# 21 Polymerization at High Pressure

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### **21.1 INTRODUCTION**

Most polymerization reactions proceed at a faster rate under high pressure. Higher molecular weights are obtained at higher pressures. High pressure polymerizations of a wide variety of vinyl type monomers and copolymerizations of two or more monomers have been investigated by many researchers around the world.<sup>1-8</sup> Such studies have been conducted with free radicals derived from oxygen and organic peroxides, photoinitiation,<sup>9,10</sup> and high energy radiation.<sup>11</sup> High pressure polymerizations have also been conducted with anionic<sup>12</sup> and cationic<sup>13</sup> initiators (catalysts) and with transition metal catalysts.<sup>14</sup>

High pressure polymerizations of bulk monomers have been conducted in the supercritical fluid state (ethylene), liquid state (for example styrene<sup>15</sup>, vinyl acetate<sup>16</sup>, methyl methacrylate<sup>11,17</sup>) and even in the glassy state (2-hydroxyethyl methacrylate and glycidyl methacrylate<sup>18</sup>) and the solid state (perfluorostyrene and several others).<sup>19,20</sup> Monomers have also been polymerized at high pressure in solution and in suspension or emulsion.<sup>21,22</sup> High pressure polymerizations have been conducted in small batch reactors in the laboratory and in very large continuous commercial reactors.

In general, any addition polymerization of vinyl type monomers can be studied as a function of pressure, just as it can be studied as a function of temperature. High pressures (above about 500 atm) do present experimental difficulties and most polymerization studies have not included effects of high pressure. Nevertheless, some general conclusions can be drawn about the effects of high pressure.

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## 21.2 ACTIVATION VOLUME FOR POLYMERIZATION

In general, increases in the pressure of polymerization result in higher polymerization rates and higher molecular weights. While most investigators have not done so, these increases can be described in terms of an activation volume, just as the increase in polymerization rates with temperature can be described in terms of an activation energy. The influence of temperature and pressure on a reaction rate constant can be written as shown in equation (1), where A is the frequency factor;  $E_A$  is the activation energy in kJ mol<sup>-1</sup> (kcal mol<sup>-1</sup>); R is the gas constant; P is the pressure;  $\Delta V^*$  is the activation volume in cm<sup>3</sup> mol<sup>-1</sup>; and T is the temperature. Table 1 shows some of the values for activation volumes reported in the literature for various free radical polymerizations.

$$x = A \exp\left\{-E_A/RT - (P\Delta V^*/RT)\right\}$$
(1)

Table 1	Activation	Volume for	High	Pressure	Polymerization	of	Various	Monomers
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	Activation volume ( $cm^3 mol^{-1}$ )						
Monomer	Propagation	Óverall	Refs.				
Ethylene			-23	a, b, c			
Ethylene			-20	a, b, c			
Ethylene			-17.5	d			
Styrene	-18.6	+ 5.8	-20.5	e			
Styrene	-17.9	+13.1	-17.1	f			
Vinyl acetate	-24.0	+16.3	-17.2	g			
Methyl methacrylate	- 19.0	+25.0		ĥ			
Butyl acrylate	-22.5	+20.8	-26.3	i			
Butyl methacrylate	-23.2	+17.8	-17.4	i			
Octyl methacrylate	-24.7	+20.8	-19.2	k			

<sup>a</sup> S. Goto, K. Yamamoto, S. Furui and M. Sugimoto, J. Appl. Polym. Sci., Appl. Polym. Symp., 1981, 36, 21.

<sup>b</sup> P. Ehrlich and G. A. Mortimer, Adv. Polym. Sci., 1970, 7, 386.

<sup>6</sup> K. H. Lee and J. P. Marano, ACS Symp. Ser., 1979, 104, 221.
 <sup>6</sup> M. Buback and H. Lendle, Makromol. Chem, 1983, 184, 193.

<sup>e</sup> P. W. Moore, J. G. Clouston and R. P. Chaplin, J. Polym. Sci., Polym. Chem. Ed., 1983, 21, 2503.

