COPOLYMERS

1. Introduction

Over the last 50 years, synthetic polymers have replaced traditional materials such as metals, ceramics, wood, and natural fibers in a large number of applications including automotive, construction, appliances, and clothing. In addition, complete new markets have been opened. This revolution has been possible because polymers have many interesting features including high strength/weight ratio, chemical inertness, and easy processability. Another important feature of the synthetic polymers is that the properties can be tuned to match the needs of a given application. This tuning process is often done by preparing new materials through copolymerization.

This article reviews the preparation, properties, use, and characterization of synthetic copolymers and discusses future trends.

2. Copolymer Structures

IUPAC (International Union of Pure and Applied Chemistry) defines a polymer (macromolecule) as: “A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass”. These molecules of low molecular mass are called monomers. Copolymers are macromolecules formed by polymerization of two or more different monomers (comonomers). Homopolymers are formed by polymerization of a single class of monomers.

Copolymers differ in the sequence arrangements of the monomer species in the copolymer chain. In terms of monomer sequence distribution different classes of copolymers can be distinguished (Table 1).

Statistical copolymers are copolymers in which the sequential distribution of the monomeric units obeys known statistical laws. Within this category, copolymers formed following a Markovian process of zero-order (Bernoullian distribution) are named *random copolymers* because the probability of finding a given monomeric unit at any given site of the chain is independent of the nature of the adjacent units. Nevertheless, the term of random copolymer is often used in a broader sense to refer to copolymers in which the comonomer units are evenly distributed along the polymer chain. This defination is the meaning used in this article.

An alternating copolymer is a copolymer comprising two species of monomeric units distributed in alternating sequence. A gradient copolymer is formed by polymer chains whose composition changes gradually along the chain.

Block copolymers are defined as polymers having a linear arrangement of blocks of different monomer composition. In other words, a block copolymer is a combination of two or more polymers joined end-on-end. Any of these polymers or blocks is comprised by monomeric units that should at least have one constitutional unit absent in the other blocks. The blocks forming the block copolymer can be different homopolymers, a combination of homopolymers and copolymers, or copolymers of different chemical composition in adjacent blocks.

Table 1. **Classes of Copolymers in Terms of Monomer Sequence Distribution**

Type of copolymer	Structure	Examples		
		Comonomers/reactants	Polymerization method	Name
statistical (random)	. . .ABBABABAAABBABAAB. . .	methyl methacrylate, butyl acrylate	free-radical polymerization	poly(methyl methacrylate-*stat*-butyl acrylate)
alternating	. . .ABABABABABAB. . .	styrene, maleic anhydride	free radical polymerization	poly(styrene-*alt*-maleic anhydride)
periodic	. . .ABBABBABB. . . or $-(\text{ABB})_n$	formaldehyde, ethylene oxide	free-radical polymerization	poly(formaldehyde-*per*-ethylene oxide-*per*-ethylene oxide)
gradient	. . .AAAABAAABAABBABBBABBBB. . .	styrene, butyl acrylate	controlled free-radical polymerization	polystyrene-*co*-butylacrylate
block	AAAAAABBBBBBBBAAAAA	styrene, butadiene	ionic polymerization	Polystyrene-*block*-polybutadiene-*block*-polystyrene
graft	AAAAAAAAAA B C B C C B	styrene/acrylonitrile, polybutadiene	free-radical polymerization	polybutadiene-*graft*-poly(styrene-*stat*-acrylonitrile)

Table 2. **IUPAC Source-Based Copolymer Classification**

Polymer type	Connective	Example
unspecified or unknown	*-co-*	poly(A-*co*-B)
random (obeys Bernoullian distribution)	*-ran-*	poly(A-*ran*-B)
statistical (obeys known statistical law)	*-stat-*	poly(A-*stat*-B)
alternating (for two monomeric units)	*-alt-*	poly(A-*alt*-B)
periodic (ordered sequence for >2 monomeric units)	*-per-*	poly(A-*per*-B-*per*-C)
block (linear block arrangement)	*-block-*	polyA-*block*-polyB
graft (side chains connected to main chain)	*-graft-*	polyA-*graft*-polyB

A graft copolymer is a polymer comprising one or more blocks connected to the backbone as side chains, having constitutional or configurational features that make them different from the main chain.

IUPAC (1–4) proposed two naming methodologies for polymers. The first methodology is the *structure-based nomenclature system* that requires naming a polymer as poly(constitutional repeating unit), wherein the repeating unit is named as a bivalent organic radical according to the rules used for organic chemistry. This nomenclature can be difficult to apply if the structure is only partly known or unknown, unless assumptions are made. The second methodology is the *source-based nomenclature system* that requires naming the polymer by adding the prefix "poly" to the name of the actual or hypothetical monomers; an infix, called a connective, is placed between them to indicate the type of sequential arrangement of the constitutional units within the chains. This nomenclature is most often employed within the scientific community. Table 2 presents a summary of the IUPAC source-based copolymer classification. Some specific examples are given in Table 1.

Copolymers can also have widely different topologies. Table 3 presents the main classes as well as some examples with the corresponding IUPAC names.

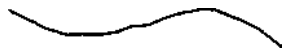
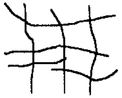
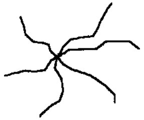
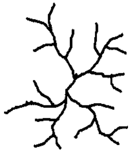
3. Copolymerization Reactions

Table 4 summarizes the different types of polymerizations (6). Chain-growth polymerization involves polymer chain growth by reaction of an active polymer chain with single monomer molecules. In step-growth polymerization, polymer growth involves reactions between macromolecules. In addition, nonpolymeric by-products may be formed in both types of polymerizations. Condensative chain polymerization is very rare.

3.1. Chain-Growth Copolymerization. In chain-growth copolymerization, monomers can only join active chains. The activity of the chain is generated by either an initiator or a catalyst. The following classes of chain-growth copolymerizations can be distinguished according to the type of active center:

- Free radical polymerization (the active center is a radical).
- Anionic polymerization (the active center is an anion).
- Cationic polymerization (the active center is a cation).
- Catalytic polymerization (the active center is an active site of a catalyst).

Table 3. **Nomenclature of Some Common Copolymers**

		Example		
	Architecture	Comonomers/reactants	Polymerization method	Name
linear		styrene	free-radical polymerization	polystyrene
branched		*n*-butyl acrylate	free-radical polymerization	*branch*-poly-(*n*-butyl acrylate)
comb		poly (methylsiloxane, styrene)	atom-transfer radical polymerization (ATRP)	poly(methyl siloxane)-*comb*-polystyrene
cross-linked/ network		butadiene	free-radical polymerization	*net*-polybutadiene
star		methyl methacrylate	ATRP	4-*star*-poly (methyl methacrylate)
hyper branched		4-(chloromethyl) styrene	ATRP	hyperbranched poly(chloromethyl styrene)[a]

[a] IUPAC nomenclature for hyperbranched polymers is not available yet, in the meantime, IUPAC recommends following the rules in Ref. (5).

Table 4. **Classes of Polymerizations**

Chain-growth polymerization	Step-growth polymerization
$P_n + M \longrightarrow P_{n+1}$ (chain polymerization) polystyrene	$P_n + P_m \longrightarrow P_{n+m}$ (polyaddition) polyurethanes
$P_n + M \longrightarrow P_{n+1} + Z$ (condensative chain polymerization)	$P_n + P_m \longrightarrow P_{n+m} + Z$ (polycondensation) poly(ethylene terephthalate)

3.2. Step-Growth Copolymerization.

Monomer molecules consisting of at least two functional groups would undergo step-growth polymerization. These functional groups would be capable of reacting with each other, eg, a $-COOH$ group would react with $-OH$ and $-NH_2$ groups. The two reacting functional groups could be on the same monomer molecule, type A–B (eg, an aminoacid) or on two separate molecules, types A–A and B–B (eg, a diacid and a diol).

Step-growth polymerization proceeds by reaction of the functional groups of the reactants in a stepwise manner: monomers react to form dimer; monomer and dimer react to form trimer; dimer and trimer form pentamer, and in general:

$$n\text{-mer} + m\text{-mer} \longrightarrow (n+m)\text{-mer} \tag{1}$$

This reaction pathway requires to achieve very high conversions in order to produce high molecular weight polymers (>98–99%). A number of different chemical reactions may be used in step-growth polymerization including esterification, amidation, the formation of urethanes, aromatic substitution, and carbonate bond formation.

4. Free-Radical Copolymerization

Free-radical copolymerization can be divided into classical free-radical polymerization and controled radical polymerization.

4.1. Classical Free-Radical Copolymerization.

The characteristics of the materials produced by free-radical copolymerization are determined by the kinetics, rather than by the thermodynamics, of the chain-growth process. Therefore, it is important to adequately describe the copolymerization kinetics. There is considerable experimental evidence (7–9) showing that in many polymerization systems, propagation depends on the nature of the monomer and on the last two units of the growing chain. This is referred to as *penultimate model*. Nevertheless, copolymer composition can be well described by considering a model in which the reactivity of the propagation reaction is governed by the nature of the monomer and the terminal unit of the polymer radical (*terminal model*). In what follows, the penultimate model will be presented first and then the terminal model will be discussed.

Penultimate Model. The features of the propagation reactions of the penultimate model for free-radical copolymerization are summarized in the following simplified reaction scheme:

$$
\begin{aligned}
&R_{11} + M_1 \xrightarrow{k_{p111}} R_{11}\\
&R_{21} + M_1 \xrightarrow{k_{p211}} R_{11}\\
&R_{11} + M_2 \xrightarrow{k_{p112}} R_{12}\\
&R_{21} + M_2 \xrightarrow{k_{p212}} R_{12}\\
&R_{12} + M_1 \xrightarrow{k_{p121}} R_{21}\\
&R_{22} + M_1 \xrightarrow{k_{p221}} R_{21}\\
&R_{12} + M_2 \xrightarrow{k_{p122}} R_{22}\\
&R_{22} + M_2 \xrightarrow{k_{p222}} R_{22}
\end{aligned}
\tag{2}
$$

where R_{ij} is a polymer radical whose last two units are of type i and j, respectively. From these reactions, four different monomer reactivity ratios (r_{ij}) and two radical reactivity ratios (s_i) can be defined as follows:

$$
r_{11} = \frac{k_{p111}}{k_{p112}} \quad r_{21} = \frac{k_{p211}}{k_{p212}} \quad r_{12} = \frac{k_{p122}}{k_{p121}} \quad r_{22} = \frac{k_{p222}}{k_{p221}} \quad s_1 = \frac{k_{p211}}{k_{p111}} \quad s_2 = \frac{k_{p122}}{k_{p222}} \tag{3}
$$

The instantaneous copolymer composition referred to monomer 1, Y_1, is determined by the relative rates of monomer consumption

$$
\begin{aligned}
Y_1 &= \frac{dM_1/dt}{dM_1/dt + dM_2/dt}\\
&= \frac{1 + \dfrac{r_{21}\frac{[M_1]}{[M_2]}\left(r_{11}\frac{[M_1]}{[M_2]} + 1\right)}{r_{21}\frac{[M_1]}{[M_2]} + 1}}{2 + \dfrac{r_{21}\frac{[M_1]}{[M_2]}\left(r_{11}\frac{[M_1]}{[M_2]} + 1\right)}{r_{21}\frac{[M_1]}{[M_2]} + 1} + \dfrac{r_{12}\left(r_{22} + \frac{[M_1]}{[M_2]}\right)}{\frac{[M_1]}{[M_2]}\left(r_{12} + \frac{[M_1]}{[M_2]}\right)}}\\
Y_2 &= 1 - Y_1
\end{aligned}
\tag{4}
$$

where $[M_i]$ is the concentration of monomer i. The reactivity ratios determine not only the instantaneous copolymer composition, but also the comonomer sequence distribution in the copolymer chain. The probability distribution function for having a sequence of x units of monomer i in the copolymer chain is

$$
F_i(x) = 1 - p_{jii} \qquad x = 1 \tag{5}
$$

$$
F_i(x) = p_{jii}p_{iii}^{x-2}(1 - p_{iii}) \qquad x > 1 \qquad i,j = 1,2 \tag{6}
$$

where

$$p_{jii} = \frac{[\mathrm{M}_i]}{[\mathrm{M}_i] + [\mathrm{M}_j]/r_{ji}} \tag{7}$$

$$p_{iii} = \frac{[\mathrm{M}_i]}{[\mathrm{M}_i] + [\mathrm{M}_j]/r_{ii}} \tag{8}$$

The penultimate model can simultaneously account for the copolymerization rate, the copolymer composition, and the sequence distribution (9). However, its usefulness is limited by the fact that for a copolymerization of two monomers, the values of eight different propagation rate constants are needed, and the number of parameters rapidly increases as a multimonomer system is considered. Therefore, there is a strong interest in using simpler models. Fukuda and coworkers (7) proposed the *implicit penultimate model* in which $r_{ii} = r_{ji}$. Although there are theoretical reasons supporting the explicit penultimate model, its superiority over the implicit penultimate model seems to be marginal in most cases (9). Even in the case of the implicit penultimate model, the number of parameters is large, and further simplification of the model is desirable. This is achieved in the *terminal model* in which the reactivity of the propagation reaction is governed by the nature of the monomer and the terminal unit of the polymer radical.

Terminal Model. According to the terminal model, the propagation reactions are as follows:

$$\begin{aligned} &\mathrm{R}_1 + \mathrm{M}_1 \xrightarrow{k_{p11}} \mathrm{R}_1 \\ &\mathrm{R}_1 + \mathrm{M}_2 \xrightarrow{k_{p12}} \mathrm{R}_2 \\ &\mathrm{R}_2 + \mathrm{M}_1 \xrightarrow{k_{p21}} \mathrm{R}_1 \\ &\mathrm{R}_2 + \mathrm{M}_2 \xrightarrow{k_{p22}} \mathrm{R}_2 \end{aligned} \tag{9}$$

In this scheme, R_i represents a polymer radical with ultimate unit of type i.

The polymerization rate referred to monomer i, R_{pi}, is

$$\mathrm{R}_{pi} = (k_{pli}p_1 + k_{p2i}p_2)[\mathrm{M}_i][\mathrm{R}^*] \qquad i = 1, 2 \quad (\mathrm{mol/Ls}) \tag{10}$$

where kp_{ij} is the propagation rate constant of radicals of terminal unit i with monomer j, $[\mathrm{M}_i]$ is the monomer concentration, $[\mathrm{R}^*]$ is the concentration of radicals, and p_i is the time averaged probability of finding an active chain with ultimate unit of type i given by (10):

$$p_1 = \frac{k_{p21}[\mathrm{M}_1]}{k_{p21}[\mathrm{M}_1] + k_{p12}[\mathrm{M}_2]} \qquad p_2 = 1 - p_1 \tag{11}$$

It is well documented that the terminal model is not adequate to describe the polymerization rate of an increasing number of free-radical copolymerizations

(7–9). However, it is widely used in practice because (a) for historical reasons, values of the terminal model reactivity ratios for many comonomer systems are available (11), and (b) in many cases, eg, emulsion polymerization, the uncertainties associated with [R*] are larger than the errors included by the terminal model.

The instantaneous copolymer composition is given by the Mayo-Lewis equation (12).

$$\begin{aligned} \mathrm{Y}_1 &= \frac{d\mathrm{M}_1/dt}{d\mathrm{M}_1/dt + d\mathrm{M}_2/dt} \\ &= \frac{1 + r_1([\mathrm{M}_1]/[\mathrm{M}_2])}{2 + r_1([\mathrm{M}_1]/[\mathrm{M}_2]) + r_2([\mathrm{M}_2]/[\mathrm{M}_1])} \qquad (12) \\ \mathrm{Y}_2 &= 1 - Y_1 \end{aligned}$$

where $r_i = k_{pii}/k_{pij}$ are the monomer reactivity ratios.

It has been found that the Mayo-Lewis equation predicts well the evolution of copolymer composition (13–15). This equation shows that the instantaneous copolymer composition depends on the reactivity ratios, which in turn mostly depend on the chemical nature of the monomers involved, and on the ratio of monomer concentrations in the polymerization loci. Figure 1 shows the effect of the monomer molar ratio on the instantaneous copolymer composition for different reactivity ratios.

The reactivity ratios also determine the comonomer sequence distribution in the copolymer chain. The probability distribution function for having a

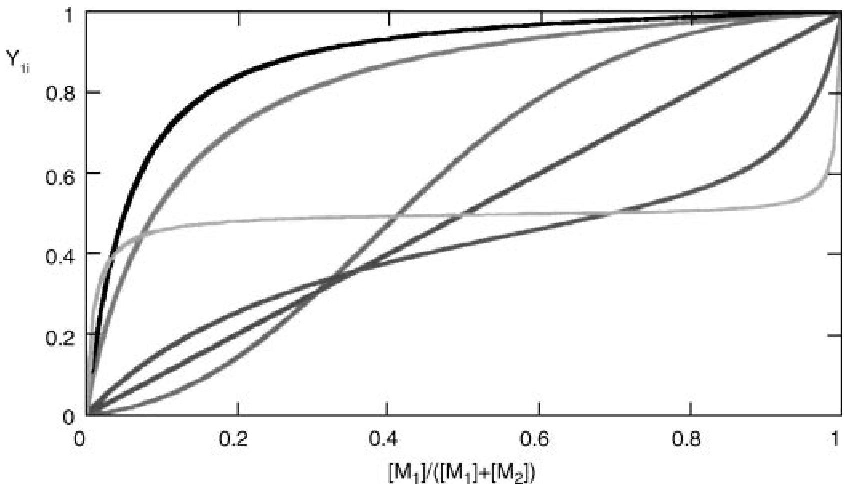


Fig. 1. Effect of the reactivity ratios on the instantaneous copolymer composition referred to monomer 1, Y_{1i}. Legend: (▬) $r_1 = 22$ and $r_2 = 0.06$; (▬) $r_1 = 10$ and $r = 0.1$; (▬) $r_1 = 10$ and $r_2 = 5$; ▬ $r_1 = r_2 = 1$; (▬) $r_1 = 0.1$ and $r_2 = 0.5$; ▬ $r_1 = 0.01$ and $r_2 = 0.02$.

sequence of x units of monomer i in the copolymer chain is

$$F_i(x) = p_{ii}^{x-1}(1 - p_{ii}) \qquad i = 1, 2 \tag{13}$$

where

$$p_{ii} = \frac{r_i[\mathrm{M}_1]/[\mathrm{M}_2]}{r_i[\mathrm{M}_1]/[\mathrm{M}_2] + 1} \tag{14}$$

The adequacy of the terminal model for describing the sequence distribution of copolymerization systems is controversial as it has been found inadequate for some systems such as α-methyl styrene–acrylonitrile (16), methyl methacrylate–acrylonitrile (17), and styrene–maleic anhydride (18), but adequate for vinyl acetate–butyl acrylate (13), and methyl methacrylate–methyl acrylate (14). Statistical methods to discriminate between the penultimate and the terminal models have been discussed (19). Certainly, until additional data are available, the terminal model seems to be a practical way for predicting copolymer composition and sequence distribution. Qualitatively, several cases may be distinguished:

- $r_1 \ll 1$ and $r_2 \ll 1$, both monomers add almost exclusively to the other monomer, and hence an alternating copolymer is obtained.

