolar interaction M_2 during the inter-crosslink chains motion; and $1/T_2 = M_2\tau_f$. The average molecular weight between crosslinks, M_c , can be calculated from Equation 9.11, assuming that the polymer chains behave according to a Kuhn statistical segment [59]:

$$M_c = \frac{3c_\infty M_{ru}}{5n\sqrt{q}} \quad (9.11)$$

where c_∞ is the number of backbone bonds in a Kuhn segment and M_{ru}/n is the mass of the chemical repeating unit per number of backbone bonds in this unit.

9.5 THEORY AND MATHEMATICAL MODELING OF CROSSLINKING

Historically, Carothers [1] was the first scientist who derived an expression to calculate the extent of reaction at which gelation occurs. He defined a polymer gel as a polymer network that has an infinitely large molecular weight. Consequently, his conception of the gelation point was based on the divergence of the number-average molecular weight (M_n). However, at the gelation point, there will be polymer molecules bigger than M_n and divergence in M_n would manifest itself, if at all observed, only after the actual gelation phenomenon has taken place. Later, Flory [60] gave continuity to the concept of infinite molecules by means of a statistical treatment on a weight basis, presenting the conditions for the onset of gelation in polycondensation systems. His work together with the work developed by Stockmayer [61, 62] for free radical polymerization with crosslinking set up the basis of what is known as the *classical theory of gelation*.

The formation of polymer networks by step-growth polymerization has been modeled using statistical theories, such as the Flory–Stockmayer classical theory [61–64], the Macosko–Miller conditional probability model [65–70], and Gordon’s cascade theory [71–74]. However, statistical methods have not been successful for modeling of polymer network formation in chain-growth polymerization systems.

To address polymer network formation from nonlinear chain-growth polymerization (or copolymerization), kinetic methods are more appropriate [23, 75–83]. Some of the most successful kinetic models to address this type of system are based on the method of moments [23, 75–77, 79, 80, 82, 84]. Some divergence problems at the vicinity of the gelation point are common with the method of moments, although there are practical ways to avoid this situation [80]. A more refined kinetic method to address the issue of modeling the dynamics of gelation in

chain-growth polymerization reactors, without divergence problems, is the numerical fractionation technique (NFT) of Teymour and Campbell [83]. In the NFT, the population of polymer molecules is divided into generations, with each generation having the same type of architecture. It is possible to calculate the full molecular weight distribution (MWD) with this technique, but to do that it is assumed that the MWD of each independent generation is well represented by the Flory–Schulz most probable distribution [83], or other pre-established theoretical distributions.

Percolation theory approaches have been extensively used to model possible deviations from the classical Flory–Stockmayer theory [85]. With Percolation theory, it is possible to obtain useful information on the microstructure and connectivity of the polymer chains [85], but it has not been proven useful for polymerization reactor design and dynamic analyses [83]. Percolation theory usually requires Monte–Carlo (MC)-type simulations, which are very demanding of computer time. The group of Peppas have presented interesting kinetic simulations for several polymerizations leading to gelation, including the homopolymerization of tetrafunctional monomers [86]. Tobita has also modeled branching and crosslinking in free radical polymerization using MC methods [87].

It is important to point out that every theory possesses its own advantages and disadvantages; the choice of the most suitable method depends on the type of system analyzed, the required information, the level of detail in the reaction scheme, and the computational resources available. Thus, up to now there is not a unified approach that can deal with every crosslinking system, considering all the implementation difficulties and taking into account all nonidealities present in these systems, such as cyclization. A few details about each theory are offered below.

9.5.1 Statistical Gelation Theories

Statistical theories are mean field theories, assuming equal reactivities of the functional groups (where each functional group reacts independently of one another) and absence of intramolecular (cyclization) reactions. In the so-called classical theory of gelation, Flory devised a simple treelike model, where branched and crosslinked structures are generated from monomer units or larger structural fragments under different reaction states. These reaction states are represented by the number and type of reacted functional groups and type of bonds that link one unit with its adjacent units.

Let us consider the nonlinear polymerization of a monomer bearing f functional groups, A_f . The simplest representation of such a concept is shown in Figure 9.6, for a three-functional unit. This unit can hold four reaction states, from 0 to 3, which indicates the number of reacted bonds that link this unit with its neighbor.