<sup>f</sup> Y. Ogo, M. Yokawa and T. Imoto, Makromol. Chem., 1973, 171, 123. <sup>8</sup> M. Yokawa and Y. Ogo, Makromol. Chem., 1976, 177, 429.

<sup>h</sup> M. Yokawa, Y. Ogo and T. Imoto, Makromol. Chem., 1974, 175, 179.

<sup>1</sup> M. Yokawa, Y. Ogo and T. Imoto, Makromol. Chem., 1974, 175, 2913.

<sup>j</sup> M. Yokawa, Y. Ogo and T. Imoto, Makromol. Chem., 1974, 175, 2903.

<sup>k</sup> M. Yokawa, J. Yoshida and Y. Ogo, Makromol. Chem., 1977, 178, 443.

The negative value for the activation volume for propagation implies that the activated reaction complex for the addition of a monomer molecule to a growing free radical occupies less volume than the two components. Therefore, an increase in reaction pressure promotes the formation of this complex and increases the polymerization rate. A positive value for the activation volume for termination implies the opposite: the activated complex occupies a greater volume than the two reacting components. Therefore, an increase in pressure results in a reduced termination rate. In combination with the increased propagation rate, this will result in an increase in the molecular weight of the polymer at higher pressures.

Of course, there are exceptions. The activation volumes may not be constant over the entire pressure range. If the pressure becomes high enough to cause a phase change in the monomer to a glassy or solid state, the polymerization rate may decline drastically. No polymerization was observed in crystalline styrene,<sup>15</sup> while very slow polymerization was observed in crystalline methyl methacrylate.23

Polymerization rates can be increased by increasing the temperature of polymerization. Activation energies for polymerization are usually large, but, in most cases, an increase in polymerization temperature alone will also cause a decrease in molecular weight, sometimes to a level below that which is desired. (Activation energies for chain transfer are positive.) If both temperature and pressure are increased, then very large increases in polymerization rates can be achieved while maintaining molecular weight within the desired range. It is this combination which makes high pressure polymerization commercially useful.

### 21.3 COMMERCIAL USES OF HIGH PRESSURE POLYMERIZATION

Although many monomers have been polymerized in the laboratory under high pressure, only the free radical polymerization of ethylene and ethylene copolymers has had sufficient utility to be used

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commercially on a large scale. Several commercial processes operate at pressures from one to a few atmospheres to contain a monomer which has a high vapor pressure or to increase the concentration of a gaseous monomer. But high pressures, typically 1000–3000 atm, and elevated temperatures, typically 150–300 °C, are required to obtain commercially useful polymerization rates and molecular weights with ethylene and free radical initiators.

### **21.4 POLYMERIZATION OF ETHYLENE**

Ethylene was first polymerized in 1933 by Fawcett in the research laboratories of Imperial Chemical Industries (ICI) in the UK.<sup>24</sup> The white waxy solid obtained from ethylene at high pressures was quickly recognized as polyethylene (PE). It gained its first commercial importance because of its remarkable properties as an electrical insulator. Since then, commercial use of PE made in high pressure processes has grown rapidly. United States consumption was  $2.8 \times 10^6$  tons in  $1984^{25}$  and worldwide consumption was more than twice that amount.

ICI's first process used an autoclave, or stirred tank reactor. Ethylene was fed continuously and mixed with the contents of the reactor by mechanical stirring. Later, both Du Pont and Union Carbide in the United States developed tubular reactors in which agitation was provided by fluid flow inside the tube. Variations on these two processes, and combinations thereof, were developed later. For example, autoclaves have been used in series.<sup>26</sup> Internal baffles have been used to form a series of reaction zones within a single autoclave pressure vessel.<sup>27</sup> In another case the initial reactor was an autoclave followed in series by a tubular reactor.<sup>28,29</sup> Details of the processes can be found in the vast patent literature on polyethylene processes.<sup>30-44</sup> Mathematical models have been constructed to describe these processes in great detail.<sup>45-50</sup>

### 21.4.1 Heat of Reaction

The polymerization of ethylene is exothermic, releasing about 94 kJ mol<sup>-1</sup> (22.5 kcal mol<sup>-1</sup>). For each one percent conversion of ethylene to polymer, the temperature rises 12-13 °C if none of the heat of polymerization is removed through the reactor walls by heat transfer. In the autoclave process, ethylene is injected at a temperature well below the polymerization temperature and is heated by the exothermic heat of polymerization. Relatively little heat can be removed through the thick walls in the autoclave. The difference between feed temperature and reaction temperature limits the conversion of ethylene to polymer to about 15% or less.