  ABABABABABABABABABABAB

- $r_1 < 1$ and $r_2 < 1$, both monomers add preferentially to the other monomer, and therefore a copolymer with some alternating character is formed. The alternating character decreases as the reactivity ratios approach unity.

  ABABAABABABBABABABAABB

- $r_1 < 1$ and $r_2 > 1$, copolymer formed by a long sequences of monomer 2 separated by single monomer 1 units.

  BBBBABBBBABBBBBABBBBBB

- $r_1 = r_2 = 1$, a random copolymer is formed.

  ABAABABBAAABABBBABAABB

- $r_1 > 1$ and $r_2 > 1$, the same monomer is added preferentially, and hence the copolymer is made of long sequences of each monomer.

  AAAABBBBAAAABBBBBAAAAABB

- $r_1 > 1$ and $r_2 < 1$, copolymer formed by a long sequences of monomer 1 separated by single monomer 2 units.

  AAAAAABAAAAABAAAAAABA

- $r_1 \gg 1$ and $r_2 \gg 1$, the same monomer is almost exclusively added and a mixture of homopolymer chains with small amounts of block copolymers is obtained

AAAAAAAAAAAAAAAAAAAAAA

BBBBBBBBBBBBBBBBBBBBBBB

BBBBBBBBBBBBAAAAAAAAAA

Factors Affecting the Reactivity Ratios. *Chemical nature:* Reactivity ratios depend on both radical and monomer reactivities. Monomer reactivity increases with its ability to stabilize by resonance the radical formed from the monomer, which depends on the substituent X in $CH_2{=}CHX$, according to the sequence (20): $-Ph, -CH{=}CH_2 > -CN, -COR > -COOH, -COOR > -Cl > -OCOR, -R > -OR, -H$. Substituents composed of unsaturated linkages are most effective stabilizing the radicals because of the loosely held π-electrons. On the other hand, resonance stabilized radicals are the least reactive. The effect of resonance is more acute in radical than in monomer reactivity. This means that copolymerization between two monomers with stabilizing substituents or between two monomers without stabilizing substituents will be favored, whereas copolymerization between a monomer with a stabilizing substituent and a monomer without it will be difficult. Steric hindrance and polar effects also affect reactivity ratios.

Arguably, the most efficient method for producing graft copolymers is copolymerizing monomers with macromonomers. The reactivity of the macromonomer is primarily determined by the chemical nature of the polymerizable group in the macromonomer, but the degree of compatibility of the macromonomer with the propagating polymer chain may affect the macromonomer reactivity(21).

Polymerization conditions: Reactivity ratios are not substantially affected by the reaction medium used, provided that the system remains homogeneous. However, in heterogeneous systems, such as in emulsion polymerization, the apparent reactivity ratios are strongly affected by monomer partitioning between different phases. Thus, when monomers with widely different water solubilities are copolymerized, the monomer molar ratio in the polymer particles may be very different from the average ratio in the reactor, affecting the apparent reactivity ratios (22). Nevertheless, when the monomer partitioning is properly taken into account, the actual reactivity ratios should be used (23). In addition, the effect of the different water solubilities decreases as the solids content increases (24). The reactivity ratios are relatively insensitive to temperature (11).

Determination of the Reactivity Ratios. The reactivity ratios can be determined from experimental data and estimated from empirical correlations.

The determination of the reactivity ratios with small confidence intervals requires a careful experimental design, sensitive analytical techniques, and the use of a good method for parameter estimation. Unfortunately, these requirements are not always fulfilled in the determination of many of the binary reactivity ratio values published. Although, traditionally low conversion data have been used, higher precision is obtained running the experiments to high conversion (25). The error-in-variable estimation method, which allows accounting properly for all sources of error, is superior to classical linear and nonlinear least squares (26–28). The error-in-variable method also allows estimating reactivity ratios in terpolymerization (29), and from emulsion polymerization data by accounting for monomer partitioning (30).

The reactivity ratios can also be estimated from empirical equations. As discussed above, propagation constants depend on resonance stabilizations, polar, and steric effects. Price (31) and Alfrey and Price (32), proposed that the propagation rate constant for polymerization of radical 1 and monomer 2 be written as

$$k_{p12} = P_1 Q_2 \exp(-e_1 e_2) \tag{15}$$

where P_1 and Q_2 are associated to the resonance stabilization, and e_1 and e_2 depend on the polarity of the macroradical and monomer. By assuming that the same e values apply to the monomer and to the corresponding radical, the reactivity ratios are then expressed in terms of the Alfrey-Price Q,e scheme:

$$r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)] \tag{16}$$

$$r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)] \tag{17}$$

$$r_1 r_2 = \exp[-(e_1 - e_2)^2] \tag{18}$$

where each monomer has a Q resonance value and an e polarity value. The Q,e scheme requires that a monomer is chosen as a reference. Styrene was chosen as the reference monomer and a Q value of unity and an e value of −0.800 were assigned. Table 5 shows a selection of Q,e values and Table 6 presents a comparison between the values of the reactivity ratios predicted with this scheme and those estimated from experimental data.

Copolymerization with Depropagation. Classical analysis of free-radical copolymerization considers that propagation occurs irreversibly. However, this is not the case for the polymerization of some monomers such as methyl methacrylate and α-methyl styrene at relatively high temperatures. The copolymerization of monomers that suffer depropagation cannot be accounted for by either the

Table 5. **Selection of *Q* and *e* Values**[a]

Monomer	Q	e
ethylene	0.016	0.05
vinyl chloride	0.056	0.16
methyl methacrylate	0.78	0.40
acrylamide	0.23	0.54
methyl acrylate	0.45	0.64
butyl acrylate	0.38	0.85
1-hexene	0.035	0.92
acrylonitrile	0.48	1.23
butadiene	1.70	−0.50
isoprene	1.99	−0.55
styrene	1.00	−0.80
vinyl acetate	0.026	−0.88
propylene	0.009	−1.69

[a] Ref. 13.

Table 6. **Comparison between the Values of the Reactivity Ratios Predicted by the *Q*,*e* Scheme and Those Estimated from Experimental Data**

Monomer system	*Q*,*e* scheme	Estimated from experimental data[a]
1. styrene	$r_1 = 0.70$	$r = 0.84$
2. butyl acrylate	$r_2 = 0.09$	$r_2 = 0.18$
1. methyl methacrylate	$r_1 = 1.91$	$r_1 = 2.15$
2. ethyl acrylate	$r_2 = 0.49$	$r_2 = 0.4$
1. styrene	$r_1 = 0.46$	$r = 0.6$
2. butadiene	$r_2 = 1.98$	$r_2 = 1.8$

[a] Ref. 11.

classical penultimate model or the classical terminal model. Lowry (33) developed models to predict the instantaneous copolymer composition when only one monomer tends to depropagate for three cases that considered different penultimate effects. Wittmer (34) and Krüger and co-workers (35) developed equations for the instantaneous copolymer composition when both monomers can depropagate. By considering the following terminal model scheme,

$$\begin{aligned} \mathrm{R}_{r,1} + \mathrm{M}_1 &\underset{k_{pr11}}{\overset{k_{p11}}{\rightleftharpoons}} \mathrm{R}_{r+1,1} \\ \mathrm{R}_{r,1} + \mathrm{M}_2 &\underset{k_{pr12}}{\overset{k_{p12}}{\rightleftharpoons}} \mathrm{R}_{r+1,2} \\ \mathrm{R}_{r,2} + \mathrm{M}_2 &\underset{k_{pr22}}{\overset{k_{p22}}{\rightleftharpoons}} \mathrm{R}_{r+1,2} \\ \mathrm{R}_{r,2} + \mathrm{M}_1 &\underset{k_{pr21}}{\overset{k_{p21}}{\rightleftharpoons}} \mathrm{R}_{r+1,1} \end{aligned} \tag{19}$$

Krüger and co-workers (35) developed the following equation for the instantaneous molar ratio of the comonomers in the copolymer:

$$\begin{aligned} \mathrm{Y}_1 &= \frac{d\mathrm{M}_1/dt}{d\mathrm{M}_1/dt + d\mathrm{M}_2/dt} \\ &= \frac{[\mathrm{M}_1]\{r_1([\mathrm{M}_1] + q_1P_{21}) + [\mathrm{M}_2] - r_1K_1P_{11}\} - q_1P_{21}(r_1K_1P_{11} + q_2P_{12})}{\begin{array}{l}[\mathrm{M}_1]\{r_1([\mathrm{M}_1] + q_1P_{21}) + [\mathrm{M}_2] - r_1K_1P_{11}\} - q_1P_{21}(r_1K_1P_{11} + q_2P_{12}) \\ \quad +[\mathrm{M}_2]\{r_2([\mathrm{M}_2] + q_2P_{12}) + [\mathrm{M}_1] - r_2K_2P_{22}\} \\ \quad -q_2P_{12}(r_2K_2P_{22} + q_1P_{21})\end{array}} \end{aligned} \tag{20}$$

$$\mathrm{Y}_2 = 1 - Y_1 \tag{21}$$

with

$$r_1 = \frac{k_{p11}}{k_{p12}} \qquad r_2 = \frac{k_{p22}}{k_{p21}} \qquad q_1 = \frac{k_{pr12}}{k_{p21}} \qquad q_2 = \frac{k_{pr21}}{k_{p12}} \qquad K_1 = \frac{k_{pr11}}{k_{p11}} \qquad K_2 = \frac{k_{pr22}}{k_{p22}} \tag{22}$$

the parameters P_{ij} are determined from a steady-state approximation on the radical species balance with the conditions that $P_{ii} + P_{ij} = 1$. By using a different analysis method, Wittmer (34) developed a different, although equivalent, equation. Palmer and co-workers (36) used the equations developed by Wittmer (34) and Kruger and co-workers (35) to analyze the copolymerization of methyl methacrylate and α-methyl styrene in a wide temperature range. It was reported that both approaches described the experimental data well with the Krüger equations being more stable and having better convergence properties. On the other hand, the data could not be fitted by the Mayo-Lewis equation (eq. 12).

Copolymer Composition Evolution. In classical free-radical polymerization, the number of polymer chains that are growing at the same time is rather small (10^{-8}–10^{-7} mol/L), and the time spent by a chain from initiation to termination is very short (typically 0.5–10 s). This means that the final copolymer is made of polymer chains formed at different moments in the polymerization process. This characteristic limits to random, alternating, and ill-defined graft the type of copolymers that are accessible using classical free-radical polymerization. This means that well-defined block and graft copolymers cannot be produced by means of classical free-radical copolymerization. On the other hand, the cumulative copolymer composition referred to monomer h, $\bar{Y}_h$, differs from the instantaneous one $\bar{Y}_{hi}$:

$$\bar{\mathrm{Y}}_{hi} = \frac{1}{X_{Tf}} \int_0^{X_{Tf}} \mathrm{Y}_{hi} dX_T \tag{23}$$

where X_T is the overall molar conversion defined as the number of moles of monomer reacted divided by the total number of moles of monomer in the formulation. Figure 2 presents the effect of the reactivity ratio values on the evolution of the instantaneous copolymer composition in a batch reactor. It can be seen that a substantial composition drift occurred for monomers with different reactivity ratios, as well as for monomers of similar reactivity but using not equimolar feed compositions. This fact and the problems associated with heat removal led to the use of semicontinuous reactors for copolymer composition control (see the section Controlling Copolymer Microstructure).

Multicomponent Copolymerization. Multicomponent copolymerization involves three or more monomers. The polymerization rate of monomer i and the instantaneous copolymer composition are given by

$$\frac{d[\mathrm{M}_i]}{dt} = \left(\sum_{j=1}^{n} k_{pji} p_j \right) [\mathrm{M}_i][\mathrm{R}^*] \tag{24}$$

$$Y_i = \frac{\left(\sum\limits_{j=1}^{n} k_{pji} p_j \right) f_i}{\sum\limits_{i=1}^{n} \sum\limits_{j=1}^{n} k_{pji} p_j f_i} \tag{25}$$

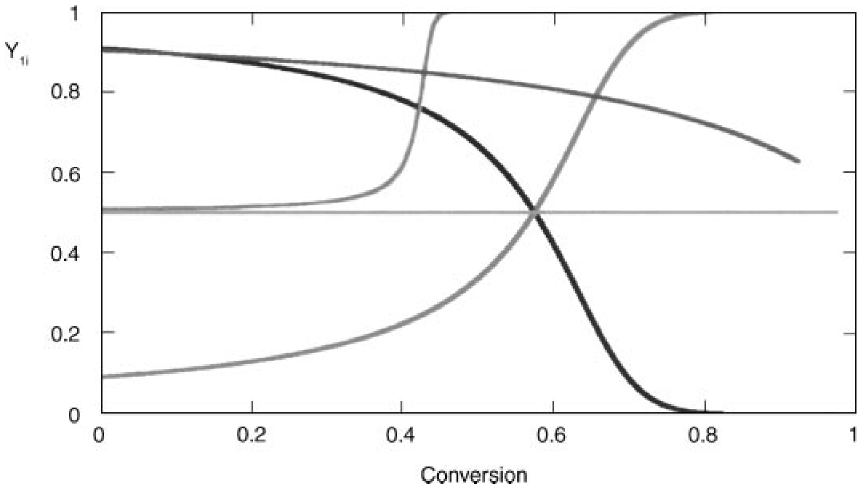


Fig. 2. Effect of the reactivity ratios on the evolution of the instantaneous copolymer composition Referred to monomer 1, in a batch reactor. For $[M_1]/([M_1]+[M_2]) = 0.5$: (▬) $r_1 = 10$ and $r_2 = 0.1$; (▬) $r_1 = 0.1$ and $r_2 = 10$; (—) $r_1 = r_2 = 0.01$; For $[M_1]/([M_1]+[M_2]) = 0.8$: (▬) $r_1 = r_2 = 0.01$; (▬) $r_1 = r_2 = 5$

where f_i is the mole fraction of unreacted monomer i at the polymerization locus.

4.2. Controlled Radical Polymerization. Free-radical copolymerization is attractive because of the huge number of monomers that can be copolymerized, the different media that can be used (both organic and aqueous), and the relative robustness of this technique to impurities. In the classical free-radical copolymerization considered above, only a few polymer chains are growing at the same time and the time spent in building a chain is very short (typically 0.5–10 s). This is convenient to produce random and alternating copolymers, but well-defined complex copolymer topologies (eg, gradient and block copolymers in Table 1) are not accessible through classical free-radical polymerization. In order to produce a well-defined block copolymer, all chains should start at the same time, and they should grow for some time in the presence of monomer 1 until the first block is formed. Then monomer 1 should be removed and a different monomer is added to produce the second block. In order to conduct such a process successfully, termination should be avoided during the polymerization.

In recent years, the development of controlled radical polymerization (CRP) methods has made it possible to conduct a free-radical polymerization minimizing the extent of termination. This allows preparing almost any kind of copolymer microstructure by means of a free-radical mechanism. All CRP methods have in common that a rapid dynamic equilibrium is established between a tiny amount of growing free-radicals and a large majority of dormant polymer chains. In these processes, each growing chain stays for a long time in the dormant state, then it is activated and adds a few monomer units before becoming dormant again. As the activation–polymerization–deactivation process is a random process, the molecular weight distribution of the growing chains becomes narrower as they grow longer. The composition of the polymer chain can be easily modified by controlling the monomer composition in the reactor. Termination between active radicals is minimized by simply maintaining its concentration at a low value. The CRP methods differ in the way in which these dormant species are formed. The most efficient CRP methods are stable free-radical polymerization best represented by nitroxide mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT).

Nitroxide Mediated Polymerization. This field has been reviewed by recently Hawker and co-workers (37). The key aspect of this process is the reversible termination of the growing polymer chain with the nitroxide radical. In this way, the concentration of active chains is very low and the extent of the irreversible bimolecular termination is minimized (Fig. 3).