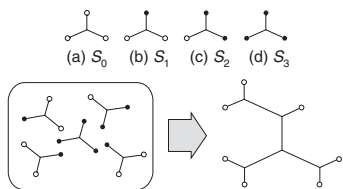


Figure 9.6 Representation of a trifunctional monomer according to the classical theory of gelation. The monomer can hold four reactive states, from 0 to 3, which indicate the number of functional groups that have been reacted, linking this unit with its neighbor. *Source:* Adapted with permission from Dusek K, MacKnight WJ. Crosslinking and structure of polymer networks. In: Labana SS, Dickie RA, Bauer RS, editors. *CrossLinked Polymers*. American Chemical Society; 1988. p. 2 [88]. Copyright 1988 American Chemical Society.

The linking process can be depicted by a tree graph in which each node represents a monomer unit. This picture is built by selecting one node at random from one polymer chain. The chosen node represents the root of the tree and, therefore, generation zero. Subsequently, the neighboring nodes linked to this node represent the first generation. Those nodes attached to this first generation represent the second generation and so on (Fig. 9.7).

In general, when a monomer unit is chosen randomly as the root of the tree in an f -functional system, the number N_r of components that can be introduced into generation g_r at conversion α is given by

$$N_r = f\alpha [(f-1)\alpha]^{r-1} \quad (9.12)$$

Once a gel is formed, the number of nodes in the rooted tree can be either finite or infinite. If it is infinite, the node chosen as the root of its tree is part of a gelled polymer chain. Flory's theory of gelation proposes that infinite network formation becomes possible when the number of units that can be added into a new generation (N_{r+1}) through branching of some of them, exceeds the value of his preceding generation (N_r). That is, if f is the functionality of the branching unit, gelation will occur when $\alpha(f-1)$ exceeds unity. Therefore, the critical value of α can be expressed by the general expression:

$$\alpha_c = \frac{1}{f-1} \quad (9.13)$$

For the case of a three-functional monomer, this will happen at $\alpha_c = 0.5$. This can be graphically expressed by means of Equation 9.12, as shown in Figure 9.8. At conversions $\alpha < \alpha_c$, N_r decreases with r . Just at $\alpha = \alpha_c$, $N_{r+1}/N_r = 1$ for any generation r , which represents the critical condition for the onset of gelation. For values of α greater than α_c , the values of N_{r+1} are always larger than N_r .

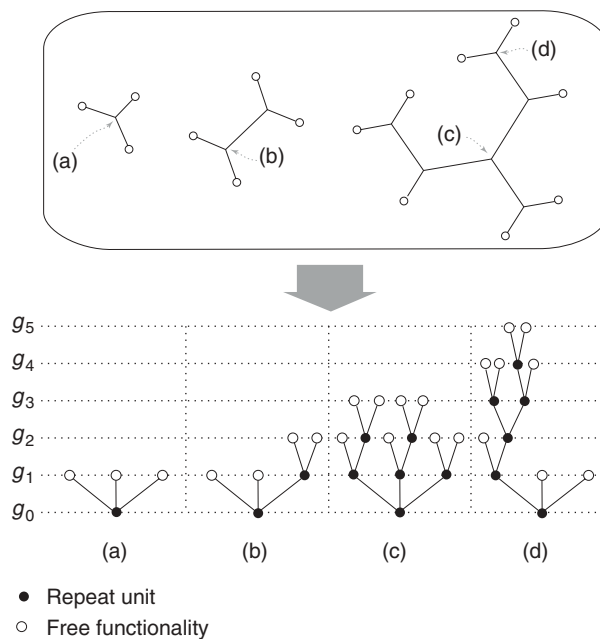


Figure 9.7 Tree plot for conceptualizing the crosslinked polymer structure, according to the classical theory of gelation. *Source:* Adapted with permission from Dusek K, MacKnight WJ. Crosslinking and structure of polymer networks. In: Labana SS, Dickie RA, Bauer RS, editors. *CrossLinked Polymers*. American Chemical Society; 1988. p. 2 [88]. Copyright 1988 American Chemical Society.

The previous observation can also be understood if we look at the expressions for the number and weight-average degrees of polymerization. For this system, these values will be respectively given by Equations 9.14 and 9.15.