In the tubular process, much more surface area is available for heat transfer and external water cooling of the tube walls is used, thus permitting higher conversions.<sup>51</sup> Even with some heat being removed through the walls, the polymerization reaction is generally so fast that there is an increase in temperature as the reacting fluid flows down the tube. To achieve even higher conversions without excessive temperature rise, some tubular processes employ multiple injections of cold ethylene and/or inert diluents at several points along the tube.<sup>52</sup> Additional polymerization initiator must also be injected. A major portion of the ethylene remains unconverted and must be recovered, cooled and recycled to the process.

### 21.4.2 Decomposition

At high temperatures (above about  $300 \,^{\circ}$ C) ethylene can undergo a decomposition reaction (equation 2). This decomposition is also exothermic, releasing about  $125 \,\text{kJ} \,\text{mol}^{-1}$  (30 kcal mol<sup>-1</sup>). Once initiated, this reaction proceeds very rapidly, consumes most of the available ethylene, and results in a very rapid rise in temperature and pressure until the pressure is released, either intentionally or accidentally. Decomposition reactions are apparently initiated by adventitious hot spots in the polymerization reactor. Ethylene can undergo thermal (spontaneous) initiation of polymerization without the addition of other initiators.<sup>53</sup> At high temperatures (above 300 °C), this spontaneous polymerization, together with polymerization caused by added initiator, can become so fast that a runaway (accelerating) reaction occurs. When the temperature becomes high enough, the decomposition reaction starts releasing heat at a still faster rate and the reaction goes to completion very rapidly.

(2)

Industrial processes utilize carefully designed rupture discs to discharge the high pressure gases very rapidly whenever the designed release pressure is exceeded in order to quickly remove unreacted ethylene from the reactor.<sup>54</sup> Much work has been done on the careful control of industrial polymerization processes so that these undesirable ethylene decompositions do not often occur.

# 21.5 MECHANISM OF FREE RADICAL POLYMERIZATION (see also Volume 3, Chapter 6 and related chapters)

The mechanism of free radical polymerization at high pressures is generally believed to be the same as the mechanism at low pressures. Because of its commercial importance, the polymerization of ethylene has been studied more extensively than other high pressure polymerizations.<sup>55-60</sup> The discussion that follows describes the free radical polymerization of ethylene at high pressures. Other monomers are believed to behave in a similar manner, though some reactions such as chain transfer to polymer and the decomposition reaction may not be important for many other monomers.

An initiator (I) (generally a peroxide or hydroperoxide) decomposes to produce two free radicals  $R_0^*$  (equation 3). An ethylene molecule adds to  $R_0^*$  to produce another free radical  $R_1^*$  equation (4). Equation (3), sometimes combined with equation (4), is called the initiation reaction. Equation (5) is called the propagation reaction, in which ethylene monomer molecules are added successively to free radicals. Equations (6) and (7) are called the termination reaction, in which two free radicals combine to form dead polymer. Equation (6) shows termination by combination, in which both free radicals combine to form one polymer molecule. Equation (7) shows termination by disproportionation or disassociation in which two free radicals combine to form two polymer molecules. Equations (8) and (9) show chain transfer to telogen, in which S–H represents a molecule having an active hydrogen; such molecules are called chain transfer agents or telogens. Telogens may be added as solvents, comonomers, or as molecular weight control agents. In equation (8), a hydrogen atom is transferred from the telogen to a growing free radical, thereby terminating its growth and producing a dead polymer molecule. This reaction also results in a free radical on the telogen molecule which can add ethylene (equation 9) and undergo further growth by the polymerization reaction (equation 5).