2,2,6,6-Tetramethylpiperidinyloxy (TEMPO) is one of the most commonly used nitroxide radicals (38), but it suffers from some serious drawbacks including the necessity of using high polymerization temperatures and its incompatibility with many important monomer families. Improved nitroxides based on phosphonate derivatives (39) and on the family of arenes (40) have been developed. With this second-generation nitroxides, a broader range of monomers including acrylates, acrylamides, 1,3-dienes and acrylonitrile, as well as monomers containing functional groups, such as amino, carboxylic acid and glycidyl, can be polymerized with accurate control of molecular weights and polydispersities. Good control of homopolymerization of methacrylates has not been achieved because these monomers are strongly affected by chain end degradation through hydrogen transfer (38). Nevertheless, random copolymers with up to 90% of methacrylate incorporation can be prepared in a controlled fashion (40); the reasons for this behavior are not clear currently. The reactivity ratios in NMP are the same as in conventional free-radical polymerization. This leads to one of the advantages of controlled radical polymerization compared to living anionic or cationic

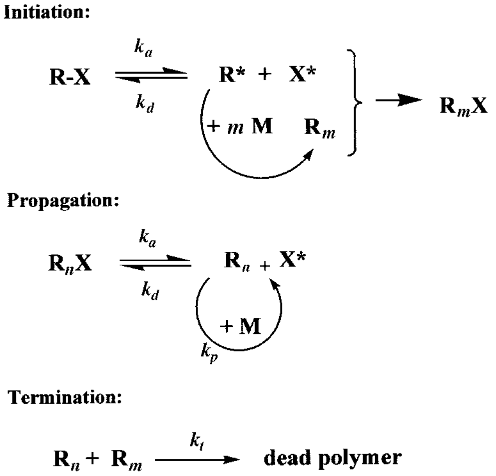


Fig. 3. Scheme of a NMP.

polymerizations, which is the ability of preparing well-defined random copolymers. In batch copolymerizations of monomers with different reactivity ratios, the chemical composition distribution of the chains formed by CRP considerably differs from that of the polymer chains produced in the classical free-radical polymerization (see the section Some Common Kinetic Features of the CRP Processes). Nitroxide mediated polymerizations allow us to produce narrow molecular weight distributions (MWD) up to a value of the number average molecular weight of ~200,000 g mol (40). At higher molecular weights, termination reactions become significant and this leads to a loss of control and the living character of the process.

ATRP. An excellent review of this process can be found in (41). In the ATRP process, the reactor is charged with monomer and a certain amount of alkyl halides that act as initiator. The alkyl halides are dormant species that can be activated through a reversible redox process catalyzed by a transition-metal complex (M_t^n–Y/ ligand, where Y may be another ligand or the counterion). The active radical adds some monomer units as in classical free-radical polymerization until it suffers a deactivation reaction. (Fig. 4).

The main role of the initiator is to determine the number of polymer chains. Termination between active radicals is minimized by maintaining a low concentration of active chains. In a well-controlled process, <5% of the polymer chains suffer termination. The molecular weight is determined by the ratio of consumed monomer and the initiator. Well-defined polymers with molecular weights between 1000 and 150,000 g/mol have been obtained, but termination and chain transfer make it difficult to obtain longer polymers of well-defined microstructure. A challenge for the ATRP process is the removal and recycling of the catalyst, which has not been adequately achieved yet. Monomers with substituents that can be stabilized by resonance of the radical formed from the monomer [(eg, styrenes (42), (meth)acrylates (43,44), (meth)acrylamides (45), and acrylonitrile (46)] can be successfully polymerized by means of ATRP. Other monomers like olefins, halogenated alkanes, and vinyl acetate have not been polymerized yet using ATRP. On the other hand, acidic monomers have not been polymerized

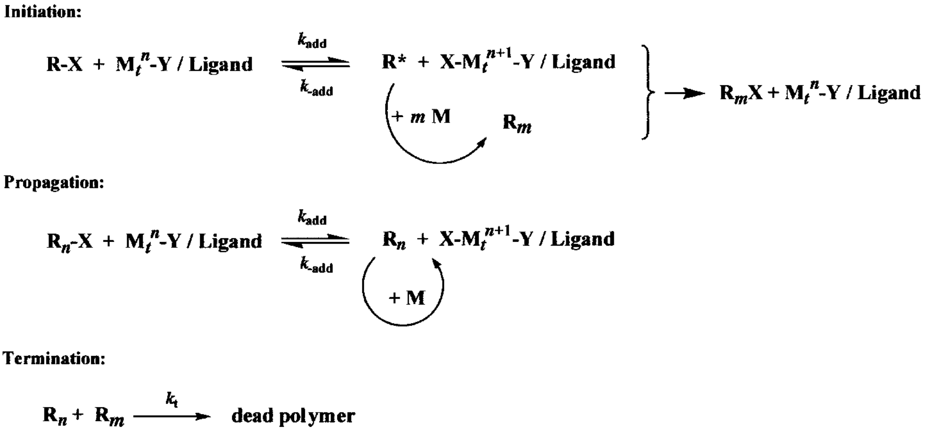


Fig. 4. Scheme of a transition metal catalyzed ATRP.

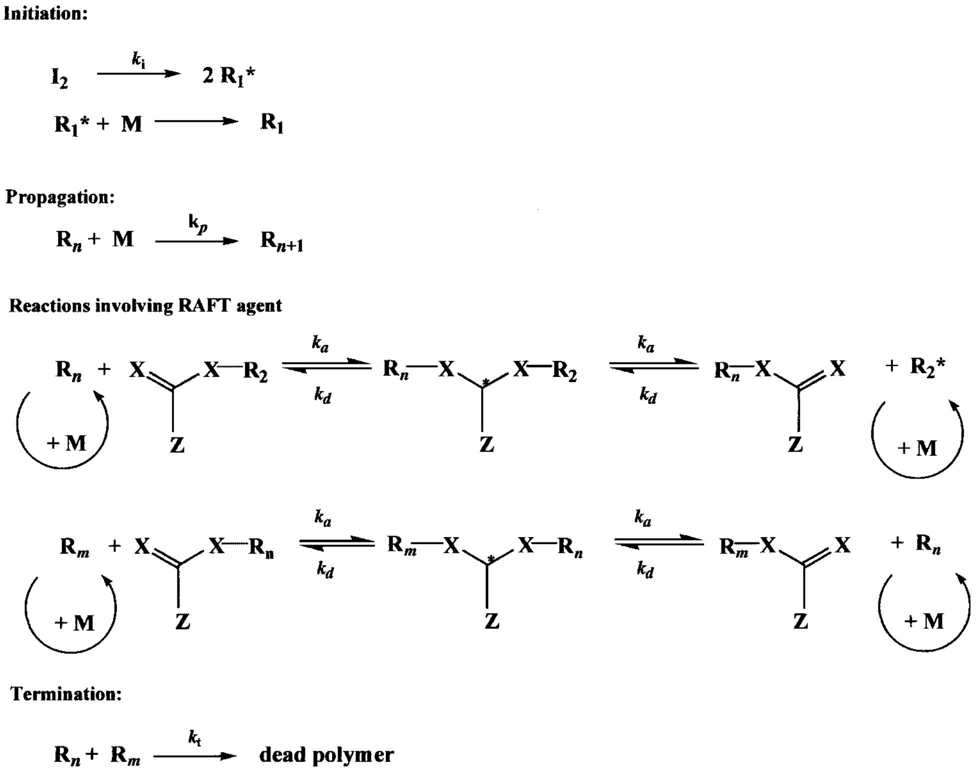


Fig. 5. Scheme of a RAFT process.

using this method because they can protonate ligands and form the corresponding salt. Nevertheless, the polymerization of the neutral salt of the acidic monomers is possible (47).

RAFT. This process is performed in the presence of certain dithio compounds (eg., dithiobenzoates), which act as highly efficient reversible addition–fragmentation chain transfers and provide the polymerization with living characteristics. The polymerization proceeds according to the scheme in Figure 5.

RAFT has a number of advantages as a synthetic method because it is applicable to a wide range of monomers (48), including many unreactive monomers, such as vinyl acetate (49). Since radicals are generated in a conventional way (eg, by means of a conventional initiator), it is tolerant of impurities. Polymerization conditions are typical of those used for classical free-radical polymerization and the process can be tailored to ambient temperatures (50). On the other hand, retardation may occur when the RAFT agent is used in high concentrations to produce low molecular weight polymers (51).

Some Common Kinetic Features of the CRP Processes. The key feature of the CRP processes is that molecular termination is minimized by maintaining the concentration of active radicals at a low value by establishing a rapid equilibrium between this small fraction of active radicals and a large majority of dormant polymer chains. The extent of bimolecular termination can be lowered by reducing the concentration of active chains, but at the expense of a longer process time. Therefore, there is a practical lower limit in the concentration of active chains. The relative influence of both bimolecular and monomolecular (eg, chain transfer to monomer) termination events on the MWD increases as longer polymer chains are produced. This represents a practical limit for the maximum molecular weight that can be achieved under controlled conditions, which currently is in the range of 150,000–200,000 g/mol (37,41).

Controlled radical polymerizations (NMP, ATRP, and RAFT) can be carried out in bulk, solution, and suspension polymerization. Mass transfer limitations of the radical trapping agent make difficult the implementation in conventional emulsion polymerization (52,53). This limitation has been overcome working in miniemulsion polymerization (51,54–60). In CRP, the reactivity ratios of the monomers are the same as in conventional free-radical polymerization (37,41). In addition, the reactivity ratios of the macromonomers are close to those of the monomers with the same polymerizable group, in contrast with classical free-radical polymerization where the reactivity of the macromonomers is substantially lower than that of the corresponding monomers. This may be due to the longer characteristic times for monomer and macroradical addition (61).

The chemical composition distribution of the chains formed by CRP considerably differs from that of the polymer chains produced in the classical free-radical polymerization. In a batch controlled process in which monomers with different reactivity ratios are polymerized, all polymer chains have a very similar chemical composition distribution (CCD) with a composition gradient along the chain. In the corresponding classical free-radical polymerization, the CCD of the chains formed at the beginning of the polymerization may greatly differ from that of the chains formed at the end of the process, and the composition along each chain is constant.

It is important noticing that the concepts of instantaneous and cumulative copolymer composition in CRP are different from those in classical free-radical polymerization. In CRP the instantaneous copolymer composition, which can be calculated with equations 4 or 12, refers to the composition of the part of the chains that is being formed in a given moment. In classical free-radical polymerization, the instantaneous copolymer composition is the composition of the chains being formed in a given moment. On the other hand, the cumulative copolymer composition in a CRP represents the average composition of the fraction of each chain formed up to the time considered, whereas in classical free-radical copolymerization, it is the average composition of all chains formed up to this time.

5. Anionic Copolymerization

Anionic polymerization is not spontaneous and requires the presence of initiators that provide the initiator anions. Anions can only attack those monomers whose electrons can be moved in such a way that a monomer anion results. Therefore, anionically polymerizable monomers should contain electron-accepting groups. These includes styrene, acrylic monomers, some aldehydes and ketones, and cyclic monomers such as ethylene oxide and other oxiranes, N-carboxy anhydrides, glycolide, lactams, and lactones that can be polymerized by ring-opening polymerization. The kinetic scheme of an anionic copolymerization may be summarized as follows:

Initiation:

$$\begin{aligned} \mathrm{RM} &\rightarrow \mathrm{R}^- + \mathrm{M}^+ \\ \mathrm{R}^- + \mathrm{M}_1 &\rightarrow \mathrm{R1}_1^- \\ \mathrm{R}^- + \mathrm{M}_2 &\rightarrow \mathrm{R2}_1^- \end{aligned}$$

Propagation:

$$\begin{aligned} \mathrm{R1}_n^- + \mathrm{M}_1 &\xrightarrow{k_{p11}} 1_{n+1}^- \\ \mathrm{R1}_n^- + \mathrm{M}_2 &\xrightarrow{k_{p12}} 2_{n+1}^- \\ \mathrm{R2}_n^- + \mathrm{M}_1 &\xrightarrow{k_{p21}} 1_{n+1}^- \\ \mathrm{R2}_n^- + \mathrm{M}_2 &\xrightarrow{k_{p22}} \mathrm{R2}_{n+1}^- \end{aligned} \tag{26}$$

This kinetic scheme does not include termination because in purified systems, most macroanions grow until all of the monomer present in the reactor is polymerized. Such polymerization is called living polymerization, because if additional monomer is added into the reactor the polymer chains undergo further growing. A characteristic of the living polymerization is that, provided that initiation is quick enough, all polymer chains grow to a similar extent yielding very narrow molecular weight distributions. In addition, block copolymers can be produced by adding a second monomer once the first one has completely reacted. Triblock and multiblock copolymers can be prepared by subsequent additions of different monomers. Also, graft, star, and hyperbranched polymers can be obtained by means of this technique by simply using suitable initiation systems (62).

The concept of reactivity ratios applies also to anionic copolymerization. However, the production of statistical copolymers in anionic polymerization is often difficult because the macroanions substantially differ in polarities yielding to widely different reactivity ratios, usually $r_1 \gg 1$ and $r_2 \ll 1$, which means that block copolymers are mainly produced. Typical reactivities encountered in anionic copolymerization are shown in Table 7 (63).

Reactivity ratios are affected by the solvent. Thus, Table 7 shows that styrene is in general less reactive than diene monomers except when tetrahydrofuran (THF) is used as a solvent, in which case the reactivity changes and styrene becomes more reactive. Statistical copolymerization of styrene and dienes with more polar monomers, which have much higher electronegativities, is unlikely to take place. For example, the copolymerization of styrene and methyl methacrylate only yields block copolymers. In general, only monomers with fairly small differences in electronegativities can be successfully copolymerized, and even in these cases the tendency is toward forming block copolymers.

Table 7. **Reactivity Ratios in Anionic Copolymerization**[a]

M_1	M_2	Solvent	Counterion	Temp°C	r_1	r_2
styrene	butadiene	hexane	Li^+	25	0.03	12.5
styrene	butadiene	benzene	Li^+	25	0.04	10.8
styrene	butadiene	THF	Li^+	−35	8	0.2
styrene	isoprene	benzene	Li^+	30	0.14	7.0
styrene	isoprene	cyclohexane	Li^+	40	0.046	16.6
styrene	isoprene	THF	Li^+	−35	40	0
isoprene	butadiene	hexane	Li^+	40	0.3	2.0
styrene	*p*-methylstyrene	benzene	Li^+	30	2.5	0.4
styrene	*p*-methylstyrene	THF	Li^+	0	1.3	0.9
styrene	*p*-methylstyrene	THF	Na^+	0	2	0.4
styrene	1,1-diphenylethylene	benzene	Li^+	30	0.7	0
isoprene	1,1-diphenylethylene	THF	Li^+, Na^+, K^+	0	0.1	0

[a] Ref. 63.

6. Cationic Polymerization

Cationic polymerization presents many similarities with anionic polymerization. Cationic initiators formed from carbocation salts, Brønsted acids, or Lewis acids, react with monomer to give monomer cations that upon addition of more monomer become macrocations. Both monomer cations and macrocations are fairly reactive and may react with the counterions instead of with monomer. Therefore, counterions should not be too nucleophilic. The nucleophilicity of the counterions depends on the solvent, and hence only a few solvents, including benzene, nitrobenzene, and methyl chloride, are suitable for cationic polymerization. Monomers suitable for cationic polymerization should have electron-donating groups: (a) olefins CH_2=CHR with electron-rich substituents, (b) compounds R_2C=Z with heteroatoms or hetero groups Z, and (c) cyclic molecules with heteroatoms as part of the ring structure. Although, there are many more cationically polymerizable monomers than anionically polymerizable ones, relatively few cationic polymerizations are performed industrially because macrocations are highly reactive and prone to suffer termination and chain-transfer reactions.

Thus, the cationic polymerization of alkenyl monomers suffers from the transfer reactions that affect the stability of the active intermediate species. Therefore, in order to minimize these transfer reactions and to produce high molecular weight polymers, very low temperatures must be used. When heterocyclic monomers are employed, higher temperatures can be used although care must be taken with the ceiling temperature that promotes depropagation in these cases.

A compilation of reactivity ratio data for styrene-like monomers are given in (62). The main trends are as follows: (a) copolymerization of styrene (A) with less basic monomers (B, obtained by adding an electron-withdrawing group, eg, *p*-halostyrene) results in $r_A > 1$ and r_B; (b) copolymerization of styrene with more basic monomers (eg, α-methylstyrene and *p*-methylstyrene) results in $r_A > 1$ and $r_B > 1$. These trends can be altered by steric effects. When other nonstyrenic monomers are employed in the copolymerization it is difficult to establish clear trends. In addition, variables such as solvent polarity, temperature, and counterion effects may significantly affect the reactivity ratios, but it is not straightforward to determine the extent of the effect (64). In the copolymerization of heterocycle monomers, care should be taken when using the Mayo-Lewis equation to calculate reactivity ratios because this equation cannot be used if depropagation reactions are relatively important (see the section Copolymerization with Depropagation). Because of the living character of the polymerization, well-defined cationic polymerization is, together with anionic polymerization, one of the typical routes to prepare block and graft copolymers. In addition, it allows the preparation of prepolymers that can be further activated to generate branched and graft copolymers (65–69).

7. Ring-Opening Copolymerization

Ring-opening copolymerization (ROP) consists in opening a cyclic compound to produce a linear polymer as shown in the following scheme:

$$C_nX \rightarrow (C_n - X)_p \tag{27}$$

The functional groups denoted as X include –CH=CH– and those that consist of one or two heteroatoms such as O, N, S, P, and Si. Ring-opening polymerization of heterocyclic monomers are classified depending on the nature of the propagating species and monomers (70). Ring-opening polymerization can proceed via (a) electrophilic propagating species, mainly cationic polymerization; (b) nucleophilic propagating species, mainly anionic polymerization; (c) zwitterion intermediates, in which the propagating chain and the monomer bear both cationic and anionic species. This type of polymerization is always catalyzed by an initiator (protonic acids including BF_3, $AlCl_3$, $AlBr_3$, and $SnCl_3$; tryalyloxonium salts; carbenium salts; and others) at very low temperatures to avoid depropagation.

Ionic ring-opening polymerization of heterocyclic compounds, such as ethylene oxide, THF, ethyleneimine, β-propiolactone, and caprolactam as well as the Ziegler-Natta ring opening of cyclic alkenes, such as cyclopentene and norbornene, are well known, but free-radical ROP is rather rare (71–73). An example of cyclic monomers that copolymerize with common monomers by radical ROP are the cyclic ketene acetals (74,75). The main deficiency of these monomers is their rather low reactivity to monomers such as styrene. Thus, for the copolymerization of 2-methylene-1,3-dioxepane and styrene in bulk at 120°C, the reactivity ratios are $r_{\text{ketene}} = 0.021$ and $r_{\text{st}} = 22.6$.