$$\overline{P}_n = \frac{1}{1 - \left(\frac{f}{2}\right)\alpha} \quad (9.14)$$

$$\overline{P}_w = \frac{1 + \alpha}{1 - (f-1)\alpha} \quad (9.15)$$

Divergence of \overline{P}_w , which sets the onset of gelation, will occur at the condition expressed by Equation 9.13. The higher the functionality of the monomer A_f , the smaller the conversion required for reaching gelation. For other special cases, such as the case of $A_f + B_g$ step polymerization, the condition for gelation will be slightly different:

$$\alpha_c = \frac{1}{[r(f-1)(g-1)]^{1/2}} \quad (9.16)$$

where r is the stoichiometric imbalance ratio, defined as

$$r = \frac{A}{B} \leq 1 \quad (9.17)$$

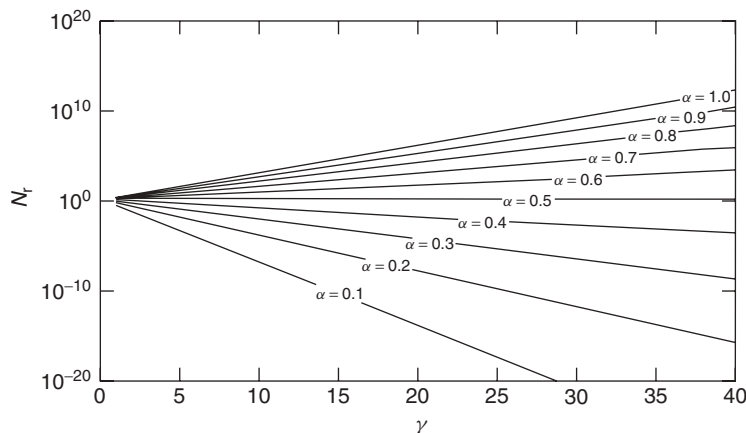


Figure 9.8 The number of components N_r that can be introduced into the generation g_r , at any given conversion α during the polymerization of a trifunctional unit. According to Flory's theory, gelation point will occur just when $N_{r+1}/N_r = 1$. In accordance with Equation 9.13, this will happen at $\alpha = 0.5$ for a trifunctional unit.

In the previous case, there is a critical stoichiometric imbalance ratio at which gelation will not occur:

$$r_c = \frac{1}{(f-1)(g-1)} \quad (9.18)$$

9.5.2 Percolation Gelation Theories

The percolation approach is a non-mean-field theory that is based on random walks in an n -dimensional space and takes spatial correlations into account. The work of Boots [89], Bansil [90], and Herrman [91] are some examples of such theory. This type of problems were first formally studied by Broadbent and Hammersley [92], but Stauffer [85] and de Gennes [2] first suggested that percolation on a three-dimensional (3D) lattice could provide a good insight into the critical phenomenon of gelation. Actually, the pioneering work of Flory and Stockmayer represents the mean field limit of percolation approaches in a Bethe lattice, a branching but loopless structure [93]. Under this approach, gel formation is visualized as a lattice model, where each lattice site with f neighbors stands for multifunctional units with f reacting sites. Two adjacent units can link each other, thus forming a bond. Let us consider, for instance, the FRC of bi- and tetrafunctional monomers producing a polymer network, as shown in Figure 9.9. Bi- and tetrafunctional monomers will be immersed within the lattice. Each monomer will occupy a lattice site. Lattice sites where a bifunctional monomer is situated can hold at most two bonds with their neighboring sites, while those sites having a tetrafunctional monomer can hold at most four bonds. Polymerization is initiated by free radicals (stars), which add to double bonds forming a growing chain that can continue this process.

During this growing process in the lattice, we can randomly select an active site and a neighboring lattice site, and examine the conditions between the two. If the adjacent site is not occupied, that is, if this site has not already undergone two or four bondings with its immediate neighbors, then the active site can be shifted to this new lattice site, thus forming a new bond. The fraction of reacted monomer will be α . At the beginning, when α is small, there will be only short chains and the entire lattice will be made out of sol. However, when a critical value of conversion, α_c , is reached, an infinite cluster is obtained. MC calculations can be performed to obtain the MWD, w_m , of this population at a certain conversion, α , which will be given by the number of clusters, each containing m sites per lattice site. Near the critical point, α_c , several properties undergo remarkable variations and the environment experienced by one molecule in one point can be noticeably different from the one experienced by any other molecule in a different point of the same system. This variation will be more evident as the system is closer to the gelation point. This non-mean-field theory allows consideration of fluctuations in chain connectivity at the vicinity of gelation. Since these fluctuations will be present during the pre- and post-gelation periods, it is useful to define a reduced conversion as

$$\varepsilon = \frac{|p_c - p|}{p_c} \quad (9.19)$$

In percolation theory, the weight-average chain length of the polymer distribution for a crosslinking system diverges according to the law:

