Chapter 4
Synthesis of Polymers for Plastic Materials

4.1 Motivation

This chapter deals with the preparation of products starting with material based on plastic polymers from fossil origin (Bruckner et al. 2001). The production route of traditional plastic polymers starts from available monomers, followed by the reaction for converting them into polymers and successive processing to obtain objects. This synthetic description is considered necessary for the general objective of the book devoted to the comparison between plastics from fossil origin and from renewable sources. The description below of the various macromolecular structures that man has produced starting with fossil feedstock gives a good insight about the molecular features necessary for a plastic behaviour and for modulating plastics properties according to the application needs. Indeed, the alternative use of plastics from renewable source is first of all depending on the evaluation of real capacity of the bio-related plastics to be produced with structures granting the basic response to use. An additional concern may arise from the real possibility to provide renewable feedstocks in an adequate amount with sustainable processes not involving significant amounts of energy and of side streams producing environmental problems. Clearly, this problem arises when monomers and polymers from bio-related starting compounds with different structures than the ones traditionally used are considered as substitute of the traditional analogues from fossil sources. These new bio-related polymers may need different production processes and then arise new sustainability problems. Moreover, the bio-related polymers will be clearly submitted to the same processing technologies as the corresponding fossil products and then must be adapted to the related thermal and mechanical treatments. This problem obviously does not exist when the monomer from natural renewable sources has very similar or identical structure as in the case of ethylene from oil or from fermentation, as both will end up with not distinguishable ethylene polymers. Then this chapter has the role of describing the state of art in established plastic polymer technology as far as polymerization reactions and material processing are concerned in order to have an insight into the

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challenge encountered by monomers and polymers from renewable sources when converted in the so-called bioplastic material.

4.2 Monomers from Fossil Resources

Monomers from fossil resources can be obtained capable to undergo either chain polymerization or stepwise polymerization. Monomers used for producing plastics are bi-functional so to give rise to linear or branched macromolecules, but without cross-linking, which would originate non-thermally processable materials.

The monomer per se cannot grant polymer plastic properties, which derive from the macromolecules structure. This last and important contribution is provided by the polymerization process as discussed in the next section.

A monomer is a molecule that can be incorporated through a polymerization reaction in a macromolecule, the long molecular chain formed by connecting one monomer after the other through covalent bonds. Clearly, the monomer when becoming part of a macromolecule must undergo structural changes for forming bonds by addition or condensation reactions. The structure assumed by the monomer when part of a macromolecular chain is indicated as the 'repeating unit' (r.u.). The product of the polymerization reaction is the macromolecule, which has high molecular mass corresponding to a multiple of finite number of the repeating unit. Note that from the same monomer, macromolecules containing a different number of repeating units can be obtained, all having the same short term molecular structure, but giving different material properties.

In a picturesque simplified representation, the monomer can be designed as the precursor of the coach (monomeric unit) constituting a long train (macromolecule). A monomer must therefore have some basic requirements of being at least bi-functional for forming chemical bonds with at least two other monomer molecules, during a specific polymerization process. The polymer with plastic behaviour must be converted in the corresponding melted material by heating at a temperature over the melting point but below the decomposition temperature of the subject polymer. This is obtained only with not cross-linked chain, and therefore, the monomer for the plastic polymer is bi-functional.

For this reason, the following presentation refers only to bi-functional monomers which are submitted to polymerization reactions according to a chain or a stepwise mechanism.

The chain polymerization is generally applied to monomers that contain a reactive double bond opening up to form a chain by repeated rapid addition. The reaction is started and developed by initiators and catalysts.

The typical monomers are alkenes or substituted alkenes. The reactions are actually fast and involve the conversion of a double π-bond of the monomer to two more stable σ-bonds in the polymer chain; therefore, the polymerization reaction is usually exothermic. A general scheme illustrating the formation of a linear macromolecule from a monomer containing a double bond (bi-functional) is reported in Fig. 4.1.

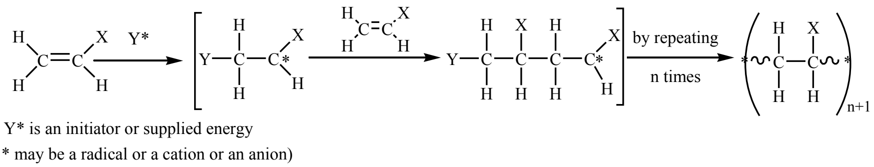


Fig. 4.1 Schematic representation of chain polymerization

Monomers with a carbon–carbon double bond can be polymerized by either free radical, ionic or metal-coordination methodologies. In fact, we can distinguish four polymerization procedures according to the following description.