Regarding copolymerization, this technique is predominantly employed to produce block and also graft copolymers. In these cases, the concepts discussed for the copolymerization via cationic and anionic polymerization are also applicable here.

8. Catalytic Polymerization

Free-radical, anionic, and cationic polymerizations proceed by addition of monomer units to the active end of the growing polymer chain that in the course of polymerization separates from the bound initiator fragment. Catalytic polymerizations proceed by an insertion mechanism, in which the monomer units are inserted between the catalytic site and the growing polymer chain. Over 40% of the yearly polymer production is obtained by catalytic polymerization (76). This includes linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), which are copolymers of ethylene and α-olefines (with decreasing amounts of α-olefines as a higher density is sought); polypropylene and high impact polypropylene; and EPDM elastomers (terpolymers of ethylene, propylene, and a nonconjugated diene, eg, 5-ethylidene-2-norbornene). Catalytic polymerizations are carried out using Ziegler-Natta, transition-metal and metallocene catalysts.

8.1. Ziegler-Natta Catalysts. A typical commercial Ziegler-Natta catalyst for ethylene polymerization is produced by reacting $TiCl_4$ with a finely divided $MgCl_2$ stabilized with an electron donor (internal donor; eg, phthalate ester, diethers, and succinates) and activating the resulting system with trialkylaluminium compounds. In propylene polymerization, the addition of another electron donor (external donor, eg, alkoxysilanes) is usually needed to achieve high stereospecifity (76).

There is some debate about the mechanisms involved in the growth of polymer chains on the active center. The most widely accepted mechanism is that proposed by Cossee (77) in which propagation occurs at the transition-metal–alkyl bond (Fig. 6). The first step of this mechanism is the complexation of the olefin in a vacant coordination site followed by migration of the polymer chain and formation of a new metal–carbon bond. An exchange of the alkyl groups and the vacancy is needed to account for the formation of stereoregular polymers (78).

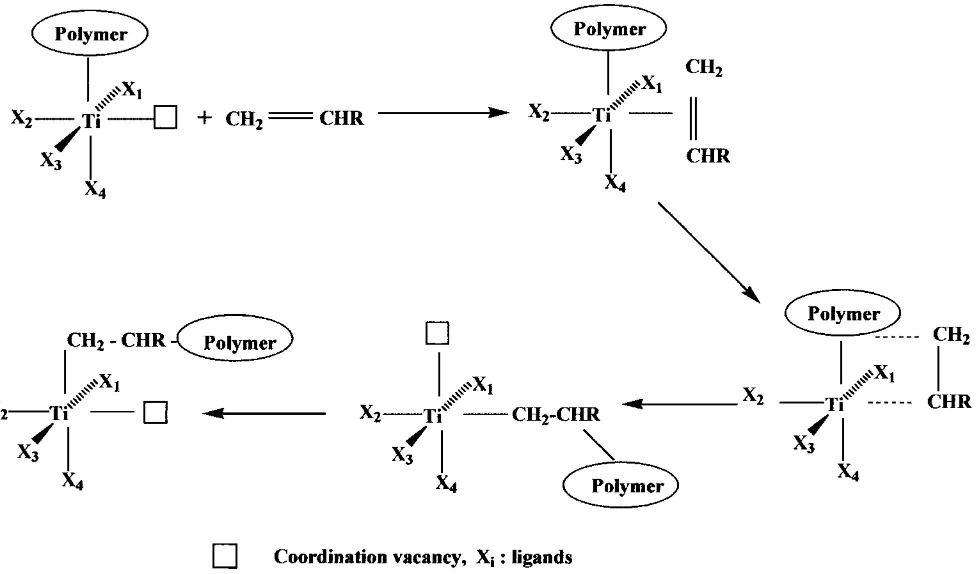


Fig. 6. Cossee's mechanism of monomer insertion.

Copolymerization adds complexity to the propagation step because four different reactions are involved

$$\begin{aligned}
&\mathbf{catalyst{-}M_1{-}Polymer + M_1 \xrightarrow{k_{p11}} catalyst{-}M_1{-}M_1{-}Polymer}\\
&\mathbf{catalyst{-}M_1{-}Polymer + M_2 \xrightarrow{k_{p12}} catalyst{-}M_2{-}M_1{-}Polymer}\\
&\mathbf{catalyst{-}M_2{-}Polymer + M_1 \xrightarrow{k_{p21}} catalyst{-}M_1{-}M_2{-}Polymer}\\
&\mathbf{catalyst{-}M_2{-}Polymer + M_2 \xrightarrow{k_{p22}} catalyst{-}M_2{-}M_2{-}Polymer}
\end{aligned} \tag{28}$$

By considering this scheme, the instantaneous copolymer composition is (79)

$$\begin{aligned}
Y_1 &= \frac{dM_1/dt}{dM_1/dt + dM_2/dt} = \frac{1 + r_1([M_1]/[M_2])}{2 + r_1([M_1]/[M_2]) + r_2([M_2]/[M_1])}\\
Y_2 &= 1 - Y_1
\end{aligned} \tag{29}$$

Note that the similarity of this equation with that giving the instantaneous copolymer composition for the terminal model of the classical free-radical copolymerization (eq. 12). However, in this case, $[M_i]$ is the concentration of monomer i at the active center, which due to mass transfer limitations may be different from that of the feed (80). On the other hand, the reactivity ratios, r_i, are a measure of the tendency for a comonomer to show preference for insertion into a growing chain in which the last inserted unit was the same, rather than the other comonomer. The effect of the values of the reactivity ratios on the chemical composition distribution is as in classical free-radical polymerization (the section Terminal Model).

Ziegler-Natta catalysts present multiplicity of active centers (81). Each centre may have a different activity, and hence different reactivity ratios. Therefore, the average copolymer composition of chains of different lengths is different, namely, there is a correlation between chain molecular weight and chain composition (Fig. 7). In addition, the catalytic activity changes with time. Consequently, the reaction scheme and the copolymerization equation may require modification to account for these features of the Ziegler-Natta catalysts. Reactivity ratios depend on operation conditions [eg, temperature (82), reactant concentrations (83,84), nature of the catalyst (85), and comonomer structure (86)].

8.2. Transition-Metal Catalysts. The Phillips catalyst discovered by Hogan and Banks (87) is the most common example of these catalysts. The Phillips catalysts encompass two families of supported chromium catalysts (88): (a) organochromium compounds, and (b) chromium oxide. Suitable supports include silica, aluminophosphates, and silica–titania. Polymerization of ethylene on these catalysts yields a linear polymer (HDPE). Copolymerization of ethylene and α-olefins yields linear polymers with short branches. The crystallinity of the copolymer, and consequently its density decreases as the copolymer content in α-olefins increases. Phillips catalysts are able to produce a wide range of polyethylenes (from HDPE to LLDPE). The chromium content of the catalyst is in the

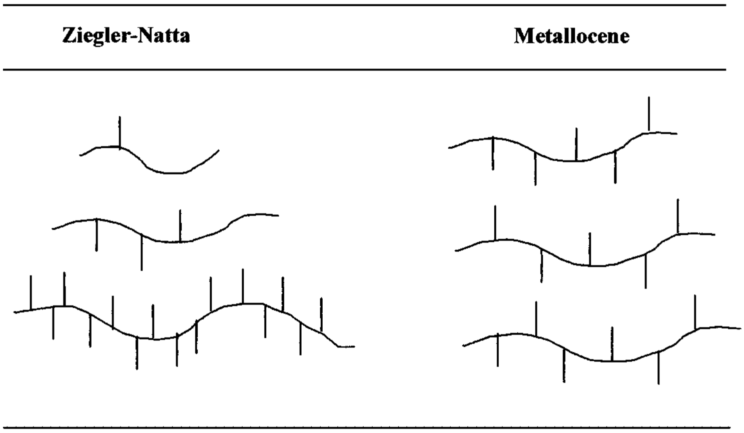


Fig. 7. Comparison between the polymers obtained using Ziegler-Natta catalysts and metallocenes.

range of 0.2–1 wt%, although only a small fraction of the chromium is active. The Phillips catalyst presents a distribution of actives sites leading to broad molecular weight distribution (89). The polymerization mechanism is still a matter of debate, although theoretical calculations (90) suggest that propagation may occur through the Cossee mechanism (77).

8.3. Metallocene Catalysts. Metallocenes are organometallic compounds that consist of a metallic atom coordinated with two cyclopentadienyl rings. Figure 8 shows the general structure of the homogeneous metallocene catalysts, where M is a transition metal, usually from Group 4 (IVB); B is a bridge formed by one or several atoms (usually C or Si); R is hydrogen, an alkyl group or any hydrocarbon group; and X is a halogen (usually Cl) or an alkyl group. Although metallocene catalyst are new in commercial applications, the first attempts to use metallocenes as catalysts for olefin polymerization were carried out in the 1950s. Natta and co-workers (91) and Breslow and Newburg (92) used metallocene activated with alkyl aluminium as catalysts in ethylene polymerization, but these systems showed a low activity and fell into oblivion until Sinn and Kaminsky (93) discovered that metallocenes activated with methyl aluminoxane (MAO) showed a high activity in olefin polymerization. Several reviews on metallocene catalysts are available (94–98). Metallocenes are single center catalysts and represent the most versatile way of synthesizing almost any kind of stereoregular polymer. Polymers with entirely new properties may be produced by varying the components (type of metal and its substituents, type and length of the bridge, and substituents of the rings) of the metallocene molecule (99,100). Metallocenes are single active center catalysts, and hence the composition of all copolymer chains is statistically the same, and independent of chain length (Fig. 7). This opens the possibility for a much tighter control of copolymer composition. In addition, metallocene catalysts exhibit higher reactivity for α-olefines than the conventional Ziegler-Natta catalysts (98). Figure 7 also illustrates that the molecular weight distribution of the polymer produced with metallocene catalysts is narrower than that obtained with Ziegler-Natta catalysts. For a given

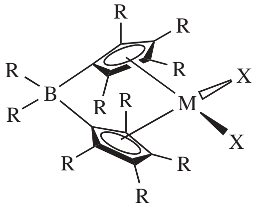


Fig. 8. General structure of homogeneous metallocene catalysts.

monomer system, the catalyst activity and the reactivity ratios strongly depend on the structure of the metallocene molecule (101), MAO/metallocene ratio (102) and temperature (102) among other variables.

The metallocene of Figure 8 is soluble in organic solvents, and hence can be directly used in solution copolymerization. However, soluble metallocenes present some serious drawbacks. First, high MAO/metallocene ratios are required to obtain adequate activity levels and stereochemical control. MAO is expensive and significantly increases production costs. In addition, most of polyolefins are produced by slurry and gas-phase processes, which need heterogeneous catalysts. Three main methods have been used to prepare supported metallocene catalysts (103): (1) direct impregnation of the metallocene on the support followed by treatment with MAO (104); (2) impregnation of the metallocene on a support previously treated with MAO (105); and (3) chemical anchoring of the metallocene on a modified support followed by treatment with MAO (106). In comparison with the homogeneous counterparts, the main advantages of the supported metallocenes are (103): (a) lower MAO/metallocene ratio; (b) higher molecular weights; (c) higher isotacticity for polypropylene, and (d) usable in slurry and gas processes. On the other hand, the supported metallocenes have a lower activity than the homogeneous ones and yield broader molecular weight distributions, likely because the interaction between the metallocene and the support leads to active centers with a distribution of catalytic activities.

Copolymerization of ethylene and α-olefins is used in the manufacture of the high tonnage LLDPE. In this process, metallocene catalysts exhibit higher reactivity for α-olefins than conventional Ziegler-Natta catalysts (98). The reactivity ratios of ethylene and α-olefins can be modified in a wide range by varying the structure of the metallocene catalyst. This allows tailoring the monomer sequence distribution in the copolymer and even alternating ethylene/α-olefin copolymers have been obtained for both long (1-octene) (107) and short (propylene) (108) α-olefins. Incorporation of styrene into ethylene/styrene copolymers is also easier with metallocene catalysts as compared with Ziegler-Natta catalysts (109). Highly syndiotactic poly(propylene-*co*-α-olefin) is one of the new polymers that can be synthesized by using metallocene catalysts (110).

There is some controversy about the mechanisms involved in polymer chain growth, and insertion mechanisms inspired in that proposed by Cossee (77) for Ziegler-Natta catalysts have been proposed (111,112). Production of EPDM by terpolymerization of ethylene/propylene/diene using metallocene catalysts has been reported (113).

One of the factors that is retarding the introduction of metallocene-based polyethylenes is the difficulties in processing caused by the narrow MWD (114). Processability is substantially improved in the case of polyethylene with long branches produced by means of the constraint-geometry catalyst (115,116). This catalyst has been used in the copolymerization of ethylene and styrene with a good incorporation of styrene (117).

9. Step-Growth Copolymerization

Step-growth polymerization proceeds by reaction of the functional groups of the reactants in a stepwise manner: monomer reacts to form dimer; monomer and dimer react to form trimer; dimer and trimer form pentamer, and in general

$$n\text{-mer} + m\text{-mer} \rightarrow (n+m)\text{-mer} \tag{30}$$

In this process, the molecular weight of the polymer continuously increases with time and the formation of polymer with sufficiently high molecular weight for practical applications requires very high conversions of the reactive groups (>98–99%). This requirement poses stringent conditions to the formation of polymers by polycondensation, such as the necessity for a favorable equilibrium and the absence of side reactions. In spite of these difficulties, a number of different chemical reactions may be used to synthesize materials by step polymerization. These include esterification, amidation, carbonate bond formation, the formation of urethanes, and aromatic ether and aromatic ketone bond formation among others.

All step polymerizations (including copolymerizations) fall into two groups depending on the type of monomer(s) employed. The first one implies the use of at least two bifunctional and/or polyfunctional monomers, each one possessing a single type of active group. In this context, a bifunctional monomer is a monomer with two functional groups per molecule and a polyfunctional monomer is a monomer with more than two functional groups. The monomers involved in this type of reaction are often represented as A–A and B–B, where A and B are the different reactive groups. An example of this reaction is the formation of polyesters from diols and diacids.

$$\begin{aligned} &\text{m HOOC-R}_1\text{-COOH} + \text{m HO-R}_2\text{-OH} \rightleftharpoons \\ &\qquad \text{HO}\!\left(\text{OC-R}_1\text{-COO-R}_2\text{-O}\right)_{\text{m}}\text{H} + 2(\text{m}+1)\ \text{H}_2\text{O} \end{aligned} \tag{31}$$

In order to form a copolymer, at least three monomers are needed (eg, two diols and one diacid or one diol and two diacids). The second type of step polymerization involves the use of monomers with different functional groups in the same molecule, A-B type. To produce a copolymer by this step polymerization at least two A–B type monomers must be used (eg, two amino acids).

In comparison with homopolymers, the structure of the step copolymers contains two repeating units as it is shown in the following schemes:

$$\text{—CO—R}_1\text{—CONH—R}_2\text{—NHCO—R}_3\text{—CONH—R}_4\text{—NH—} \tag{32}$$

$$\text{—NH—R}_1\text{—CO—NH—R}_2\text{—CO—} \tag{33}$$

Structure 32 can be synthesized by using two diacids and two diols, and structure 33 by using two different aminoacids.

Different types of copolymers, as those discussed in chain-growth polymerization, are possible depending on the arrangement of the repeating unit on the chain. Thus, alternating, statistical (random) and block copolymers can be formed by step-growth copolymerization.

9.1. Kinetics of Step-Growth Copolymerization.

The kinetic analysis of the copolycondensations of two different diol diesters of dibasic diacids (118) can be used as an example of other copolycondensation kinetics. For this case and assuming that the hydroxyl chain ends attack the terminal ester groups of the chain through irreversible reactions (viz, it is assumed that the diols formed in the process are continuously removed), the following kinetic scheme can be written:

$$\text{—COOR}_1\text{OH} + \text{HOR}_1\text{OOC—} \xrightarrow{k_{11}} \text{—COOR}_1\text{OOC—} + \text{HOR}_1\text{OH} \qquad (34)$$

$$\text{—COOR}_1\text{OH} + \text{HOR}_2\text{OOC—} \xrightarrow{k_{12}} \text{—COOR}_2\text{OOC—} + \text{HOR}_1\text{OH} \qquad (35)$$

$$\text{—COOR}_2\text{OH} + \text{HOR}_1\text{OOC—} \xrightarrow{k_{21}} \text{—COOR}_1\text{OOC—} + \text{HOR}_2\text{OH} \qquad (36)$$

$$\text{—COOR}_2\text{OH} + \text{HOR}_2\text{OOC—} \xrightarrow{k_{22}} \text{—COOR}_2\text{OOC—} + \text{HOR}_2\text{OH} \qquad (37)$$

Reactions 35 and 36 are cross-reactions while reactions 34 and 37 are homoreactions. If $[\text{OH}]_1$ and $[\text{COO}]_1$ and $[\text{OH}]_2$ and $[\text{COO}]_2$ are the concentrations of hydroxyl and ester groups on chains 1 and 2, respectively, the formation rates of the diols ($\text{HO}R_1\text{OH}$ and $\text{HO}R_2\text{OH}$) are given by

$$\frac{d[\text{HOR}_1\text{OH}]}{dt} = k_{11}[\text{COO}]_1[\text{OH}]_1 + k_{12}[\text{COO}]_1[\text{OH}]_2 \qquad (38)$$

$$\frac{d[\text{HOR}_2\text{OH}]}{dt} = k_{21}[\text{COO}]_2[\text{OH}]_1 + k_{22}[\text{COO}]_2[\text{OH}]_2 \qquad (39)$$

At the initial stage of the process, the following condition is satisfied

$$\frac{[\text{monomer 1}]}{[\text{monomer 2}]} = \frac{[\text{OH}]_1}{[\text{OH}]_2} = \frac{[\text{COO}]_1}{[\text{COO}]_2} = a \qquad (40)$$

Dividing equations 38 and 39; rearranging the terms using the condition of equations 40 and considering $b = d[\text{HOR}_1\text{OH}]/d[\text{HOR}_2\text{OH}]$, the following equation is obtained

$$ak_{11} - \frac{b}{a}k_{22} = bk_{21} - k_{12} \qquad (41)$$

The values of k_{11} and k_{22} can be obtained from homopolycondensation kinetics (118,119). If the left-hand term of equation 41 is plotted against b, the slope and intercept give the rate constants k_{21} and k_{12} of the cross-reactions. In a similar way, the rate of incorporation of the diols is

$$-\frac{d[\text{—OR}_1\text{O—}]}{dt} = k_{21}[\text{COO}]_2[\text{OH}]_1 + k_{11}[\text{COO}]_1[\text{OH}]_1 \tag{42}$$

$$-\frac{d[\text{—OR}_2\text{O—}]}{dt} = k_{12}[\text{COO}]_1[\text{OH}]_2 + k_{22}[\text{COO}]_2[\text{OH}]_2 \tag{43}$$

and setting diol ratios in the copolymer as c, dividing equation 42 by equation 43, and rearranging leads to

$$c = \frac{d[\text{—OR}_1\text{O—}]}{d[\text{—OR}_2\text{O—}]} = a \cdot \frac{k_{21} - ak_{11}}{ak_{12} + k_{22}} \tag{44}$$

Equation 44 allows us to built the copolymer composition diagram by calculating the ratio of diols in the polymer, c, for a given monomer ratio, a. This is equivalent to the analysis carried out in the section on the Terminal Model for the chain-growth polymerization that led to the Mayo-Lewis equation (eq. 12) (12). Han (118) demonstrated that the assumptions made to obtain equations 41 and 44 were in good agreement with the low conversion experimental data obtained in the copolycondensation of bis(2-hydroxy ethyl) terephthalate (HET) and bis(2-hydroxy-1-propyl) terephthalate (HDT) carried out in bulk at 160°C. This polycondensation obeys a second-order kinetics with respect to the concentration of ester and hydroxyl groups and the copolymer composition diagram shows an azeotrope composition at 29.5 mol% of HET.