$$\overline{P_w} \cong \varepsilon^{-\gamma} \quad (9.20)$$

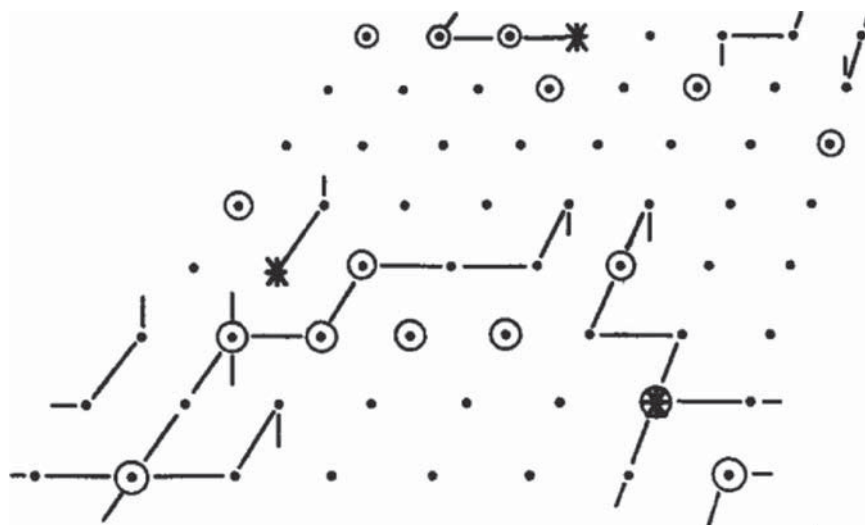


Figure 9.9 Schematic representation of a lattice considered in the percolation method. Bifunctional monomers are indicated by dots, tetrafunctional monomers by dots with circles, and active centers by stars. *Source:* Reprinted with permission from Herrmann HJ, Landau DP, Stauffer D. *Phys Rev Lett* 1982;49:412–415 [91]. Copyright 1982 American Physical Society.

where the exponent γ is in the order of 1.7–1.8, which differs from the critical value obtained with mean-field theories for chain connectivity $\gamma = 1$, where it is assumed that average properties are maintained throughout the whole system, even at the vicinity of gelation. However, with percolation theory, a wide range of values for γ have been obtained for several systems. For further discussion about percolation theory, the reader is referred to de Gennes [2].

9.5.3 Kinetic Theories

Kinetic approaches represent realistic and comprehensive description of the mechanism of network formation. Under this approach, reaction rates are proportional to the concentration of unreacted functional groups involved in a specific reaction times an associated proportionality constant (the kinetic rate constant). This method can be applied to the examination of different reactor types. It is based on population balances derived from a reaction scheme. An infinite set of mass balance equations will result, one for each polymer chain length present in the reaction system. This leads to ordinary differential or algebraic equations, depending on the reactor type under consideration. This set of equations must be solved to obtain the desired information on polymer distribution, and thus instantaneous and accumulated chain polymer properties can be calculated. In the introductory paragraphs of Section 9.5, we have already mentioned some of the characteristics of the kinetic theories, and mentioned some groups that have used them.

A common feature in the traditional modeling of FRC with crosslinking with kinetic theories is the use of the

“monoradical assumption”, that is, it is assumed that each polymer molecule can possess only one radical site, thus considering that polymer chains are either living or dead (in MC simulations, there is no such distinction). However, strictly speaking, this assumption is acceptable for linear polymerizations with monofunctional initiators. If cyclic multifunctional initiators are used, then multiradicals can also be present even in linear polymerizations. In nonlinear polymerizations, the presence of polymer chains with more than one radical center is expected, especially if gelation takes place.

By assuming multifunctional polymer molecules in the proposed reaction scheme for nonlinear polymerization, several imposed restrictions caused by the use of the monoradical assumption can be overcome. A single polymer population can be used instead of splitting the polymer population into classes based on functionality (i.e., labeling the polymer molecules as living, dead, or dormant, as typically done). Some important aspects of FRC with crosslinking, such as the presence of multiple living or dormant radical sites per macromolecule, the presence of multiple terminal double bonds per polymer chain, as well as the possibility of branching and crosslinking occurring not only in dead polymer molecules, but also in living or dormant ones, can be adequately modeled by using a multifunctional polymer molecule approach. In addition, when using this approach, the use of empirical closure expressions can be avoided.