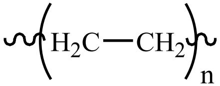
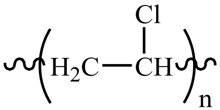
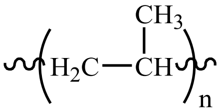
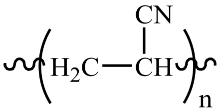
- Free radical polymerization: the initiator is a molecule generating free radicals or energy supply, and the propagating site (marked with *) is a free radical derived from the monomer.
- Cationic polymerization: the typical initiator is a protonic acid or a Lewis acid, and the propagating site (marked with *) is a carbocation.
- Anionic polymerization: the initiator is a molecule capable of generating an anion and the propagating site (marked with *) is a carbanion.
- Coordination catalytic polymerization: the initiator is a transition metal complex with, in general, an organometallic co-catalyst, and the propagating site is the catalytic complex with the monomer bearing connected the growing chain.

As a result of this polymerization, the polymer is formed of repeating units with similar structure as the monomer (without obviously the double bonds) and has a higher molecular mass (Table 4.1). The chains forming the polymer are long but not infinite and have two terminal groups derived from the initiator and from the chain termination mechanism.

The stepwise polymerization generally proceeds by the reaction between two complementary functional groups present on the same molecule (for example one amino acid or a hydroxyl acid) or formed in situ from two complementary bi-functional molecules (a diamine and a dicarboxylic acid or a diol and dicarboxylic acid). The reaction steps leading to a macromolecule can occur with loss of a small molecule (polycondensation), such as water or ammonia, but also by the addition of a functional group to a reactive unsaturated group as diol addition to diisocyanates to give polyurethanes (Table 4.2).

The examples of monomers and polymers reported in Tables 4.1 and 4.2 indicate the broad structural and chemical variability of the synthesized structures where carbon–carbon bonds, oxygen, nitrogen atoms and aromatic groups can be present in the main chain or as side groups. This in turn gives different chemical and physical properties as well as mechanical and thermal properties in assembled materials, polymer packing, going from soft to rigid plastic polymer up to fibres. Apolar/aliphatic polymers have mostly applications as soft plastics. Whereas, heteroatoms and aromatic groups give a more rigid structure, contributing to more performing plastics in

Table 4.1 Examples of monomers giving chain polymerization and the corresponding polymers

Monomer	Formula	Polymer	Trivial name	Structure of repeat unit
Ethene	$H_2C{=}CH_2$	High density poly(ethene)	High density poly(ethylene), HDPE	 $\sim\!\!\left(H_2C{-}CH_2 \right)_n\!\!\sim$
Chloroethene	$H_2C{=}CHCl$	Poly(chloroethene)	Poly(vinyl chloride), PVC	 $\sim\!\!\left(H_2C{-}\overset{\overset{\textstyle Cl}{\vert}}{C}H \right)_n\!\!\sim$
Propene	$H_2C{=}CH{-}CH_3$	Poly(propene)	Poly(propylene), PP	 $\sim\!\!\left(H_2C{-}\overset{\overset{\textstyle CH_3}{\vert}}{C}H \right)_n\!\!\sim$
Propenenitrile	$H_2C{=}CH{-}CN$	Poly(propenonitrile)	Poly(acrylonitrile), PAN	 $\sim\!\!\left(H_2C{-}\overset{\overset{\textstyle CN}{\vert}}{C}H \right)_n\!\!\sim$

(continued)

Table 4.1 (continued)

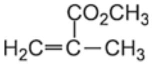
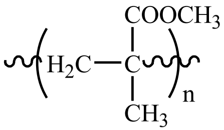
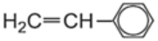
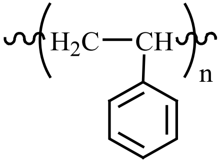
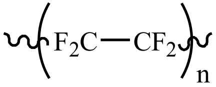
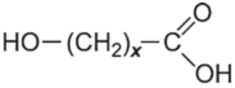
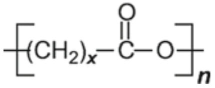
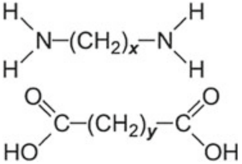
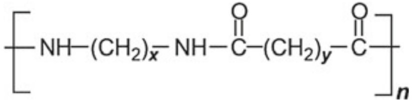
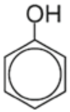
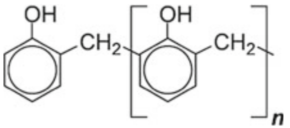
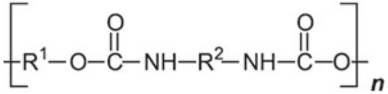
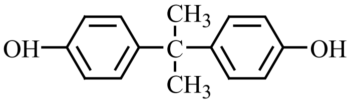
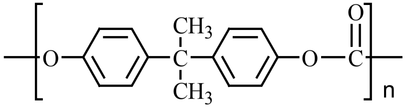
Monomer	Formula	Polymer	Trivial name	Structure of repeat unit
Methyl 2-methylpropenoate	 $H_2C{=}C(CO_2CH_3){-}CH_3$	Poly(methyl 2-methylpropenoate)	Poly(methyl methacrylate), PMMA	
Phenylethene		Poly(phenylethene)	Poly(styrene), PS	
Tetrafluoroethene	$F_2C{=}CF_2$	Poly(tetrafluoroethene)	Poly(tetrafluoroethylene), PTFE	