$$I \rightarrow 2R_0^{\bullet}$$
 (3)

$$\mathbf{R}_{0}^{\bullet} + \mathbf{CH}_{2} = \mathbf{CH}_{2} \rightarrow \mathbf{R}_{0}\mathbf{CH}_{2}\mathbf{CH}_{2}^{\bullet}(=\mathbf{R}_{1}^{\bullet})$$

$$\tag{4}$$

$$\mathbf{R}_{N}^{\bullet} + \mathbf{CH}_{2} = \mathbf{CH}_{2} \rightarrow (\mathbf{R}_{N+1}^{\bullet})$$
(5)

$$\mathbf{R}_{N}^{\bullet} + \mathbf{R}_{M}^{\bullet} \to \mathbf{P}_{N+M} \tag{6}$$

$$\mathbf{R}_{N}^{\bullet} + \mathbf{R}_{M}^{\bullet} \rightarrow \mathbf{P}_{N-1}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{3} + \mathbf{P}_{M-1}\mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H}_{2}$$
(7)

$$\mathbf{R}_{N}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}^{\bullet}+\mathbf{S}-\mathbf{H}\rightarrow\mathbf{P}_{N}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{3}+\mathbf{S}^{\bullet}$$
(8)

$$S \cdot + CH_2 = CH_2 \rightarrow S - CH_2 CH_2^{\bullet}$$
(9)

$$\mathbf{R}_{N}\mathbf{CH}_{2}\mathbf{CH}_{2}^{*}+\mathbf{CH}_{2}=\mathbf{CH}_{2}\rightarrow\mathbf{R}_{N}\mathbf{CH}=\mathbf{CH}_{2}+\mathbf{CH}_{2}\mathbf{CH}_{3}^{*}$$
(10)

In much of the early work, the initiator was oxygen, present as an impurity in the ethylene or intentionally added. Oxygen combines with hydrocarbons to form hydroperoxides which decompose at high temperatures to produce free radicals.<sup>61</sup> Later, ethylene was better purified to effectively remove the oxygen. When peroxides and hydroperoxides became commercially available, they became widely used because they offer advantages in handling and process control. Because they decompose at lower temperatures and can initiate polymerization at lower temperatures, polymers having different properties can be made.<sup>62-65</sup>

All organic molecules which contain hydrogen can be thought of as telogens, since, in principal, any hydrogen atom can participate in equation (8). However, the rate of this hydrogen transfer can vary greatly with the type of bond and the molecular structure of the telogen molecule. Hydrogens attached to carbons in an aromatic ring react very slowly, if at all. Primary hydrogens in a methyl group react more slowly than secondary hydrogens in a methylene group which, in turn, are slower than tertiary hydrogens on a carbon atom which has three other carbon atoms attached. Other atoms can also enter into a telogenic chain transfer. Generally, polyethylene processes are operated with no added telogens or with hydrocarbons as telogens. Ethylene itself can enter into telogenic chain transfer (equations 8 and 9). When ethylene enters into a telogenic chain transfer reaction, the end group on one polymer molecule is unsaturated as shown in equation (10).

# 21.5.1 Short Chain Branching (Intramolecular Chain Transfer) (see also Volume 3, Chapter 13)

The growing polymer molecule can itself act as a telogen. In equation (11), the growing free radical can assume conformations in which the free radical on the carbon at the end of the chain comes close to a hydrogen on a carbon that is part of the same chain. When that hydrogen transfers, a different free radical forms (equation 12). When this free radical adds ethylene through the propagation reaction (equation 5), the net result is a side chain on the PE molecule (equation 13). Steric factors favor six-membered rings and four-carbon side chains, though other structures can also be formed.<sup>66–68</sup> Higher polymerization temperatures result in a greater frequency of short chain branches. Since these branches interfere with the crystallization of PE, the density of the PE decreases as short chain branching increases. Conversely, higher pressures increase the rate of the propagation reaction and the ratio of short chain branching to polymer decreases as pressure increases, resulting in PE with higher densities. Both the temperature and pressure of polymerization must be controlled to obtain the desired degree of short chain branching, crystallinity, density, and those product properties which are affected by crystallinity.