Zhu and Hamielec [94] studied the FRC of vinyl monomers with chain transfer to polymer and the copolymerization of vinyl/divinyl monomers using a multiradical approach. They used the method of moments and focused on the pre-gelation period. They concluded that

the presence of multiradical macromolecules is an important feature of FRC with branching/crosslinking. However, they observed that the effect of multiradicals is not important if the propagation/terminations coefficient ratio (k_p/k_t) is smaller than 10^{-3} . Dias and Costa [95, 96] developed a kinetic model for calculation of average molecular weights based on the moment generation function (MGF). They took into account the presence of different types of radicals in the mechanism of FRC of vinyl/divinyl monomers, thus following a multidimensional approach. Korolev and Mogilevich [97] investigated the FRC with crosslinking of vinyl/divinyl monomers using MGF. They used a three-dimensional mass balance approach to take into account number of monomers, radical centers, and pendant double bonds. Recently, Iedema and Hoefsloot [98] employed the Galerkin finite-elements method (GF) to assess the importance of multiradicals on the chain length distribution (CLD) in FRC with branching by solving a set of two-dimensional balance equations. They compared their results to those obtained with a MC simulation of the same system, obtaining identical results of gelation point and evolution of the gel fraction.

9.5.4 Crosslinking and Controlled-Living Radical Polymerization

Controlled/"living" radical polymerization (CLRP) processes are well-established synthetic routes for the production of well-defined, low-molecular weight-dispersity polymers [99]. The types of CLRP processes (initiator-transfer agent-terminator (INIFERTER), atom transfer radical polymerization (ATRP), nitroxide-mediated radical (NMRP) polymerization, reversible addition-fragmentation transfer (RAFT)) and their characteristics are described in Section 3.8 of Chapter 3 and in Section 14.8 of Chapter 14.

Ide and Fukuda [100] studied the FRC of styrene with a small amount of 4,4'-divinylbiphenyl at 125 °C in the presence of an oligomeric polystyryl adduct with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (PS-TEMPO), with the aim of estimating the pendant double bond reactivity in such a system. They were able to mathematically describe that system by means of a simple reaction mechanism, assuming a random distribution of double bonds. They claimed that such system leads to a more homogeneous polymer network compared to those obtained by FRC. Later, they collected further experimental evidence that confirmed their initial hypothesis [101]. For the networks synthesized by regular FRC, they observed an insoluble fraction (microgels) at very low conversion, which grew up abruptly at the gelation point. In contrast, in the networks synthesized in the presence of PS-TEMPO, no microgels at low conversions were observed and the gel fraction grew gradually after the gelation point. In addition, they found that in the systems in the presence of PS-TEMPO, the critical conversion for

the onset of gelation can be described with certain degree of precision with the classical Flory–Stockmayer theory of gelation [60]. Since then, important research activity in the field of CLRP with crosslinking has emerged, addressing the INIFERTER, NMRP, ATRP, and RAFT techniques. The study of such systems has already been reviewed [102–106].

The use of CLRP as a novel approach to polymerize multifunctional monomers has gained relevance in the last few years. The reports concerning crosslinked polymers synthesized by CLRP have demonstrated that important differences exist between polymer networks synthesized by conventional free radical polymerization and those synthesized by CLRP techniques. These differences include a significant delay in the onset of the gelation point, steady increase of gel content with monomer conversion, and higher swelling ratios of the gels produced. These differences arise from the fact that the presence of CLRP reagents modifies the crosslinking process and thus, gelation occurs by a rather different mechanism. In CLRP with crosslinking, the fast and reversible equilibrium between active radicals and dormant species, coupled with fast initiation and negligible irreversible termination, results in a low and constant concentration of growing radicals. This situation reduces to some extent the heterogeneous nature of polymer gels synthesized by conventional FRC. In contrast to conventional FRC with crosslinking, the growth of polymer chains in CLRP with crosslinking is slow (in the order of hours, whereas it takes only seconds in conventional FRC), as a consequence of the activation–deactivation cycles undergone by the growing chains. During these dormant periods, the polymer molecules do not propagate but they have enough time for chain relaxation and diffusion, allowing the few radical centers to eventually and randomly react with the available pendant double bonds. Because of the high initiation rates present in CLRP, a high concentration of short polymer chains will be attained from the beginning of the reaction, thus favoring intermolecular (over intramolecular) crosslinking (Fig. 9.10). These characteristics of statistical crosslinking with low cyclization rates approximate the ideal conditions assumed in the Flory's mean-field theory of gelation. However, it is important to point out that cyclization will unavoidably occur, and polymer gels will show certain degree of heterogeneity, irrespective of the synthetic route of gel formation. Factors such as dilution, crosslinker content, and CLRP reagent concentration will play an important role in the extent of intramolecular crosslinking and, therefore, in the homogeneity of the resultant polymer network. Moreover, the higher reactivity of the crosslinker, which causes significant compositional drift, will contribute to the heterogeneity of the produced polymer network. This situation can be minimized by implementing adequate monomer feeding policies such as those proposed by Dubé et al. [19] and Enright and Zhu [107].