Other systems that were accounted for by equations 41 and 44 are the polyamides synthesized by amide interchange reactions [*N*,*N*′-bis(2-aminoethyl)decandiamide (AES) and *N*,*N*,*N*′, *N*′-bis(diethyleneiminodecandiamide) (DEIS)], and polyester amides synthesized by copolycondensation of a diamine amide of a diacid [AES and bis(2-hydroxyethyl) decandioate (HES)], although for those cases no azeotrope was obtained in the composition diagram (119,120). Table 8 shows the reactivity ratios obtained for these three systems.

In the works discussed above (118–120), the concept of equireactivity, namely, that all functional end-groups attached to the same residue have the

Table 8. **Reactivity Ratios and Homoreaction Rate Constants of Different Copolycondensations Carried Out in Bulk**[a]

Comonomer system	Temperature °C	Homocondensation rate constants kg/mol h	Reactivity ratios
HET (1)	160	1.69	$r_1 = 4.23$
HDT (2)		1.39	$r_2 = 1.70$
AES (1)	200	3.01	$r_1 = 1.30$
DEIS (2)		1.70	$r_2 = 0.59$
AES (1)	200	3.01	$r_1 = 10.03$
HES (2)		34.70	$r_2 = 0.19$

[a] Refs. (118–120).

same reactivity, was used. However, the penultimate effect can be important in some copolycondensation systems such as in phosgene, chloroformates, and phthalates (121).

Turska and co-workers (122–125) found that the composition of the copolymer varied during the solution copolycondensation of terephthaloyl chloride, 2,2-bis(4-hydroxyphenyl) propane and 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane in α-chloronaphthalene at 220°C. Theoretical considerations (123) demonstrated that it is possible to control the average composition of the copolymer by manipulating the reaction conditions for the case of three monomers. Moreover, these authors were able to show that if the homopolycondensations of monomer 1 with monomers 2 and 3 satisfy the Arrhenius dependence with temperature and have different activation energies, there is a temperature at which the rate constants are equal to each other. This temperature is called isokinetic temperature, and at this temperature, the composition of the copolymer is independent of the extent of the reaction. This was experimentally verified for the copolymerization of phenolphthalein, dichloro-3,3′-bisphenol A and terephthaloyl dichloride, which has a isokinetic temperature of 242°C (124). Boryniec (126) has developed kinetic equations for the copolycondensation of three bifunctional monomers when there is a change in reactivity of the intermonomer after reaction of the first functional group. The same author (127) has developed kinetic equations for the copolycondensation of a bifunctional monomer with two other monomers not reacting with each other considering invariable reactivity of the functional groups.

10. Random Copolymers

Random copolymers are by far the largest class of copolymers made and used today. They are mainly produced by catalytic polymerization and by classical free-radical polymerization. Some copolymers are also produced by ionic polymerization.

10.1. Catalytic Random Copolymers.

Polyolefins produced by catalytic polymerization account for more than one-third of the yearly production of synthetic polymers (128). Polyolefins are made from a surprisingly short list of monomers, mainly ethylene and propylene, but also α-olefins (1-butene, 1-hexane, 1-octane), isobutylene and a few other monomers. These monomers are produced in large-scale petrochemical units, and hence they are available in large quantities at low cost. Polylefins are extremely versatile materials with properties ranging from elastomers to thermoplastics to high strength fibers (129). One of the key characteristics of the polyolefins is crystallinity, which depends on the regularity of the chemical structure of the polymer chains. Highly regular polymers such as linear polyethylene and isotactic polypropylene are crystalline polymers, whereas some copolymers of ethylene–propylene and ethylene–α-olefin are amorphous materials.

Catalyst development and polymerization technology have made possible the continuous expansion of the properties of the polyolefins (130). The development of high mileage highly selective Ziegler-Natta catalysts allowed a control of the polymer microstructure (composition, CCD, MWD, tacticity, etc.) and polymer macrostructure (morphology, phase distribution, crystallinity) not achieved previously (76). This trend has been reinforced with the development of metallocene catalysts (131).

Polyolefins are mainly produced by means of particulate polymerization processes: gas-phase and slurry polymerizations. In these processes, the polymerization takes place inside each polymer particle and the properties of the final product strongly depend on the way in which the particle grows. The scientific understanding of the polymer growth mechanisms is critical to control both polymer microstructure and particle morphology, and to achieve the ultimate goal of improving and expanding the polymer properties envelope toward new specialty materials (132).

The main olefin copolymers are LLDPE, some grades of HDPE, ethylene–propylene elastomers, propylene copolymers, and high impact polypropylene (hiPP).

Copolymerization of ethylene and α-olefins lead to LLDPE. The crystallinity, and consequently the density of the polyethylene, is controlled by the amount and type of α-olefin incorporated to the backbone. Decreasing contents of α-olefin lead to higher densities. Thus, HDPE is produced at low or nil α-olefin content. On the other hand, ultralow density polyethylene is produced by copolymerizing ethylene and octane (eg, Attane, Dow Chemical). Comparing with low density polyethylene (LDPE) produced by free-radical polymerization, LLDPE exhibits a higher melting point (objects can be used at higher temperatures), is stiffer (thinner walls can be used), and presents higher tensile and impact strengths (more resistant films). However, the processability of the LLDPE is worse than that of the LDPE. A way of improving processability is to produce bimodal molecular weight distributions. This can be achieved by using dual-site catalysts such as a metallocene supported on a Ziegler-Natta catalyst (133), two different metallocenes on the same support (134), and a single metallocene activated with a mixture of two cocatalysts (135). Another alternative is to use two reactors in series producing different molecular weights in each reactor by using different hydrogen concentrations (hydrogen is an efficient chain-transfer agent) (136). In this case, the polymer particle consists of a blend of polymers of different molecular weights, and when there is a large difference in molecular weights, the effective mixing of the polymer fractions during melt processing may be limited. This limitation may be overcome by means of the "multizone circulating reactor" technology (137,138). This is a loop-like reactor in which different reaction conditions are maintained in each leg of the loop. Continuous circulation of the polymer particles allows the production of intimate blends of polymer chains having different molecular weights and/or compositions. It is claimed that this technology significantly expands the properties envelope (139).

LLDPE is mainly used in film applications with smaller markets in injection molding and wire-cable. Some important producers of LLDPE are Basell (Lupolex), Dow Chemical (Dowlex), ExxonMobil (LL grades), BP Solvay Polyethylene (Innovex), Chevron Phillips Chemicals (Marflex), Equistar Chemicals (Petrothene), Borealis (Borstar) and Atofina. Metallocene-based grades (mLLDPE) are also available in the market (Exceed, ExxonMobil; mPact, Chevron Phillips Chemicals; Boracene, Borealis; Evolue, Mitsubitsi Chemicals; Luflexen, Basell; Umerit, Ume Chemicals). Compared to conventional grades, mLLDPE provides a higher schock resistance (downgauged films), lower content of extractables (better organoleptic properties), and better optical properties (clarity and gloss). However, the processability of the mLLDPE is in general worse than that of the conventional LLDPE. Long branching mLLDPE produced with constraint geometry catalysts (115,116) exhibit LDPE-like processability with LLDPE-like performance (Elite, Dow Chemical).

Ethylene/propylene elastomers (EPM) are copolymers of ethylene and propylene with intermediate levels of each comonomer. These materials are completely amorphous and rapidly recover its shape after removal of a strain of at least 50%. In order to make these elastomers cross-linkable a nonconjugated diene is introduced in the formulation. These products are called EPDM for ethylene, propylene, diene monomer. Ethylidene norbornene and 1.4-hexadiene are common choices for the diene monomer. EPDMs are produced by using both Ziegler-Natta and metallocene catalysts. Some producers are DSM (Keltan), DuPont-Dow Elastomers [Nordel IP (metallocene)], ExxonMobil (Vistalon), and Enichem (Dutral). EPDMs are used in construction (roof sheeting, insulation sponge, seals, hoses-tubes, reservoir linings), automotive (sealing systems, hoses), impact modification of plastics, and wire and cable.

In propylene–ethylene copolymers with a low ethylene content, the insertion of ethylene in the propylene chain reduces the regularity of the chain leading to a semicrystalline polymer. The properties of these materials, called propylene random copolymers, depend not only on the total ethylene content, but also on the monomer sequence distribution (140). Other monomers such as 1-butene and 1,3-butadiene may be incorporated (141). Some producers are Basell (Moplen), Dow Chemical, Equistar (Petrothene), and ExxonMobil (PP9000 Series). The main uses are cast film and rigid and flexible packing.

High impact polypropylene is a multiphase material in which an ethylene–propylene elastomeric phase is finely dispersed in an isotactic polypropylene matrix. In principle, hiPP can be produced by blending iPP and the elastomeric copolymer, but it is simpler and more versatile in terms of product properties achievable to produce the heterophase material during polymerization. Thus, in the Spheripol process (Basell, 142) isotactic polypropylene particles are first produced in a slurry of liquid propylene, and then, the particles are transferred to a gas-phase fluidized bed reactor where the elastomeric material is produced by polymerizing an ethylene-propylene monomer mixture. Figure 9 illustrates the evolution of the particle morphology in this process. In the first reactor, the catalyst forced by the pressure exerted by the polymer that is being formed undergoes a rupture process leading to a porous particle composed of polymer microparticles containing catalyst fragments. In the second stage, because polymerization proceeds by an insertion mechanism, the newly formed elastomeric phase grows inside of the polypropylene microparticles becoming encapsulated by the polypropylene. The encapsulation may not be possible if the volume fraction of the elastomeric phase increases, and then the particle pores become filled with the ethylene–propylene elastomer. If the elastomeric phase reaches the surface of the particle, particle agglomeration may occur leading to reactor fouling and eventually to blocking. Therefore, the characteristics of the catalysts particle and the way in which the operation is conducted are critical for the success of the operation. In order to accommodate large amounts of elastomeric phase,

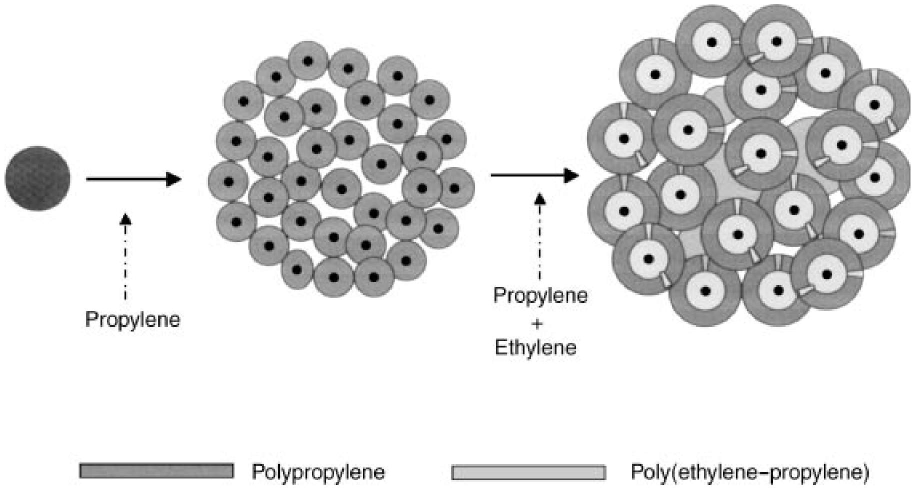


Fig. 9. The hiPP morphology development in a two-stage polymerization process.

particle porosity should be the maximum possible without compromising the particle mechanical integrity.

The ability of dissipating the impact energy, likely via both crazing and shear yielding, is the key property of hiPP. It has been established that the optimal balance of properties can be achieved when the compositions of the rubber fraction is in the range of 50–60 wt% of ethylene and the diameter of the elastomeric domains is ~1 μm (142). In addition, the crystallinity of the polypropylene matrix also plays an important role (143) and it is possible to improve the stiffness–impact performance by increasing crystallinity. This can be achieved by manipulating the molecular weight distribution of the polypropylene, because broad MWDs leads to higher stiffness, due to the effect of the MWD on the kinetics of crystallization (143).

The main applications of hiPP are automotive (interior and exterior trims, bumpers), rigid packaging, consumer goods, pails, and corrugated pipes. Grades containing ~70 wt% of amorphous, propylene-rich ethylene–propylene copolymers are supersoft polypropylene alloys suited for roofing and geomembranes. Some important producers are Basell, Atofina, Borealis, BP Amoco, ExxonMobil, Dow Chemical, and DSM.

10.2. Random Free-Radical Copolymers. Styrene–butadiene rubbers (SBR) is the largest volume synthetic rubber. It is produced in emulsion polymerization by free-radical polymerization and in solution by means of an anionic polymerization mechanisms. The large-tonnage grades of emulsion-polymerized SBR are produced in continuous stirred tank reactors in series. Conversion is maintained below 70% to avoid the formation of branches and gel that have a deleterious effect on rubber properties. There are two broad SBR types. The so-called “cold” grades that are produced at low polymerization temperatures (~5°C) and the “hot” grades produced at ~50°C. The tensile strength of SBR vulcanites increases with decreasing temperature (144) presumably because the molecular weight increases, the tendency for branching and cross-linking reactions decreases, and the ratio *trans*-1.4/*cis*-1.4 increases (145). The styrene/butadiene ratio for general purpose rubbers is in the region of 25/75, wt/wt. At higher contents of styrene, the elastic character of the material decreases and its plasticity increases. At the end of the polymerization, the latex is coagulated, washed, dried, and baled. Polymers with very high molecular weight that are difficult to process with ordinary equipment, can be processes upon addition of oils (oil extended SBR).

The main use of the cold SBR is for tires. Other applications include conveyor belts, rubber articles, and footwear. Hot polymerized SBR is used in sporting goods, shoe soles, and adhesives. Some important producers of SBR are Ameripol Sympol, Bayer, Dow Chemical, Enichem, Firestone Polymers, Goodyear Tire and Rubber, Japan Synthetic Rubber, Korea Kumho, Petroflex, Sinopec, and Zaklady.

Carboxylated styrene–butadiene latexes containing 50–60 wt% of styrene are directly used as dispersions for carpet backing (146) and paper-coating (147,148). Carboxylated styrene–butadiene latexes are produced by BASF, Dow Chemical, and Rhodia among others.

The production method of acrylonitrile–butadiene rubbers (NBR) is similar to that of the emulsion SBR. The properties of this material are strongly affected by its acrylonitrile content, which ranges from 10 to 50 wt%. As the acrylonitrile content increases the processability and oil resistance increase, but the low temperature flexibility decreases. The main use is in applications that require a rubber having good resistance to swelling in organic liquids. Aging and ozone resistance of NBR can be improved by selective hydrogenation of the double bonds of the butadiene units (hydrogenated nitrile rubber). The main producers are Bayer, Enichem, Goodyear, Japan Synthetic Rubber, Nitriflex, Uniroyal, and Zeon. Hydrogenated nitrile rubber is produced by Bayer and Zeon.

Styrene–acrylonitrile copolymers (SAN) are manufactured by emulsion, suspension, and bulk free-radical polymerization. Emulsion and bulk processes can be continuous. The properties of the SAN copolymers strongly depend on copolymer composition. Incorporation of acrylonitrile improves the chemical resistance, the barrier properties, the scratch resistance, and rigidity of polystyrene. Most SAN resins contain 15–30 wt% of acrylonitrile. SAN is used in applications that require better chemical resistance, toughness, and heat distortion temperature such as shower doors, cosmetic bottles, and toys. Most SAN is consumed in the production of acrylonitrile–butadiene–styrene (ABS resins) copolymers. Other applications are appliances, housewares, automotive, and packaging. Grades containing a high amount of acrylonitrile (60–80%) are used as barrier plastics. Some producers are Aiscondel (SAN 44), BASF (Lilerum), Daicel (Cevian), Dow Chemical (Tyril), and Mitsubitsi Chemicals (Saurex).