$$R_{N}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2} \longrightarrow R_{N}CH_{2} \longrightarrow CH_{2}$$
(11)

$$\rightarrow \mathbf{R}_{N} \mathbf{CH}_{2} \dot{\mathbf{C}} \mathbf{H} \mathbf{CH}_{2} \mathbf{CH}_{2} \mathbf{CH}_{3}$$
(12)

$$\xrightarrow{\text{CH}_2=\text{CH}_2} \mathbb{R}_N \text{CH}_2 \text{CH}_2 \text{CH}_2 \cdot (13)$$

# 21.5.2 Long Chain Branching (Intermolecular Chain Transfer) (see also Volume 3, Chapter 13)

Dead polymer molecules can also act as telogens. Previously formed polymer molecules contain many carbon-hydrogen bonds which can undergo telogenic chain transfer. In equations (14) and (15), a polymer chain is represented by a line and a free radical by a dot.

After the hydrogen transfers from a dead polymer molecule to a growing free radical (equation 14), the dead polymer molecule becomes a free radical which, by the addition of ethylene, can then grow a new PE chain. The length of this chain depends on how many ethylenes are added before growth is terminated, either by equation (6) or equation (7), or by a telogenic chain transfer (equation 8). Thus, side chains are formed having lengths comparable to the lengths of polymer molecules. This phenomenon is called long chain branching. Each of these long chains also has short chain branches, and long chain branches can form on polymer molecules which already have one or more long chain branches. The amount of long chain branching relative to the total amount of polymer increases with polymerization temperature, decreases with polymerization pressure, and increases with the dead polymer to ethylene ratio. This ratio is essentially constant in a stirred autoclave, but continually increases along a tubular reactor as ethylene is converted to polymer.



### 21.5.3 Molecular Weight and Molecular Weight Distribution

Detailed mathematical analyses  $^{69-71}$  have been made of the effects of reaction kinetics and long chain branching on molecular weight and molecular weight distribution (see Volume, 3, Chapter 18). Only a few qualitative conclusions are presented here.

The number average molecular weight of the polymer is determined by the ratio of the rate of the propagation reaction (equation 5) to that of all reactions that result in new molecules (initiation and chain transfer to telogen). Chain transfer to polymer (both short and long chain branching) which does not result in additional polymer molecules will not affect number average molecular weight. However, the probability that a polymer molecule will grow a long chain branch increases as the size of the molecule increases (more carbon-hydrogen bonds become available for transfer). This has a large effect on the weight average molecular weight (and higher moment averages). Molecular weight distributions are broadened by long chain branching. Long chain branching also has important effects on melt rheology, or the melt flow characteristics of the polymer. In general, increasing long chain branching will make the polymer melt in a more non-Newtonian way; the apparent viscosity will change more rapidly with shear rate.

In a well-stirred autoclave reactor, there is a very broad distribution of residence times. Those polymer molecules which remain in the reactor for long times have the opportunity to participate in intermolecular chain transfer and to grow long chain branches many times before being removed from the reactor. A very broad distribution of molecular sizes and number of long chain branches per molecule results from these reactions.

In a tubular reactor approximating plug flow, the polymer molecules produced in the earlier portion of the reactor are exposed to more opportunities to grow long chain branches than the polymer molecules produced in the latter portions of the reactor. Ethylene conversions and polymer concentrations are higher in tubular reactors. Since long chain branching depends on polymer concentration, this higher concentration will result in more such branches being formed. Again, very broad distributions of molecular sizes and number of long chains per molecule can be formed. The changing reaction temperature in the tubular reactor also has an important effect on the molecular structures which are formed. The net result is that the molecular structures formed in each type of reactor are very complex, but are different in the two types of reactor. Two autoclaves in series, which can be operated at different temperatures and conversion levels (polymer concentrations), have been used to produce PE products having properties that match those of tubular reactor products.<sup>72</sup> Molecular structures of these products must differ in detail, but product properties, which depend on an averaging of molecular structures, could be matched.