Table 4.2 Examples of monomers giving stepwise polymerization and the corresponding polymers

General polymer	Monomer	Polymer formula
Polyesters	 $HO-(CH_2)_x-C(=O)OH$	 $-[(CH_2)_x-C(=O)-O]_n-$
Polyamides	 $H_2N-(CH_2)_x-NH_2$ $HO(O=)C-(CH_2)_y-C(=O)OH$	 $-[NH-(CH_2)_x-NH-C(=O)-(CH_2)_y-C(=O)]_n-$
Phenol–methanal plastics	 CH_2O	
Polyurethanes	$HO–R^1–OH$ $O=C=N–R^2–N=C=O$ R1 and R2 alkyl and/or aromatic substituents	 $-[R^1-O-C(=O)-NH-R^2-NH-C(=O)-O]_n-$
Polycarbonates	 (Bisphenol A) $X_2C=O$ (X = $O–CH_3$ or Cl)	

term of applications temperature and mechanical performances and are used as rigid plastic materials or fibres (Young 1987).

4.2.1 Hydrocarbon Monomers from Oil

The viscous component necessary for plastic properties is fluid when strong interactions are lacking as in hydrocarbon macromolecules. For this reason, most common monomers polymerized for plastics are hydrocarbon molecules containing a single double bond per molecule and are made of linear chain without any cross-links. These monomers preferably contain a terminal double bond, that is a vinyl group attached to a hydrogen atom in ethylene or to alkyl or aryl groups in aliphatic and aromatic mono-olefins, respectively. These monomers have a high reactivity for surviving in the natural environment and were obtained through several man-made preparative processes starting from fossil resources. Now we are facing the real possibility to produce these monomers from renewable sources, such as fermentation, to save non-renewable resources maintaining products with exactly the same performances.

The hydrocarbon monomers used for producing the corresponding plastic materials are ethylene and monosubstituted 1-olefin, having the molecular formula reported in Fig. 4.2.

It is of interest to note that these monomers contain carbon and hydrogen only, and thanks to the reactivity of the double bond present in each olefin molecule, can be converted into macromolecules polymers, the polyolefins, by activators of the polymerization reaction. The polymerization converts the double bond in a saturated structure; thus, the resulting polymer is formed of saturated hydrocarbon macromolecules that is high molecular weight paraffins. Therefore, the polyolefins maintain the hydrophobic character of the monomer being paraffin with additional chemical inertness as the double bond disappears during the polymerization process. Due to their reactivity, olefins are not present in the major hydrocarbon sources used, such as natural gas and crude oil. Fractions of these last are then processed by steam cracking to provide petrochemicals like as olefin and diolefins (dienes) to be employed as monomers (Fig. 4.3).

Aliphatic mono-olefins (ethylene, propylene, 1-butene, etc.) are directly obtained by dehydrogenation of C2–C4 natural gas ethane, propane, and butanes, while the steam cracking of higher molecular weight saturated species present in petrol produces additional olefins and aromatics. Schematically, as shown in Fig. 4.3 a process