Ethylene–vinyl acetate copolymers are produced to practically cover the whole range of comonomer ratios from 98/2 (ethylene–vinyl acetate) to 4/96. Control of copolymer composition is easy because the reactivity ratios are close to 1.0. Bulk (mainly) and solution (in less extent) polymerization is used to manufacture copolymers containing 5–50% of vinyl acetate. Emulsion polymerization is used for copolymers with higher vinyl acetate content. Copolymers containing 3–25 wt% of vinyl acetate (EVA copolymers) are used in film applications (blow and cast films, shrink films, stretch film, disposable surgical gloves). Grades with higher vinyl acetate content are used as adhesives, diesel fuel additives, and asphalt modifiers. Dupont (Elvax), Equistar Chemical (Ultrathene), Polimeri (Greeflex), and Sumimoto (Evatate) manufacture EVA copolymers.

Vinyl acetate–ethylene dispersions are used in paint and coatings, adhesives, paper coating, and binders for nonwoven materials such as needlet felt carpet, cleaning cloths and sanitary products, moist wipes, bed covers, winter clothing, and tablewear. Air Products Polymers (Airflex) is the leading producer of these dispersions. Redispersable powder (Vinnapas, Wacker Polymer Systems) based on vinyl acetate–ethylene dispersions (in some cases including also vinyl esters of versatic acid (Veova monomers, Resolution Research) are used in construction (ceramic tile adhesives, mortars, plasters) and as powder paints. Redispersable powders for nonwoven are also available (Vinnex, Wacker Polymer Systems). Copolymers of vinyl acetate and branched vinyl esters are used for architectural paints. Marketed under the name of Veova 10 (Resolution Research) the most distinguishing feature imparted by this branched vinyl ester to the polymer is its resistance to hydrolysis. Some producers of these latexes are BASF, Clariant, Dow Chemical, Rhodia and Wacker Polymer Systems.

Dispersions of vinyl chloride and ethylene are used for paints and flame retardant systems (Airflex, Air Products Polymers). Redispersable powders based on vinyl chloride–ethylene copolymers are also available (Vinnol, Wacker Polymer Systems).

Acrylic copolymers are used for high temperature automotive coatings. Coating quality requires the use of solvent-borne systems, but the use of solvents is limited by environmental regulations. Therefore, there is a strong pressure to increase the solids content. In order to increase the solids content maintaining the viscosity in manageable values, low molecular weight ($\bar{M}_w$: 1000–10000 g/mol) is used. These low molecular weight copolymers are obtained copolymerizing a mixture of methacrylates and acrylates at high temperature (up to 150°C) (149). Monomers containing functional groups (eg, hydroxyl and carboxyl) are included in the formulation to allow cross-linking with suitable cross-linking agents (melamine and isocyananate for $-$OH, and epoxy for $-$COOH). A relatively large fraction of these functional monomers should be used to ensure that most of the short chains contain functional groups.

Acrylic dispersions are extensively used for coatings textiles and nonwoven fabrics, adhesives, floor care, caulks, and sealants. A typical formulation includes a hard (high T_g) monomer such as methyl methacrylate, a soft monomer (low glass transition temperature, T_g) such as butyl acrylate or 2-ethylhexylacrylate, and functional monomers to impart special characteristics (colloidal stability, adhesion, cross-linking) (147,150). The use of styrene as a hard monomer leads to styrene–acrylic latexes. Vinyl acetate is used in vinyl–acrylic latexes. The comonomer ratio is chosen to meet the required for the application. Thus, pressure sensitive adhesives must be soft and tacky ($T_g \cong -50$ to -25°C), architectural paints should form a continuous nonsticky film at room temperature (T_g from 5 to 30°C) and industrial coating and floor polishes should be hard and withstand exigent use (147,150). The T_g depends on copolymer composition and can be estimated using the Fox equation (151).

$$\frac{1}{T_g} = \sum_i \frac{w_i}{T_{g_i}} \tag{45}$$

where w_i is the weight fraction of monomer i in the copolymer and T_{g_i} the glass transition temperature of its homopolymer. Monomer composition also affect another important characteristics. For example, all acrylic paints show a good weatherability and durability but styrene–acrylic latexes with >20 wt% of styrene do not present a good exterior durability (150). Latex performance is also affected by copolymer microstructure (molecular weight distribution, branching, gel content, etc). Thus, in the case of pressure sensitive adhesives, high molecular weights provide resistance to shear, whereas resistance to peel is maximized for intermediate molecular weights, and tackiness requires low molecular weights (152). On the other hand, increasing the gel fraction from 1 to 32% leads to an increase of the shear resistance but further increase of the gel content to 55% results in a severe decrease of the shear resistance (153). Some important producers of acrylic latexes are Akzo-Nobel, Atofina, BASF, Dow, Rohm and Haas, and UCB.

Fluorinated polymers give excellent performance under highly demanding conditions requiring resistance to high temperature, chemical inertness, and low surface tension. Fluorinated homopolymers are often crystalline and copolymerization induces disorder of the polymer chain and consequently reduces crystallinity. Depending on the copolymer composition, fluorinated copolymers range from thermoplastic to elastomers. Thermoplastic fluoropolymers are produced by co(ter)polymerization of a main monomer with a relatively low amount of other monomer(s). Some thermoplastic fluoropolymers are

1. Tetrafluoroethylene (TFE)–hexafluoropropylene (HFP) copolymers (Teflon FEP, DuPont; Neoflon, Daikin).
2. TFE–perfluoropropyl vinyl ether (Teflon PFA, DuPont; Neoflon AP, Daikin; Hostaflon TFA, Ticona).
3. Vinylidenefluoride (VDF)–HFP (Kynarflex, Atofina).
4. VDF–TFE (Kynar SL, Atofina).
5. VDF–Chlorotrifluoroethylene (CTFE) (Foraflon, Atofina; Solef, Solvay).
6. VDF–TFE–HFP (Hostaflon TFB, Dyneon).

Fluoroelastomers require a high degree of disorder of the polymer chain, and hence 35–50% of the second comonomer is needed. These products are designed to maintain rubber-like elasticity under extremely severe conditions (high temperatures and in contact with chemicals). To prevent flow deformation under an imposed force, the fluoroelastomers are cross-linked. An excellent review on fluoroelastomers has been recently published (154). Some commercial products are

1. VDF–HFP (Daiel 801, Daikin; Fluorel, 3M/Dyneon, Viton A, DuPont).
2. VDF–CTFE (Kel F, Dyneon; Voltalef, Atofina).

3. TFE−perfluoromethyl vinyl ether (Kalrez, DuPont).
4. VDF−TFE−HFP (Tecnoflon, Ausimont; Viton B, DuPont).

Fluorinated copolymers are produced by free-radical polymerization in both aqueous and non-aqueous media. In aqueous media, perfluorocarbon surfactants are used and the polymer is separated and converted into various forms. Some products are sold as latexes. The product is recovered from nonaqueous polymerization by evaporating the fluorinated solvent.

Thermoplastic fluoropolymers are used in applications that require chemical inertness, excellent dielectric properties, nonaging characteristics, antistick properties, low coefficient of friction, and performance at extreme temperatures. These applications include electrical applications (wire-cable, molded electrical parts), lined pipes and fittings, heat exchangers, and conveyor belts.

The main uses of the fluorinated elastomers are O-rings and gaskets, shaft and oil seals, diaphgrams, hoses, and profiles.

10.3. Random Copolymers Produced by Ionic Polymerization. Butyl rubber is a copolymer of isobutylene and isoprene (1−3%) formed by cationic polymerization. The polymerization is carried out in a continuous slurry process with methyl chloride as the diluent. Isoprene is a strong chain-transfer agent and very low temperatures (−90°C) are used to produce high molecular weight polymer. The insaturared sites of the isoprene units enable vulcanization, and butyl rubber cures well although more slowly than polyisoprene and polybutadiene. This causes problems when butyl rubber is blended with these polymers. Halogenation of some of the isoprene groups greatly increases the cure rate of butyl rubber. Substitution of isoprene by brominated *p*-methyl styrene leads to a copolymer more stable oxidatively, and with a good curing reactivity. The applications of polyisobutylene copolymers take advantage of the low permeability of these copolymers. The main application is for the inner-liners of tubeless tires and inner tubes of tires. Other uses are adhesives, binders, pipe wrap, caulking, and sealing compounds. ExxonMobil and Bayer are the main producers.

SBR can be also be produced by a solution process using organolithium initiators. These anionic systems show a marked sensitivity of the reactivity ratios to solvent type. Nonpolar solvents favor the incorporation of butadiene while polar solvents lead to styrene- rich copolymers (144). The main application is for tires. Firestone polymers, American synthetic rubber, Michelin, Repsol YPF, and Negromex are producers of this rubber. It is claimed that solution SBR gives low rolling resistance (less fuel consumption), improved wet grip, and good wear properties.

10.4. Controlling Copolymer Microstructure. The application properties of copolymers are mostly determined by their microstructure (copolymer composition, monomer sequence distribution, molecular weight distribution, branching, cross-linking, etc.). Therefore, the final properties can be improved by controlling copolymer microstructure. Copolymers are "products-by-process" materials, and consequently their microstructure, and hence their final properties, are determined by the process variables in the reactor (in a broad sense process variables include the type of polymerization process, catalysts, etc.). Competition and margin reduction are pushing polymer producers to achieve an efficient and consistent production of polymers with improved properties under safe and environmentally friendly conditions. Therefore, there is a strong interest in developing strategies for on-line control of polymerization reactors. Reviews discussing the field up to 1998 are available (155–160).

On-line control of copolymer microstructure is, in a large extent, associated to random copolymers produced by catalytic polymerization and classical free-radical polymerization. Catalytic polymerization is conducted in large scale continuous reactors, and hence grade transition is an important issue. On the other hand, due to proprietary reasons, data from those processes are not freely available to academic researchers, and this limits the number of works published in the open literature. Böhm and co-workers (161) developed a strategy to control the density (copolymer composition) and melt flow index (molecular weight) of a HDPE produced in a continuous slurry reactor. An on-line state estimator for the density and the melt flow index was developed based on measurements of the composition of the gas phase. A fuzzy-logic controller was used for grade transition. Control strategies for gas-phase production of LLDPE in a fluidized bed reactor have also been proposed (162–164). In these works, an extended Kalman filter was used for inferring the values of the density and melt flow index, and a model-based controller was employed to track the optimal trajectories in grade transition. Dynamic matrix control has been used to control product quality (terpolymer composition and Mooney viscosity) during changes in product specifications and in production rate and catalyst activity for an EPDM continuous stirred tank reactor (165).

Successful strategies for on-line control of copolymer (166–172) and terpolymer composition (173–175) of random free-radical copolymers have been implemented. On-line closed-loop control of the molecular weight distribution of linear polymers has been achieved (168,176–180). Open-loop strategies have also been proposed (181). The simultaneous closed-loop control of copolymer composition and MWD of linear polymers has been recently reported (182), as well as some open-loop strategies for this purpose (183,184). The application of the control strategies developed for linear polymers fail to control the polymer microstructure of nonlinear polymers (185) and although some success has been obtained in open-loop control based on complete mathematical models (186) the control of the microstructure of nonlinear polymers (MWD, branching, gel) still is an unresolved issue.

The implementation of strategies for on-line control of copolymer microstructure requires the availability of appropiate sensors. The development of on-line sensors for polymerization reactors have been difficult in comparison with other chemical processes because of the physical characteristics of the polymerization mixture that makes it difficult to use in-line sensors or circulation loops due to fouling and clogging of pipes, pumps, and the sensor itself (187,188). In the lab reactors, copolymer composition and conversion were monitored by gas chromatograph and densimeters (167,189), but these devices are not robust enough for application in industrial scale reactors. On-line reaction calorimetry and spectroscopic techniques [eg, Raman and near infrared (nir) spectroscopies] are more promising (190–192). Some success has been reported for the on-line measurement of the molecular weight distribution in solution polymerization processes (168), but in disperse systems, this is still an unresolved issue. Therefore, soft-sensors and/or state estimation techniques have been proposed to on-line infer the molecular weights (161,182).

11. Alternating Copolymers

There are several ways in which alternating copolymers can be produced. Thus, free-radical copolymerization of electron-donor monomers (such as styrene and α-olefins) and electron-acceptor monomers (such as maleic anhydride and fluorinated alkenes) yields alternating copolymers. These copolymerizations deviate from the predictions of the terminal model (193) and it occurs through the formation of a donor–acceptor charge-transfer complex between the two participating monomers, which enters into the propagation step as a single unit (194).

Alternating ethylene–α-olefin copolymers can be obtained using Ziegler-Natta catalysts at very low temperature (−70°C) (193) as well as at higher temperatures (0°C) using metallocene catalysts (107,108,195–197). Alternating CO–olefin copolymers can be produced in a methanol slurry phase using a catalyst system that includes a palladium salt of a carboxylic acid, a phosphorous or nitrogen bidendate base, an anion of an organic acid, and an oxidant such as 1,4-benzoquinone (198).

A limited number of alternating copolymers are commercially available. Alternating styrene–maleic anhydride copolymers (SMA) are produced by free-radical copolymerization. Low molecular weight SMA with a high maleic anhydride content (25–50 wt%) is alkali soluble and used in paper and textile sizing, floor polishes, printing ink, pigment dispersants, and coatings. High molecular weight SMA with low maleic anhydride content (<25 wt%) is used for molding and extrusion applications. Bayer (Cadon) and Nova Chemicals (Dyrlak) are producers of styrene–maleic anhydride copolymers.

Fluorinated alternating copolymers are produced by free-radical copolymerization of electron-withdrawing fluorinated alkenes with electron-donating monomers. Tetrafluoroethylene and ethylene are copolymerized in emulsion (using fluorinated surfactants) or in a non–aqueous media (using a fluorinated solvent) to yield an alternating copolymer that has a high tensile strength, moderate stiffness, outstanding impact strength, low dielectric constant, excellent resistivity, good thermal stability, and excellent chemical resistance. This copolymer can be cross-linked with electron beam and γ-ray radiation. The main uses of this copolymer are power and automotive wiring, injection-molded electrical components, pump impellers, and molding articles. Some producers are DuPont (Telzel), Asahi Glass (Aflon COP), Ausimont (Halon ET), and Daikin (Neoflon EP). Asashi Glass also produces TFE–propylene alternating copolymer (Aflon). Emulsion copolymerization of chlorotrifluorethylene (CTPE) with vinyl ethers leads to commercial alternating copolymers (Lumiflon, Asashi Glass; Zeffe, Daikin; Fluonate, Dainippon Ink; DX 2000, Atofina).

Alternating ethylene–CO copolymers are not of practical relevance because it is difficult to process without degradation (198). On the other hand, ethylene–propylene–CO terpolymers are perfectly alternating aliphatic polyketones that exhibit moduli, impact, and thermal characteristics of amorphous polymers with the chemical resistance of crystalline polymers while processing like a polyolefin. Shell commercialized these products under the trade name of Carilon, but the product was withdrawn from the market in February 2000.

12. Block Copolymers

12.1. Synthetic Methods.

Block copolymers can be produced by means of several polymerization mechanisms including anionic polymerization, ring-opening polymerization, step-growth polymerization, catalytic polymerization, controlled free-radical polymerization, and combinations of some of these polymerization methods.

Anionic Polymerization. Anionic polymerization proceeds in the absence of termination and transfer reactions allowing the synthesis of block copolymers of the desired molecular weight, composition, and structure. The different synthetic methods are shown below for the case of styrenic thermoplastic elastomers (199)

(a) Succesive polymerization of monomers (200).

$$\begin{aligned}&\mathrm{R^{-}Li^{+}} \xrightarrow{+n\mathrm{S}} \mathrm{R{-\!\!-}(S)_{\mathit{n}}^{-}Li^{+}} \xrightarrow{+m\mathrm{M}} \mathrm{R{-\!\!-}(S)_{\mathit{n}}{-\!\!-}(M)_{\mathit{m}}^{-}Li^{+}} \xrightarrow{+n\mathrm{S}}\\ &\quad \mathrm{R{-\!\!-}(S)_{\mathit{n}}{-\!\!-}(M)_{\mathit{m}}{-\!\!-}(S)_{\mathit{n}}^{-}Li^{+}}\end{aligned} \tag{46}$$

(b) Coupling diblock copolymers (200)

$$\begin{aligned}&\mathrm{2(S)_{\mathit{m}}{-\!\!-}(M)_{\mathit{m}}^{-}Li^{+} + X{-\!\!-}R{-\!\!-}X} \rightarrow\\ &\quad \mathrm{(S)_{\mathit{m}}{-\!\!-}(M)_{\mathit{m}}{-\!\!-}R{-\!\!-}(M)_{\mathit{m}}{-\!\!-}(S)_{\mathit{n}} + 2LiX}\end{aligned} \tag{47}$$

(c) Multifunctional initiation (201)

$$\begin{aligned}&\mathrm{Li^{+\,-}R^{-}Li^{+}} \xrightarrow{+2n\mathrm{M}} \mathrm{Li^{+\,-}(M)_{\mathit{n}}{-\!\!-}R{-\!\!-}(M)_{\mathit{n}}^{-}}\\ &\quad \mathrm{Li^{+}} \xrightarrow{+2m\mathrm{S}} \mathrm{Li^{+\,-}(S)_{\mathit{m}}{-\!\!-}(M)_{\mathit{n}}{-\!\!-}R{-\!\!-}(M)_{\mathit{n}}{-\!\!-}(S)_{\mathit{m}}^{-}Li^{+}}\end{aligned} \tag{48}$$

where M is either butadiene of isoprene. In this case, the block copolymers are termed S–B–S and S–I–S, respectively. The polybutadiene and polyisoprene blocks contain double bonds that limit the stability of the products. Hydrogenation of S–B–S yields S–EB–S and hydrogenation of S–I–S gives S–EP–S.

Anionic polymerization requires ultrapure reagents and solvents, low temperature, and the absence of oxygen. An important limitation of anionic polymerization is that it can only be applied to a limited number of monomers (styrene, butadiene, isoprene, and cyclic monomers such as epoxides, anhydrides, lactones, and siloxanes). Nevertheless, polystyrene-*block*-polybutadiene-*block*-polymethylmethacrylate copolymers produced by anionic polymerization have been commercialized by Atofina (SBM).