#### **21.6 DETERMINATION OF MOLECULAR STRUCTURE OF POLYETHYLENE**

Because polyethylenes can be produced under a wide range of conditions, the molecular structures obtained also vary over a wide range. Published results of measurements of molecular structures do not show good agreement, probably because the samples measured were made under different conditions.

Short chain branches have been measured by IR and <sup>13</sup>C NMR.<sup>73</sup> Structures so identified are ethyl, *n*-butyl (which predominates), *n*-pentyl, 2-ethylhexyl and 1,3-diethyl. In 13 commercial samples, 7–17 short chain branches were found per 1000 carbon atoms.<sup>74</sup> The number of long chain branches (more than six carbon atoms) varied between 0.5 and 2.2 per 1000 carbon atoms.

Free radical polymerized PE made at low temperature  $(50-80 \,^{\circ}\text{C})$  and very high pressures (505-707 MPa) (5000-7000 atm) has a density of about 0.955 cm<sup>-3</sup> and less than 0.8 branches per 1000 C atoms based on IR determination of methyl groups.<sup>75</sup> Commercial PEs (made at 200-300  $^{\circ}\text{C}$  and 200-300 MPa) have densities of 0.912-0.935 with 10-35 methyl groups per 1000 carbon atoms. Short chain branches interfere with crystallinity; therefore, density varies inversely with short chain branching. Since density is so much easier to measure, it is usually used as an indication of the amount of short chain branching. The number of long chain branches is small compared to the number of short chain branches; the effect of long chain branching on crystallinity and density is too small to measure in the presence of the much larger effect of the greater number of short chains.

### 21.6.1 High Pressure Polyethylene vs. Linear Polyethylene

Ethylene can be polymerized at low to moderate pressures with transition metal catalysts which operate by an entirely different mechanism (see also Volume 4, Chapters 1 and 2). These catalysts

have been used at high pressures<sup>76,77</sup> but normally, for economic reasons, only sufficient pressure is used to maintain the desired concentration of ethylene monomer in the gas phase or in solution in an inert solvent. Such catalysts produce very few short chain or long chain branches (densities are about 0.95 to 0.965). PE made with these catalysts is called linear polyethylene or high density polyethylene (HDPE). PE made with free radicals at high pressure is often called low density polyethylene (LDPE), but, as cited above, by operating at low temperatures and at very high pressures, high pressure polyethylene can be made which is essentially linear and which has a density comparable to HDPE.

When these transition metal catalysts are used to copolymerize ethylene with  $\alpha$ -alkenes, side chains are introduced into the structure and crystallinity and density are reduced. Such copolymers have been made with densities down to 0.90 and even lower. Polymers in the lower part of the density range are often referred to as linear low density polyethylene (LLDPE). Because of other differences in molecular structure and because of important property differences, density and molecular weight (or melt viscosity) cannot adequately characterize a PE or fully describe its end use properties. No simple set of measurements can fully characterize all important end use properties. Commercial products are defined by product names and codes and quality control is assured by a combination of process conditions, manufacturing practices and standard quality control tests on the finished products. Different kinds of PE are preferred for different end uses and the several different processes continue to be used commercially.

### 21.7 COPOLYMERS (see Volume 3, Chapter 15)

Ethylene has been copolymerized with many vinyl type monomers at high pressure. In general, transition metal catalysts can be used with hydrocarbon monomers but cannot be used with polar type comonomers because they poison or kill the catalyst. In contrast, free radical initiators work well with polar type comonomers but with  $\alpha$ -alkene comonomers, only very small amounts of comonomers can be incorporated into the polymer. Comonomers used in the greatest quantities commercially are vinyl acetate, methyl acrylate, ethyl acrylate, acrylic acid, and methacrylic acid. Another commercial copolymer, ethylene/vinyl alcohol copolymer, cannot be made directly because vinyl alcohol (CH<sub>2</sub>=CHOH) does not exist. This copolymer is obtained by hydrolyzing ethylene/vinyl acetate copolymers so that the acetate groups are converted to hydroxyl groups. The ethylene/acrylic acid and ethylene/methacrylic acid copolymers can be partially or fully neutralized to make salts with metal ions, the so-called ionomers.