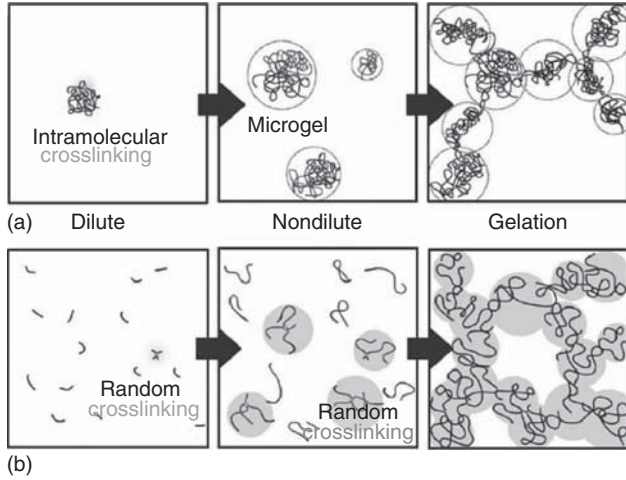


Figure 9.10 Comparison between the network formation mechanism through regular FRC and CLRP with crosslinking. (a) Conventional FRP with crosslinking; (b) CLRP with crosslinking. *Source:* Adapted with permission from Norisuye T, Morinaga T, Tran-Cong-Miyata Q, Goto A, Fukuda T, Shibayama M. Comparison of the gelation dynamics for polystyrenes prepared by conventional and living radical polymerizations: a time-resolved dynamic light scattering study. *Polymer* 2005;46:1982–1994 [108]. Copyright 2005 Elsevier.

APPENDIX A CALCULATION OF AVERAGE CHAIN LENGTH

The classical theory of Flory–Stockmeyer [60–62] (FS) provides the basis for calculation of the molecular size distribution of crosslinked polymer molecules holding an *arbitrary* initial size distribution. Let us consider an original set of polymer molecules (known as *primary chains*). The initial weight fraction of these primary chains, w_{mp} , will be simply given by

$$w_{mp} = \frac{mN_m}{\sum_{m=1}^{\infty} mN_m} \quad (9.A.1)$$

The number and weight-average chain lengths will be given by Equations 9.A.2 and 9.A.3, respectively:

$$\overline{P}_{np} = \frac{\sum_{m=1}^{\infty} mN_m}{\sum_{m=1}^{\infty} N_m} \quad (9.A.2)$$

$$\overline{P}_{wp} = \frac{\sum_{m=1}^{\infty} m^2 N_m}{\sum_{m=1}^{\infty} mN_m} = \sum_{m=1}^{\infty} m w_{mp} \quad (9.A.3)$$

In this system, the polymer chains bear functional groups that can be randomly linked to others by covalent bonds, thus allowing the formation of a polymer network at some point of the reaction. As the crosslinking reaction proceeds, the CLD will be modified, and therefore, it will be a function of the number of crosslink points that have been produced. Let us define $\bar{\rho}$ as the average number of crosslinked units (or crosslinking points) per polymer chain. Note that in the case of crosslinking of tetrafunctional units, as the case of vulcanization or free radical polymerization of vinyl/divinyl systems, every connection (crosslinkage) of primary chains attaches two crosslinking points and then $\bar{\rho}/2$ is the average number of crosslinkages per polymer chain. The extent of crosslinking is sometimes expressed in reduced form as the crosslink index γ (Eq. 9.A.4):

$$\gamma = \bar{\rho} \overline{P}_{wp} \quad (9.A.4)$$

According to the FS theory, the number and weight-average chain lengths of the new polymer CLD will be given by [4]:

$$\overline{P}_n = \frac{\overline{P}_{np}}{1 - \frac{\bar{\rho} \overline{P}_{np}}{2}} \quad (9.A.5)$$

$$\overline{P}_w = \frac{\bar{\rho} \overline{P}_{wp}}{1 - \bar{\rho} \overline{P}_{wp}} \quad (9.A.6)$$

$$\overline{P}_Z = \frac{\overline{P}_{zn}}{(1 - \bar{\rho} \overline{P}_{wp})^2} \quad (9.A.7)$$

$$\overline{P}_{Z+n} \propto \frac{1}{(1 - \bar{\rho} \overline{P}_{wp})^2}, \quad n = 1, 2, \dots \quad (9.A.8)$$