Catalytic Polymerization. Polyolefin block copolymers are obtained by successive polymerization of different monomer mixtures on Ziegler-Natta catalyst under conditions in which chain termination by chain-transfer reactions is minimized (202–204) Isotactic–atactic stereoblock polypropylene have been synthesized by using a non–bridged metallocene catalyst in which the rotation of the indenyl ligands during chain growth allows the transition between blocks (205).

Controlled Free Radical Polymerization. The block copolymers produced by CRP are not as well defined as those produced by anionic polymerization, but have the advantage that almost any of the huge number of monomers that can be polymerized by free-radical polymerization can be used to synthesize block copolymers. Polystyrene-*block*-poly(*n*-butyl acrylate) (40), poly(butyl methacrylate)-*block*-poly(methyl methacrylate) (206), poly(methyl methacrylate)-*block*-poly(butyl methacrylate)-*block*-poly(methyl methacrylate) (207), poly(n-butyl acrylate)-*block*-poly(acrylic acid) (208), and polyHEMA-*block*-polyMMA-*block*-polyHEMA (208) are examples of diblock and triblock copolymers produced by succesive addition of the monomers using monofunctional and difunctional CRP agents.

One of the interesting features of synthesizing block copolymers by means of CRP is that the initial block can be produced and stored before proceeding to the second block. In addition, CRP allows the incorporation of random copolymers as blocks (209).

Ring-Opening Polymerization. Some ring-opening polymerizations proceed by a living mechanism, which enables the preparation of block copolymers. The main difficulty being the rather limited choice of initiator catalysts that allow the living character of the polymerization to be met. Examples of block copolymer produced by anionic and cationic ring-opening polymerization have been reported in the literature (210–214): polyether-*block*-polyesther (213,214), polyester1-*block*-polyester2 (215), polyester-*block*-polycarbonate (216) polyvinyl-*block*-poly(ε-caprolactone) (217,218), polyvinyl-*block*-polycyclic amine (219), block copolymers of different caprolactones and ε-caprolactone and butadiene (219–222), and block copolymers of lactides and cyclic monomers (223).

Step-Growth Polymerization. Multiblock copolymers are produced by condensation reactions from polyurethanes, polyesters, and polyamides prepolymers. These copolymers are produced in a two-step process that for polyurethanes involves a first stage in which a long-chain diol is reacted with an excess of disocyanate yielding a soft prepolymer with isocyanate end groups. This prepolymer is reacted with a short-chain diol and additional diisocyanate, leading to a multiblock copolymer in which the ratio hard segments/soft segments is determined by the ratio short-chain diol/long-chain diol (224). Multiblock polyester copolymers are produced by a similar method using diacids (or diesters) and diols (225). Similarly, multiblock polyamide copolymers are prepared from diacids and diamines (226).

Combining Polymerization Techniques. Block copolymers can also be obtained by forming one block by means of a given polymerization method and the second one through a different polymerization mechanism. Some representative examples are given in Table 9.

12.2. Properties and Commercial Products. Block copolymers present unique structure–property relationships that are useful for a variety of applications including thermoplastic elastomers (TPE), elastomeric fibers, toughened thermoplastic resins, adhesives, compatibilizers for polymer blends,

Table 9. **Synthesis of Block Copolymers Combining Different Polymerization Techniques**

Block 1		Block 2		
Monomer 1	Polymerization mechanism	Monomer 2	Polymerization mechanism	Reference
ε-caprolactone	anionic ring-opening polymerization	styrene	CRP-nitroxide	227
2,5-dioctyloxy-1,4-phenylene vinylidene	condensation	*n*-butyl acrylate	CRP-nitroxide	228
styrene	cationic	methyl acrylate	ATRP	229
THF	cationic ring opening	styrene	ATRP	230
MMA[a]	ATRP	ε-caprolactone	Anionic ring-opening polymerization	227
4-fluorophenyl sulfone	step growth	*n*-butyl acrylate	ATRP	231
isoprene	anionic	ethylene	Ziegler-Natta	232

[a] MMA = methyl methacrylate.

membranes, and surfactants. Table 10 presents some commercially available block copolymers.

Thermoplastic elastomers is the main application of block copolymers. These materials are composed of hard and soft segments, which form a processable melt at high temperatures and transform into a solid rubber-like object upon cooling. The transition between the strong elastic solid and the processable melt is reversible. Figure 10 illustrates this phase transition for an A–B–A block copolymer, where A is a short hard segment and B is a long soft segment. At low temperatures, the hard segments segregate forming a three-dimensional network with physical cross-links that act as the sulfur cross-links in vulcanized rubber. When temperature is increased above the T_g of the polymer forming the hard segments, the physical cross-links soften and a polymer melt is formed. Styrenic thermoplastic elastomers are commercially important A–B–A block copolymers. Polybutadiene and polyisoprene are common elastomeric midsegments. The presence of double bonds in the elastomeric part of these triblock copolymers limits the stability of the product. More stable polymers are produced by hydrogenation of S–B–S that yields polystyrene-*block*-poly(ethylene-butylene)-*block*-polystyrene. Similarly hydrogenation of S–I–S leads to polyisobutylene mid-segments.

Because polystyrene is an amorphous polymer soluble in many solvents, the styrenic thermoplastic elastomers present a poor oil and solvent resistance. This resistance can be improved by compounding and in some cases is an advantage because it allows the application from solution (199).

Polyethylene-*block*-poly(ethylenic-*stat*-α-olefin) copolymers produced by catalytic polymerization present a better resistance to oil and solvent because the hard segments (polyethylene) form crystalline aggregates. Multiblock copolymers formed by step-growth polymerization are high performance elastomers.

Table 10. **Commercially Available Block Copolymers**

Hard segments	Soft segments	Type	Trade name	Applications
styrene	butadiene or isoprene	A–B–A	Kraton D (Kraton polymers)	footwear, bitumen/asphalt modification, adhesives, sealants, household appliances, toys, tubing
styrene	ethylene–butylene isobutylene	A–B–A	Kraton G (Kraton polymers)	bitumen/asphalt modification, sealants, high performance adhesives, automotive, sports, medical equipment
styrene (high styrene content)	butadiene	triblock	Finaclear (ATOFINA)	health products, packaging
styrene	butadiene	linear/Star	Finaprene (ATOFINA)	footwear, compounds, bitumen modification, adhesives, plastic modification
polyamide	polyether	multiblock	Pebax (ATOFINA)	footwear, sporting goods, protective films, waterproof breathable materials
polyester	polyether	multiblock	Hytrel (DuPont)	automotive, fluid power, sporting goods, furniture and off-road transportation. Thin flexible membranes, tubing, hose jackets, wire and cable electrical connectors
polyamide	polyether	multiblock	Vestamid (Degussa-Hüls)	fuel lines, air brake tubing, hydraulic tubes, catheters, cable and wire, plastic-rubber components for the automotive industry, sport shoes
polyurethane	polyester/polyether/poly carbonate	multiblock	Estane/Estagrip/Estaloc (Noveon)	automotive, power and handtools, wire and cable, footwear, consumer goods, health care
polystyrene/poly-(methyl methacrylate)	polybutadiene	A–B–C	(SBM) ATOFINA	nanostructurated thermoplastic and thermoset materials, compatibilization of minerals and carbon black with polymers
polyester	polyester	multiblock	Arnitel V (DSM)	automotive, tubing, cable insulation, injective molding, films
poly(ethylene oxide) (hydrophilic block)	poly(propylene oxide) (hydrophobic block)	diblock	Synperonic (Uniquema)	surfactants for resin emulsification and emulsion polymerization

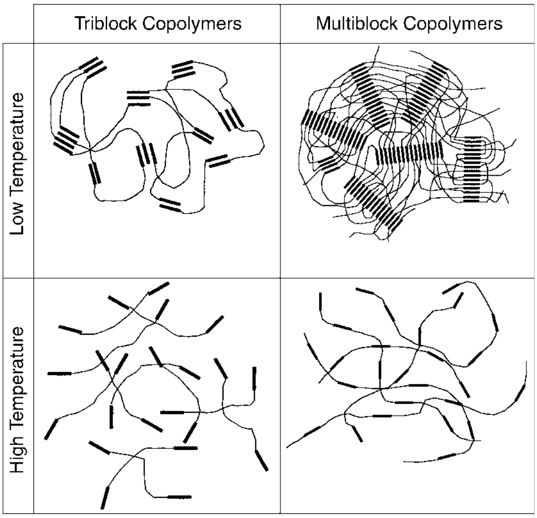


Fig. 10. Phase transition of thermoplastic elastomers.

Figure 10 illustrates the phase transition of a multiblock thermoplastic elastomer. In this case, the number of hard segments involved in each physical cross-link is much higher than for the A–B–A block copolymers. The hard segments of the multiblock copolymers of commercial importance are crystalline thermoplastics (polyurethanes, polyesters, and polyamides), therefore the cross-links are crystalline regions that provide a good oil and solvent resistance. Upon heating, the crystalline regions melt and a processable fluid is obtained. The soft segments are polyesters and polyethers.

The service temperature range of the thermoplastic elastomers spands from a temperature slightly above the T_g of the soft rubbery phase to a temperature slightly below the T_g or T_m of the hard segments. Values for the T_g and T_m of the different segments are given in Table 11.

The hardness of the thermoplastic elastomers depends on the ratio between soft and hard phases (199). The hardness range is very broad for styrenic triblock

Table 11. **Glass Transition and Melting Temperatures for Soft and Hard Segments**

Soft segment	T_g (°C)	Hard segment	T_g, T_m (°C)
butadiene	−90	styrene	95 (T_g)
isoprene	−60	polyurethane	190 (T_m)
ethylene-butylene	−60	polyester	180–220 (T_m)
isobutylene	−60	polyamide	220–275 (T_m)
polyethers	−40	polyethylene	70 (T_m)
polyesters	−60		
poly(ethylene-*stat*-α-olefin)	−50		

copolymers, in which at high styrene contents a clear flexible thermoplastic is obtained (eg, Finaclear from ATOFINA). Thermoplastic elastomers with crystallizable hard segments have limits on softness because a minimum length of the hard segment is required for crystallization.

Block copolymers, particularly styrenic triblock copolymers, are used as adhesives and sealants. The role of the chain architecture in the adhesion properties have been studied (233,234). Block copolymers are efficient compatibilizing agents for polymer blends. As little as 0.5–2% of diblock copolymers may be sufficient to achieve a good phase dispersion (235). Block copolymers are used in the surface modification of fillers (236) and as coatings for metal and glass surfaces (237). Amphiphilic block copolymers consist of hydrophilic polyoxyethylene segments and various hydrophobic parts (polypropylene oxide, polystyrene, etc) are efficient surfactants (238). New nanostructured materials can be prepared by assembly of block copolymers (239).

13. Graft Copolymers

High impact polystyrene (HIPS) and ABS resins are important graft copolymers produced by polymerizing vinyl monomers in the presence of polybutadiene through a free-radical mechanism. Grafting occurs by participation of the double bonds of the polybutadiene in the propagation reaction and by chain transfer to the polybutadiene followed by addition of monomer to the resulting allylic radical.

HIPS polymerization is carried out by first dissolving 4–12% by weight of polybutadiene rubber in a styrene monomer and adding a free-radical initiator. At the early stages of the polymerization, polybutadiene dissolved in styrene forms the continuous phase, whereas the newly formed polystyrene (swollen with styrene monomer) forms a separate phase stabilized with the grafted butadiene–styrene copolymer. As polymerization proceeds, the polystyrene phase becomes the major component and phase inversion leading to a multiphase material occurs. Figure 11 shows a transmission electron micrograph of a HIPS in which the rubber particles (dark areas) with polystyrene inclusions (clear areas) are dispersed in a continuous polystyrene matrix (clear background). Particle size severely affects the performance of HIPS. Small particles provide rigidity and gloss, whereas larger particles improve toughness (240). On the other hand, as the rubber content increases, impact strength increases while rigidity, heat distortion temperature, and clarity decrease. HIPS meets the application needs across a broad range of market segments including appliances, consumer electronics, packaging, housewares, disposables, and toys. Some important HIPS producers are BASF (Polystyrol), Dow Chemical (Styron, Aim), Nova Chemicals (Zylar), L.G. Chemical (Alphalac), and Hong Kong Petrochemical (SR and SRL grades).

ABS copolymers are produced in bulk polymerization by means of a process almost identical to that of the HIPS, but using styrene and acrylonitrile as polymerizing monomers. ABS polymers can also be produced in emulsion polymerization by polymerizing styrene and acrylonitrile on a polybutadiene seed. Commercial ABS is often a blend of this reactor produced ABS with SAN. The

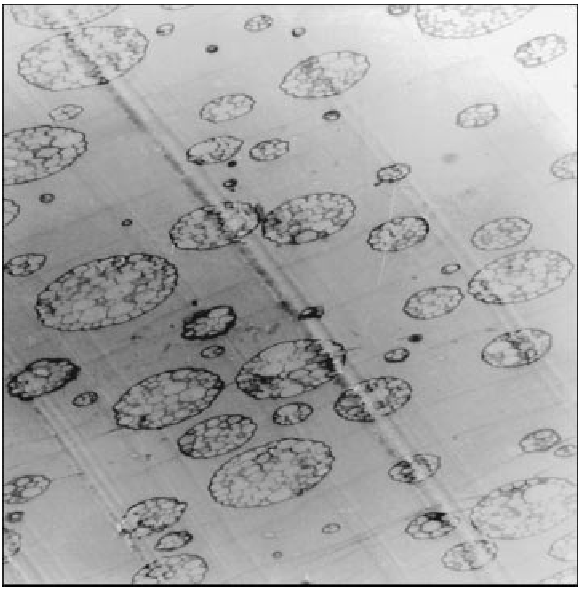


Fig. 11. Structure of HIPS.

properties of the ABS copolymers can be modified by varying the relative amounts of the components, the degree of grafting, and the molecular weight. Thus, increasing the rubber content reduces tensile strength and increases impact strength. The effect of the rubber particle size is similar to that in HIPS, small particles lead to rigid and good surface aesthetics and large particles improve toughness. A combination of good properties is usually found with particles in the range of 0.3–0.5 μm (241). Table 12 summarizes some properties of ABS and HIPS. The ABS copolymers are used in electrical and electronic equipment, house and office appliances, and the automotive industry. Some trade names are Terluran (BASF), Magnum (Dow Chemical), Diastat (Mitsubishi Rayon), Cycolac (GE Plastics), Lustran (Bayer), and Estadine (Cossa Polimeri). Other producers and trade names are available at the web site http://www.ets-corp/tradenames/. Central Soft from Central Glass is a graft fluoropolymer (VDF/CTFE)-*graft*-VDF produced by free-radical polymerization.

Polyolefin-based graft copolymers can be produced polymerizing a mixture of ethylene and α-olefin in the presence of two different metallocene catalysts (242,243). One of these catalysts has a low αolefin incorporating capability and produces primarily double-bond terminated polyethylene macromonomers. The

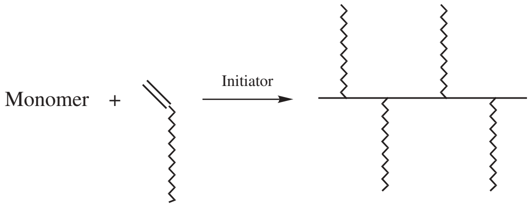
Table 12. **Properties of ABS and HIPS**

	ABS	HIPS
tensile strength (MPa)	27–55	16–28
izod impact (J/m)	106–640	58–150
vicat heat distortion (°C)	80–115	90–106

other catalyst has a higher affinity for α-olefins and also consumes macromonomers leading to a graft copolymer composed by a soft ethylene-α-olefin backbone with crystalline polyethylene branches. Polyolefin graft copolymers have also been produced via constraint geometry catalyst (242). Engage (DuPont-Dow Elastomers), Affinity (Dow Chemical), and Exact (ExxonMobil) are examples of commercial polyolefin-based graft copolymers.

Classical free-radical polymerization and catalytic polymerization only allow a limited control of the polymer architecture. Therefore, new and more selective grafting methodologies have been developed, which can be summarized by the three following main methods.

(1) "Grafting from" method. This method consists in initiating a polymerization of a monomer at some suitable reactive groups (Z) attached onto a prepolymer (PA) or from a macroinitiator with pendant functionality as indicate in the following scheme:

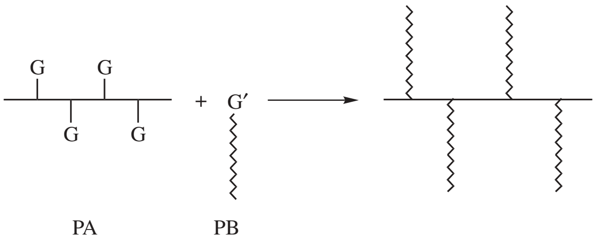


The control of the molecular weight of the grafted chains is not straightforward and can only be achieved if initiation is much faster than propagation reactions. Ionic grafting meets this requirement but the choice of monomers is limited (245,246). The grafting reaction can be done by radical polymerization [eg, using a polymer containing halogen with metal carbonyls such as molybdenum hexacarbonyl (247)], but care should be taken with the termination reaction that may produce cross-linked graft copolymer if it is by combination.

Controlled radical polymerization has opened a wide range of possibilities to graft a large number of monomers into prepolymers conveniently modified. Graft copolymers have been produced by means of a three-step nitroxide mediated radical polymerization. In the first step, a linear copolymer of styrene and *p*-chloromethylstyrene is obtained. In the second step, reaction of this copolymer with the sodium salt of a hydroxyl functionalized nitroxide yielded initiation sites for the third step that is a CRP grafting process (248). Graft copolymers can be easily produced by ATRP (41). An example of this method is the formation of graft copolymers by ATRP of vinyl monomers from pendant-functionalized poly(vinyl chloride) (PVC) (249)· In this case, polymerization was initiated by the chloroacetate moieties attached to the backbone. Monomers such as methyl acrylate (MA), *n*-butyl acrylate (*n*-BA), and styrene were grafted to PVC and graft copolymers of different T_g value than that of the PVC were produced. The decrease of T_g achieved for *n*-BA and MA grafts led to self-plastified PVC polymers.