Some monomers which cannot be homopolymerized can be copolymerized with ethylene at high pressures. Examples are maleic anhydride, carbon monoxide<sup>78</sup> and sulfur dioxide.

In general, the incorporation of a comonomer into polyethylene leads to reduced crystallinity and stiffness. The chemical nature of the comonomer can also have a large effect on polymer properties. By choosing the type and amount of comonomer, copolymers can be optimized for a wide variety of end uses.

### 21.7.1 Comonomer Reactivity Ratios (see also Volume 3, Chapter 2)

When two monomers,  $M_1$  and  $M_2$ , are polymerized together, they may both enter the chain to form a copolymer. The number of each and their arrangement are controlled by four reaction rate constants. The two types of polymer radicals with different monomer units at the end of the growing chains are designated as  $M_1^{\circ}$  and  $M_2^{\circ}$ ; each kind of monomer can add to each kind of radical, though the reaction rates can be different. [This simplified reaction scheme (equations 16–20) neglects the effects of the polymer chain composition beyond the terminal radical-containing monomer unit.]

$$\mathbf{M}_{1}^{*} + \mathbf{M}_{1} \xrightarrow{k_{11}} \mathbf{M}_{1} - \mathbf{M}_{1}^{*}$$
(16)

$$\mathbf{M}_{1}^{\bullet} + \mathbf{M}_{2} \xrightarrow{k_{12}} \mathbf{M}_{1} - \mathbf{M}_{2}^{\bullet}$$

$$\mathbf{M}_{2}^{*} + \mathbf{M}_{1} \xrightarrow{k_{21}} \mathbf{M}_{2} - \mathbf{M}_{1}^{*}$$
(17)

$$\mathbf{M}_{2}^{\bullet} + \mathbf{M}_{2} \xrightarrow{k_{22}} \mathbf{M}_{2} - \mathbf{M}_{2}^{\bullet}$$
(18)

### Free-radical Polymerization

$$r_1 = k_{11} / k_{12} \tag{19}$$

$$r_2 = k_{22}/k_{21} \tag{20}$$

If ethylene is designated as  $M_1$ , then the reactivity of ethylene relative to that of a comonomer toward the ethylene type radical is  $r_1$ . This relative reactivity toward the comonomer type radical is  $r_2^{-1}$ . The values of the reactivity ratios indicate the distribution of monomers within the chains.

If the product  $r_1 r_2$  is close to unity, then the two comonomers are arranged randomly along the chain. If the product  $r_1r_2$  is less than unity, the monomers tend to alternate along the chains. In this case, if  $r_1$  is greater than unity, the amount of  $M_1$  in the copolymer is greater than its relative amount in the feed; if  $r_2$  is greater than unity, the amount of  $M_2$  in the copolymer is greater than its relative amount in the feed. If both  $r_1$  and  $r_2$  are zero, then the alternation is perfect. Finally, if the product  $(r_1r_2)$  is greater than one, block polymerization is favored. Such block copolymerization has not been clearly established in high pressure free radical copolymerization.

High pressures can have different effects on the reactivity of different monomers.<sup>79-82</sup> The reactivity ratios can change considerably with pressure, especially when ethylene is one of the monomers. Table 2 shows some reactivity ratios for ethylene and other monomers.