Strictly speaking, the weight-average chain length is given by $\overline{P}_w = \frac{\overline{P}_{wp}}{1 - \bar{\rho}} / [1 - \bar{\rho}(\overline{P}_{wp} - 1)]$. However, since generally $\overline{P}_{wp} \gg 1$, the expression shown in Equation 9.A.6 is widely used. After successive crosslinking, the number of polymer chains will decrease constantly as they bond to each other, and polymer chains will start growing in size. These polymer chains can grow to the point where a giant molecule of remarkable molecular weight is formed. The solubility of the polymer molecules is significantly reduced, thus forming a polymer network. Hence, two clear stages can be identified: the pre- and post-gelation periods. The onset of gelation is characterized for some critical changes, as the divergence of higher order-average molecular weights. From Equation 9.A.6, the required condition for weight-average chain length to diverge is:

$$\bar{\rho} \overline{P}_{wp} = 1 \quad (9.A.9)$$

The physical meaning of Equation 9.A.9 is that an incipient polymer network will come up when, in a weight

average basis, each primary chain bears one crosslinking point (or half of a crosslinkage for crosslinking with tetrafunctional monomers). Thus, during the pre-gelation period, there will be many more primary chains than crosslink points, while the opposite happens during the post-gelation period. It is worthy of attention that all higher order-average values of the resultant weight distribution after crosslinking will diverge at the same crosslink density, regardless of the primary chain distribution, as can be deduced from Equations 9.A.5–9.A.8. This derivation is of general application and applies to both nonlinear step growth and FRC and to any other crosslinking system. For instance, in the case of A_f step-growth polymerization, the crosslink density can be basically considered equal to monomer conversion, that is, $\bar{\rho} = \alpha$. This can be also applied to end-linking systems, as the copolymerization of long primary chains of B_f with a nonpolymeric crosslink agent A_g , connect randomly to form A–B bonds. In this case, $\bar{\rho} = \alpha_A \alpha_B$. This can represent, for instance, the polymerization with crosslinking of poly(vinyl alcohol) with adipic acid.

APPENDIX B CALCULATION OF SOL AND GEL FRACTIONS

Before the gelation point is reached, all polymer molecules have finite lengths and will be dissolved by any appropriate solvent. Therefore, the weight fraction of sol is equal to unity. However, at the onset of gelation, not all the polymer molecules are totally converted into an infinite molecule in a step-wise manner, but a portion of soluble low molecular weight polymer immersed in the incipient polymer network still remains. This soluble fraction will incorporate into the gels clusters just formed, increasing its molecular weight and, therefore, the amount of insoluble (gelled) polymer. If the average crosslinking density $\bar{\rho}$ is much smaller than unity, the weight fraction of sol, w_s , expresses the probability that a randomly selected unit belongs to the sol fraction. This random selection depends on chain length. Thus, the weight fraction distribution of primary chains, w_m , will be required. A primary chain will be part of the sol fraction provided that none of the units in this chain are connected to the gel. On the other hand, one chain will be part of the gel (with a probability w_g) only if it possesses crosslinking points (where the probability for this event is given by $\bar{\rho}$). Thus, the probability that a mer selected at random does not take part in a crosslink is $1 - \bar{\rho}$. The probability that it does, but that crosslinking point is not connected to the gel, is the product $\bar{\rho}(1 - w_g)$. The addition of these probabilities, namely, that one randomly selected mer is not crosslinked or it is crosslinked but it is not part of the gel, $1 - \bar{\rho} + \bar{\rho}(1 - w_g) = 1 - \bar{\rho}w_g$, represents the probability that such mer is not directly linked to the gel. Therefore, the probability that a mer in

a polymer chain with length m belongs to the sol fraction is given by $(1 - \bar{\rho}w_g)^m$. By summing the weight fraction of chains of all lengths that are not connected to the gel, the weight fraction of the sol is obtained and is given by Equation 9.B.1.

$$w_s = \sum_{m=1}^{\infty} w_m [1 - \bar{\rho}w_g]^m \quad (9.B.1)$$

Depending on the specific distribution w_m followed by the primary chains, the recursive equation for sol fraction can take several forms. If primary chains follow an exponential distribution (Flory distribution), Equation 9.B.1 can be expressed as:

$$w_s = \frac{1}{\left(1 + \frac{\bar{\rho}P_{wp}w_g}{2}\right)^2} \quad (9.B.2)$$

which can be rearranged as:

$$w_s + w_s^{1/2} = \frac{2}{\gamma} \quad (9.B.3)$$

Equation (9.B.3) represents the Charlesby–Pinner's equation [109], which is widely employed to analyze the gel curve.