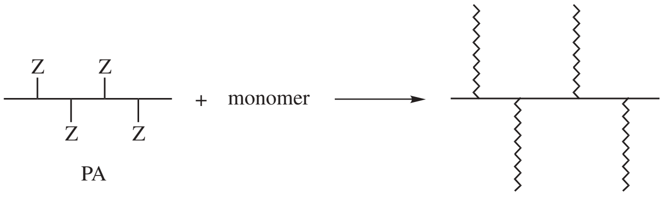
In the CRP grafting processes, bimolecular termination of growing branches limits the number of grafts per chain. Thus, it has been found that for more than six initiating sites per backbone, bimolecular termination of adjacent growing chains is important (248).

(2) "Grafting onto" method. In this method, a prepolymer (or end-reactive oligomer–telechelic polymer), PB, containing a reactive functional group (G') reacts with the groups randomly attached (G) to a backbone of a second preformed polymer, PA, as shown in the following scheme:



This method allows good control of the polymer microstructure because prepolymers with controlled structures can be employed. Both anionic and cationic techniques can be used to produce the backbone prepolymer with functionalized groups and also to couple the grafted polymer (produced by an ionic technique) onto the backbone. Examples of this method are grafting of living anionic polymers (eg, polystyril lithium) onto polymer backbones with reactive halogen or epoxide functionalities (250) and the grafting of living polytetrahydrofuran cations that can be grafted onto chlorohydroxylated polybutadiene and nitrile rubbers (251).

(3) "Grafting through" method. This is a popular approach because it can overcome some of the difficulties inherent to the other techniques. In this method, a macromonomer (viz, an oligomer bearing a polymerizable end-group) copolymerizes with a suitable monomer to form comb-like graft copolymers as shown in the following scheme:



Macromonomers can be prepared by ionic (252,253), free radical (254), and catalytic chain-transfer polymerization (255).

The interest of well-defined graft copolymers is due to the multiple properties that they may have in a single molecule. This feature opens the possibility of using this specialty and expensive polymers in applications that cannot be achieved with other polymers. Thus, graft copolymers have been used for improving processability, compatibility, dyeability, and water repellency (256–258). Because of their inherent surface activity, other uses for these copolymers are coatings, adhesives, fibers, films, and moldings (257). Recently, applications of graft copolymers for 100% solids *in situ* curing resins (by using macromonomers that cure under electron beam or ultra violet, uv, radiation) have been reported (259). The low cost and nonpolluting nature of the resulting coatings and the possibilities to improve film properties such as adhesion, tensile strength, and flexibility make them very attractive products.

Also, hydrogels were recently formed by grafting hydrophobic polymers in hydrophilic backbones. For example, graft copolymers of polystyrene and vinylpyrrolidone (NVP) were produced by using ATRP techniques (260), and also styryl-telechelic-polyisobutylene (PIB), and methacryloyl-telechelic-PIB have been copolymerized with NVP and 2-(dimethylamino)ethyl methacrylate to produce graft copolymers (261–263). These hydrogels have been employed for biomedical applications such as controlled release of drugs, enzyme immobilization, and contact lenses.

14. Star and Hyperbranched Copolymers

Star copolymers, from a wide range of monomers can be prepared by controlled radical polymerization. Thus, star copolymers can be synthesized by coupling alkoxyamine terminated linear copolymers with cross-linking agents (264). Heterogeneous star-block copolymers may be produced using linear polymers of different composition. Multifunctional small molecule initiators allow synthesizing star copolymers by using ATRP. Thus, six armed star-block copolymers of poly(methyl acrylate) and poly(isobornyl acrylate) (265) and eight armed star-block copolymers of PMMA and PBA have been produced (266). By using appropriate precursors containing multiple thiocarbonylthio groups, star polymers are also accessible by means of the RAFT process (267). Star copolymers were produced by Phillips Petroleum (268) by reacting a polystyrene-*block*-polybutadiene anion with $SnCl_4$. Some Kraton grades (Kraton polymers) are star copolymers produced by polymerizing divinylbenzene containing block copolymers to yield a cross-linked core from which block copolymer arms radiate outward. This method of producing the arms in the first place and then coupling them is called “arm first”. Core first methods based on multifunctional initiators from which the arms are grown have been reported (269).

Hyperbranched polymers are commonly produced by (a) step-growth polycondensation of AB_x monomers, (b) self-condensing vinyl polymerization of AB* monomers, and (c) multibranching ring-opening polymerization of AB_x monomers (270). Hyperbranched polymers can also be prepared by means of controlled radical polymerization. Thus, nitroxide mediated polymerization of self-condensing monomers that contain a double bond and an alkoxyamine initiating center yields to this type of topology (271). Similarly, hyperbranched polymers containing a large amount of halogen end groups can be produced by ATRP of monomers containing a double bond and an initiator fragment (272). The terminal halogens may be replaced by other functionalities such as azido, amino, hydroxy, and epoxy by means of radical addition reactions (273).

Special attention must be paid to bimolecular termination when preparing stars, combs, dendritic, and hyperbranched topologies by means of controlled radical polymerization, because a relatively small fraction of terminated chains, which can be easily tolerated in the case of linear polymers, may have a catastrophic effect in complex architectures. Thus, for polymer chains growing in five directions, 5% of bimolecular termination will lead to 25% of chains linked together, and for chains growing in 20 directions this level of termination may lead to complete cross-linking and gelation (41). Hyperbranched polyethylene are produced by low pressure polymerization of ethylene on palladium and nickel catalysts (274,275).

Hyperbranched copolymers can, in general, be considered a subclass of dendritic polymers with the advantage that their production is less costly and more suitable for mass production. The unique properties of hyperbranched polymers are mainly due to their globular structure and to the large number of terminal functional groups. Hyperbranched polymers, in comparison to their counterpart linear polymers, offer better solubility in organic solvents, lower viscosities because of their spherical shape, and the choice of controlling the T_g by chemical modification of the end functional groups. Hyperbranched polymers cannot engage in chain entanglements, and hence their use in conventional structural applications is futile (276). Hyperbranched polymers with acrylate, vinyl ester, alkyl ether, epoxy, and OH functions are used as cross-linkers in coatings and thermosets (277). Very high functionality leads to a too fast cross-linking, and therefore an optimal number of reactive groups exists (278). Hyperbranched polymers provide an exceptional film hardeness that allows the use of low viscous–high solids–low molecular weight resins without compromising the coating performance, and also allows the use of entirely aliphatic monomers, which in turn resulted in excellent weatherability (279). Hyperbranched polymers are used as melt modifiers. Thus, strong reduction of the melt viscosity of linear polyamide has been observed when a small amount of hyperbranched polymer was added (280).

Hyperbranched polymers increase the toughness of glass and carbon-reinforced composites (281) and have also been used as dye carriers (282), for nonlinear optical materials (283), in molecular imprinting (284), and for the synthesis of nanoporous polymers with low dielectric constant (285).

Astramol and Hybrane from DSM are examples of the still limited number of commercially available hyperbranched polymers.

15. Characterization of Copolymers

Polymers are complex materials whose complete characterization requires the determination of a number of characteristics, which in turn determine the application performance. Polymer characteristics can be classified into four groups.

(*a*) Molecular structure. This characteristic refers to the arrangement and type of monomeric units in the polymer chain and includes copolymer composition, chemical composition distribution, and monomer sequence distribution. The techniques used to measure these characteristics are summarized in Table 13 and include solution fractionation methods, spectroscopic methods such as nuclear magnetic resonance (nmr), uv, infrared (ir) and Raman, pyrolysis GC, mass spectroscopy, and chemical tests.

Table 13. **Experimental Techniques Used to Determine the Most Important Copolymer Characteristics**

Characteristic	Property	Experimental technique
molecular structure	average composition, chemical composition distribution and monomer sequence distribution	infrared spectroscopy, ir
		nuclear magnetic resonance, nmr (^{13}C and ^{1}H nmr)
		raman spectroscopy
		cross-fractionation techniques (for CCD): SEC/TLC, HPLC/SEC, and SEC/SEC
		pyrolysis/GC (average composition)
		uv Spectroscopy
		X-ray Spectroscopy
		inverse gas chromatography, IGC
		size-exclusion chromatography (for CCD) uv and RI detectors
		MALDI–TOF mass spectrometry
molecular size	molecular weight and molecular weight distribution	size-exclusion chromatography (MWD) (refractive index, viscosity, and light scattering detectors are mostly used)
		light scattering (measurements in three different solvents are required for the apparent molecular weight)
		end-group determination ($\bar{M}_n$) (spectroscopic techniques and titration)
		colligative properties ($\bar{M}_n$) (membrane osmometry and vapor pressure osmometry are the most suitable ones)
		viscosity ($\bar{M}_v$)
		ultracentrifugation ($\bar{M}_w$)
		field-flow fractionation (MWD)
		neutron scattering
		field desorption mass spectroscopy (MWD, limit on 30.000 g/mol)
		liquid adsorption chromatography at the critical point conditions, LACCC (MWD of block copolymers)
		MALDI–TOF mass spectroscopy (averages and MWD of blocks)
molecular organization	crystallinity	inverse gas chromatography, IGC
		differential scanning calorimetry, DSC
		dynamic mechanical analysis, DMA
		crystaf, X-ray scattering, polarized optical microscopy

	glass-transition temperature	inverse gas chromatography, IGC
		differential scanning calorimetry, DSC
		dynamic thermal analysis, DTA
		thermal mechanical analysis, TMA
	cross-linking	IGC
		raman spectroscopy
		X-ray diffraction
	branching	SEC/LLALS; SEC/MALLS; SEC/RI and viscosity and SEC/triple detector
		^{13}C nmr and ^{1}H nmr (liquid and solid state)
		viscometry
	copolymer structure (block, graft. . .) and conformation	^{13}C nmr and ^{1}H nmr (dyads, triads, . . . pentads), LACCC, static and dynamic
		light scattering
		ir, X-ray diffraction, neutron scattering, SAXS, WAXS Raman, TEM, SEM, MALDI–TOF MS
		pyrolysis/GC
	morphology	solid-state ^{13}C nmr, TEM, and SEM, neutron scattering, SAXS, DMA, Atomic force microscopy (AFM)
	purity and separation (block and graft copolymers)	thin-layer chromatography
		SEC/GPC, turbidimetry titration
		solvent extraction, ultracentrifugation, density gradient Centrifugation
mechanical, electrical and physical properties	stress–strain tests	Instron instrument
	crep tests	dynamic and mechanical thermal analysis, DMTA
	stress–relaxation tests	
	dynamical mechanical tests	
	impact tests	Izod and Charpy tests, falling-weight test
	dielectric relaxation	bridge method, resonance method, time domain reflectometry
	electrical breakdown	
	softening points	
	melt flow	Brookfied and Money viscometers
	melt viscosity	Bradender plasticgraph, capilary viscometers
	solubility	Inverse gas chromatography
	permeability	Wheather-Ometers
	stability	
	flammability	ignition tests, burning tests, oxigen redox tests

(*b*) Molecular size. The molecular size is defined by the average molecular weights, the MWD, degree of polymerization, hydrodynamic volume, radius of gyration, or other measurements relating to molecular dimension. There are a number of techniques that can be used to measure these characteristics such as: size-exclusion chromatography, membrane osmometry, vapor-pressure osmometry, end-group determination, light scattering, ultracentrifugation, and dilute-solution viscosity.

(*c*) Molecular organization. This group includes stereochemical configuration, isomerism, tacticity, branching, and cross-linking, which are of paramount importance for certain applications because they determine properties such as crystallinity and T_g, that definitely have a strong influence on mechanical properties. Molecular organization can be characterized by a number of techniques such as: thermal methods (differential scanning calorimetry, differential thermal analysis, thermogravimetry, etc), X-ray diffraction, solid-state nmr, ir and Raman spectroscopy, microscopy (optical and electron), inverse GC, neutron scattering, and others (see Table 13).

(*d*) Mechanical, electrical, and physical properties. These properties include crystallinity, T_g, and T_m, stress–strain, creep tests, impact tests, dynamic mechanical tests, dielectric relaxation, melt flow or viscosity, solubility, and others. The techniques used to determine these properties are summarized in Table 13. These properties are application specific and the experimental techniques are not always available commercially.

Table 13 presents a summary of the techniques used to characterize the copolymers. Additional information about these techniques can be obtained in (286–291). Nevertheless, the use of some of these techniques for copolymer characterization deserves some comments.

Size exclusion chromatography (SEC), also called gel permeation chromatography (GPC), is employed to determine molecular weight distributions and average molecular weights. This type of equipment separates the polymer molecules according to their molecular size, which means that at each elution time the polymer in the detection cell has the same molecular size. This is the basis of the so-called universal calibration that is a relationship between $[\eta]\,M$ and the retention time (where $[\eta]$ is the intrinsic viscosity and M is the molecular weight). The universal calibration assumes that a unique relationship between molecular weight and molecular size exists. However, the molecular size of a copolymer macromolecule depends not only on its size, but also on its composition, monomer sequence distribution, and topology (branched, grafted, etc). For example, the number of long-chain branches can be determined by SEC chromatograms if a combination of viscosity and light scattering detectors are used (287). However, this calculation usually requires us to assume the type of branching (star, bifunctional, tetrafunctional, etc.) (287), and hence special calibration curves should be developed for these copolymers (287,292).

SEC instruments can also be used to measure the copolymer composition distribution. In this case, a technique called orthogonal chromatography consisting in a set of two SEC systems is applied. The exit of the first one is connected to the injection valve of a second SEC system. The first SEC system is operated in a conventional way. The second one utilizes a HPLC-type separation mechanism by employing a weaker solvent mixture as the mobile phase (286,287). Other configurations of two separation techniques such as SEC–thin-layer chromatography (TLC), SEC–gradient high performance ligvid chromatography (HPLC) and HPLC–SEC have also been used to determine the chemical composition distribution (286–287). The main drawback of these techniques is that they are rather time consuming.

In the characterization of block and graft copolymers, the first concern is usually related to the separation of the block and graft copolymers from impurities such as homopolymers. Even if living anionic or controlled radical polymerization is used in the preparation of such copolymers, homopolymers are produced. The most useful techniques to carry out the fractionation are ultracentrifugation, density gradient centrifugation, TLC, GPC with dual or multiple detection systems, and turbidimetry. After fractionation according to the structure, the isolated block or graft copolymer is usually characterized by its overall composition and molecular weight. Composition can be determined by means of elemental analysis, uv, ir, nmr, and Raman spectroscopies; refractive index; pyrolysis–GC, and GC; X-ray fluorescence; and inverse GC. Determination of the molecular weight of block copolymers can be carried out by means of osmometry, viscometry, light scattering, and centrifugation, but the most widely employed technique is SEC (287) or more recently liquid adsorption chromatography under critical conditions (LACCC) (293,294). In the last few years, the structure and molecular weight distribution of the different segments composing block copolymers is being determined by matrix assisted laser desorption/ionization–time of flight (MALDI–TOF) mass spectroscopy. This technique is used alone or coupled with SEC instruments and also with LACCC chromatographic techniques (295–300). SEC techniques with refractive index (RI) and uv detectors for composition and low angle laser light scattering detector for branching have been used to determine the CCD and MWD of block copolymers (301).

16. Future Trends

Projections of future trends in polymers are highly speculative. Thus, in the prediction made in 1975 about the distribution of the market of plastics at the end of the twentieth century, the expectations were that most of the market would be taken by engineering and high performance plastics. However, the reality is that commodity plastics have extended their dominant position in the market with a share of ~88% of the total market (302). Therefore, let this be a warning for this section.

For high tonnage copolymers, olefin-based copolymers will likely remain and even further strengthen their position in the market by entering other fields by out-performing other plastic materials or replacing more expensive and/or problematic conventional materials (132). The potential of the polyolefins is based on the easy availability of cheap monomers, the economics of the large-scale production, and the fact that they are both environmentally benign and extremely versatile in properties and applications. Developments in catalysts and polymerization processes have expanded the properties envelope making it possible for the polyolefins share of the global plastics market to have grown from 35 to 62% (132) in the last 25 years. This process will be reinforced with the development of new metallocene catalysts (131), which may be accelerated by the extensive application of high throughput screening techniques (303). Combinatorial materials research will have an important impact in the development of new polymeric materials. However, the development of new materials produced by new monomers is not expected unless these materials adapt to the existing production technologies and/or facilities. The development of water-resistant catalysts (304,305) will bring new products to the market.

Metallocene catalysts will also affect nonolefinic polymers because the highly ordered polymers obtained, eg, sindiotactic polystyrene (Questra, Dow Chemical; Xarec, Idemitsu) have properties not attained by traditional products.

Nanotechnology will likely have a critical influence on polymeric materials. Polymer nanocomposites will further expand the properties envelope bringing dramatic improvements in stiffness and gas-barrier properties (131).

In the specialty market, commercialization of controlled radical polymerization processes will bring a whole portfolio of new polymer materials. Block, graft, and hyperbranched copolymers of well-defined topology will have opportunities in markets such as coatings, adhesives, elastomers, sealants, lubricants, imaging materials, powder binders, dispersants, personal care products, detergents, photopatternable materials, and biological sensors. In order to fully exploit the potential of the controlled radical polymerization processes, more efficient, more selective, less expensive, and environmentally sound controlling agents are needed (41). In addition, these new materials will face strong competition from existing polymers to establish themselves in the market.

Polymer producers will continue to suffer strong competition and increasing social pressure to achieve a sustainable growth. Therefore, polymerization processes will be run more efficiently to achieve a consistent production of high performance polymers under safe and environmentally friendly conditions. This will require the development of robust and accurate on-line sensors for polymerization monitoring and efficient on-line optimization and control strategies.

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