Comonomer $(M_2)$	r <sub>1</sub>	<i>r</i> <sub>2</sub>	Pressure (MPa)	Temperature (°C)	Refs.
Propylene	$3.1 \pm 0.2$	$0.77 \pm 0.05$	103–172	130-220	a, b
1-Butene	$3.4 \pm 0.3$	$0.86 \pm 0.02$	103-172	130-220	a, b
Vinyl acetate	$1.07 \pm 0.06$	$1.09 \pm 0.2$	101	90	c, d
Acrylic acid	$0.09 \pm 0.02$	6			d
•	0.02	4	118-207	140-226	c, d, e
Methacrylic acid	0.1	6			d
•	0.008	4	122-127	202-231	c, d, e
Methyl acrylate	$0.042 \pm 0.004$	$5.5 \pm 1.5$			d
	0.05	8	138	130-152	c, d, e
Ethyl acrylate	$0.19 \pm 0.04$	$2.2 \pm 0.7$			d
5 5	0.04	15	207	180	c. d. e
N-Butyl acrylate	0.03 + 0.01	11.9 + 2.5	101	70	c, d
Vinyl chloride	$0.24 \pm 0.07$	$3.6 \pm 0.3$	101	90	c, d
Carbon monoxide	0.15	0.0	92	130	f

**Table 2** Reactivity Ratios for Ethylene  $(M_1)$  and Comonomers  $(M_2)$ 

<sup>a</sup> L. Bogetich, G. A. Mortimer and G. W. Daues, J. Polym. Sci., 1962, 61, 3.

<sup>b</sup>G. A. Mortimer, J. Polym. Sci., Part B, 1965, 3, 343.

<sup>e</sup> R. D. Burkhart and N. L. Zutty, J. Polym. Sci., Part A, 1963, 1, 1137.

<sup>d</sup> P. Ehrlick and G. A. Mortimer, *Adv. Polym. Sci.*, 1970, 7, 386. <sup>e</sup> L. J. Young, *J. Polym. Sci.*, 1961, **54**, 411.

<sup>f</sup> D. D. Coffman, P. S. Pinkney, F. T. Wall and H. S. Young, J. Am. Chem. Soc., 1952, 74, 3391.

Ethylene and vinyl acetate have nearly equal reactivities at pressures within the commercial range. Copolymers of ethylene and vinyl acetate have nearly the same relative composition as feed streams. This means that such copolymers can be produced in either tubular or autoclave reactors.

However, most comonomers have different reactivity ratios. This difference in reactivity presents a special problem in tubular reactors. In commercial products, a comonomer will usually be present in a minor amount (less than about 20%). If it reacts faster than ethylene, it will be present in the feed stream in an even smaller ratio. As copolymer is produced, the comonomer will be depleted more rapidly than the ethylene. Consequently, the composition of the copolymer produced as the reaction mixture advances in a tubular reactor keeps changing toward lower comonomer content. This change in composition is undesirable for many uses.

In a well-stirred autoclave reactor, the feed stream is rapidly mixed with the contents of the reactor and steady state is rapidly reached. The comonomer ratio is nearly constant throughout the reactor and the polymer has a uniform componer composition when a uniform feed is maintained.<sup>83</sup> The autoclave process is generally preferred for making copolymers from monomers which do not have similar reactivity ratios.

### 21.7.2 Chain Transfer Activity of Comonomers (see also Volume 3, Chapter 17)

Most comonomers contain hydrogen atoms which can enter into telogenic, or chain transfer reactions (see above). At the same polymerization temperature and pressure, the molecular weight of the polymer would be reduced by this chain transfer activity.<sup>84</sup> To maintain the desired molecular weight, the polymerization temperature must be reduced as more comonomer is used; this results in a reduction of short chain branching.

When  $\alpha$ -alkenes are used as comonomers, their telogenic activity, combined with a polymerization rate slower than that of ethylene, severely restricts the amount that can be incorporated into the copolymer in high pressure free radical polymerizations. With the more reactive polar comonomers, sufficient amounts can be readily copolymerized so that the copolymer is less crystalline than the homopolymer. However, the density of a polar copolymer is no longer a reliable measure of crystallinity since it is directly affected by the density contributions of the polar comonomer itself.

This reduction in polymerization temperature for copolymers means that the exothermic conversion must be limited. This reduction in conversion will add to the cost of production of copolymers, in addition to the cost of the comonomer itself.

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