If it is assumed that scission can occur with a probability $\bar{\beta}$, then Equation 9.B.3 becomes:

$$w_s + w_s^{1/2} = \frac{\bar{\beta}}{\bar{\rho}} + \frac{2}{\gamma} \quad (9.B.4)$$

On the other hand, the expression for uniform polymer chains is given by Equation 9.B.5 and represents the simplest form of Equation 9.B.1.

$$w_s = \exp(-\bar{\rho}P_{wp}w_g) \quad (9.B.5)$$

The proper knowledge of the functional form of w_m followed by every polymerization scheme would be the key factor for describing the evolution of gel content according to Equation 9.B.1. For a conventional free radical polymerization, the weight length distribution for primary chains that are formed at $x = \theta$ is given by [110]:

$$w_m(\theta) = (\tau(\theta) + \beta(\theta)) \left[\tau(\theta) + \frac{\beta(\theta)}{2} \right. \\ \left. \times [\tau(\theta) + \beta(\theta)](m-1) \right] m \Phi^{m+1}(\theta) \quad (9.B.6)$$

where

$$\Phi(\theta) = \frac{1}{1 + \tau(\theta) + \beta(\theta)} \quad (9.B.7)$$

$$\tau(\theta) = \frac{R_f(\theta) + R_{td}(\theta)}{R_p(\theta)} \quad (9.B.8)$$

$$\beta(\theta) = \frac{R_{tc}(\theta)}{R_p(\theta)} \quad (9.B.9)$$

m is chain length, $R_p(\theta)$ denotes polymerization rate, $R_f(\theta)$ denotes rate of chain transfer to monomer and small molecules, $R_{td}(\theta)$ represents rate of termination by disproportionation, and $R_{tc}(\theta)$ represents rate of termination by combination. All these reaction rates are to be evaluated at conversion $x = \theta$.

Conversely, under the assumption of very low molar-mass dispersity (\bar{D}_M) of primary chains, the weight-average chain length of the primary chains can be approximated by its number-average value, that is,

$$\overline{P}_{wp} \cong \overline{P}_{np} \quad (9.B.10)$$

This assumption has been proved to be a straightforward but useful mathematical expression for depicting the gel curved in reaction systems in which the molar-mass dispersity of primary chains is close to unity, as in the case of polymer networks obtained by CLRP. This equation can presumably be also applied to gels formed by living techniques, such as anionic, carbocationic, group transfer, and ring opening metathesis polymerizations. In a living polymerization, the probability that a monomer is connected to a chain end is the same for every growing chain, and therefore, the Poisson distribution can be used [111]. However, some deviations are expected to occur as a consequence of various nonideal effects.

Some other distribution functions have been proposed for living systems. For example, Müller et al. [112, 113] have reported an analytical solution for the molar mass distribution in a polymerization with degenerative transfer between active and dormant chain ends. Goto and Fukuda [114] presented a chain length distribution function based on a bivariate probability $N(x, y)$, considering that during a time t the chain experiences a number of y activation–deactivation cycles, while a total of x monomer units are added to the growing chain, as given in Equation 9.B.11:

$$N(x, y) = \frac{e^{-y_n} y_n^y}{y!} (1 - p)^y p^x \binom{x + y - 1}{x} \quad (9.B.11)$$

where y_n is the mean value of y .

Tobita [115–117] derived a fundamental weight fraction distribution represented by a hypergeometric function. He

combined the most probable and the Poisson distributions, the former expressing the CLD and the later indicating the distribution of the number of active periods of the growing chain. Nonetheless, this distribution is only applicable at constant monomer concentration. Dias and Costa [118] applied a kinetic approach based on the use of MGF for linear and nonlinear CLRP's. However, a simple kinetic scheme was considered, not taking into account termination or chain transfer reactions. They obtained a general solution for the CLD in a CLRP. Their results were similar to those described by Tobita [115–117] under similar conditions. Their treatment was generalized for nonlinear CLRP, obtaining a multimodal CLD. However, for systems considering monomer consumption, analytical solutions cannot be obtained because of the complexity of the problem; only numerical calculations can be applied in those cases.

ACKNOWLEDGMENTS

The authors acknowledge financial support from Consejo Nacional de Ciencia y Tecnología (CONACYT, México) (Project CONACYT 101682 and a Ph.D. Scholarship to J.C.H.-O., through *Beca Nacional para Estudios de Posgrado*, 202907), DGAPA-UNAM (Project PAPIIT 119510), and Instituto de Ciencia y Tecnología del Distrito Federal (ICyTDF, México) (Project PICSA11-56).

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