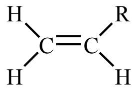


Fig. 4.2 Mono-olefins general structure

where R= H, -CH_3, -C_2H_5, and few longer alkyl group, -C_6H_5

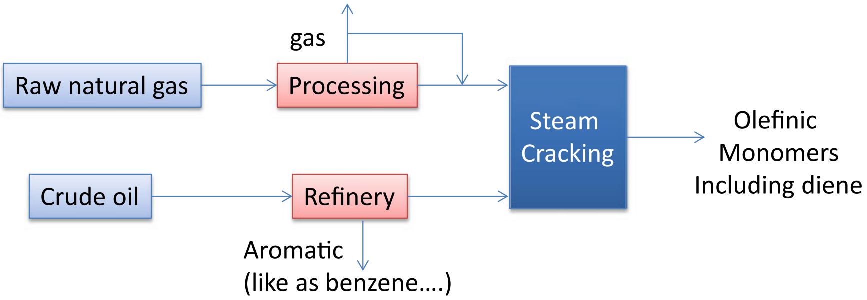


Fig. 4.3 Schematic representation of conversion of crude oil and natural gases into monomers

can be directed to produce several intermediate petrochemical feedstocks including ethylene, propylene, butenes, butadiene and benzene. The first three are, as said, very important for direct polymerization to the corresponding plastics polymers. Butadienes are interesting for producing synthetic rubber, while benzene is the basic molecule for aromatic mono-olefins.

The two most important monomers ethylene and propylene are produced in steam crackers in amount that toady are over 200 Mt overall with ethylene/propylene ratio 1.6–1.7. The plants involved in this very impressive production are very large up to as much as 1.0–1.5 Mt per year. It is evident then how difficult can be to replace in short time this remarkable production from fossil with that of the same monomers from sugar fermentation.

Even if, as mentioned before, mono-olefins do not exist in nature being too reactive, ethylene was demonstrated to be an intermediate in some fruits such as apples and pears as ripening begins but it cannot be present in the final fruit. Clearly, it would not easy to collect this ethylene in a sustainable way to feed the Industry to an acceptable level. One could argue way Nature never produced from this available monomer the corresponding polymer. The explanation could be that there was no need in nature for a filmable and processable durable plastic material with high hydrophobic character, which on the other side became very popular in the present times. The most popular aromatic mono-olefin is styrene. It is not produced directly from petrol and must be prepared according to two industrial processes starting from benzene and ethylene. The first step consists of the alkylation of benzene to ethylbenzene with ethylene under cationic catalysis and the second final step is the dehydrogenation of ethylbenzene to styrene at high temperature and in the presence of metal oxides as catalyst.

Ethylbenzene produced as reported in Fig. 4.4 can also be converted in styrene by treatment with oxygen to form the ethylbenzene hydroperoxide. This last is reacted with propylene to give propylene oxide and 1-phenylethanol, which can be successively dehydrated to styrene.

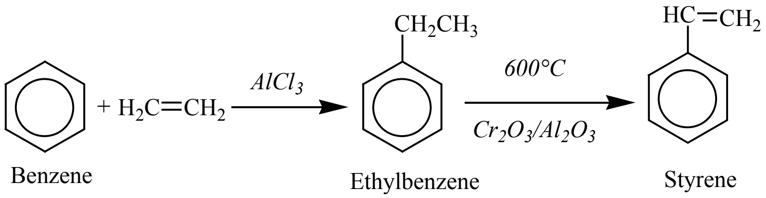


Fig. 4.4 Synthesis of styrene monomer

4.2.2 *Monomers Containing Heteroatoms*

In addition to hydrocarbon monomers providing by polymerization a number of paraffinic stable and hydrophobic plastic materials, monomers containing heteroatoms are also used to produce plastic polymers with expanded performances towards different directions. Indeed, a group of these monomers is formed by the hetero-substituted mono-olefins having the molecular structure similar to that indicated in Fig. 4.2 with the substituent R containing in general oxygen and nitrogen or a halogen atom. Typical examples are the acrylic and methacrylic monomers. In the former case, R has the structure –COOR, where R, can be alkyl or aryl, –COOH, CN or more or less substituted organic groups. Similar monomers are the methacrylic derivatives where the vinyl group of acrylates is instead a 2-propenyl group. Other used unsaturated monomers are vinyl chloride, vinylidene fluoride and tetrafluoroethylene. All the above monomers can be polymerized by chain mechanism. This last is also valid for heterocyclic compounds such as epoxides, lactones and lactams, but in these cases, the polymerization starts with ring opening instead of attack to the double bond. The resulting polymer from heterocyclic monomers clearly has heteroatoms in the macromolecules backbone.

Additional plastic polymers can also be obtained by stepwise polymerization from monomers containing two complementary functional groups, such as amino acids, hydroxy acids or by a mixture of two bi-functional compounds, with complementary functionalities such as diamine plus dicarboxylic acid or diol plus dicarboxylic acid, through a stepwise polycondensation process (Table 4.2). All these monomers are mainly produced from oil feedstocks according to various consolidated industrial processes, but some of them can also derive from renewable sources.

4.3 Polymerization Processes

4.3.1 *General Aspects*

According to the main objective of the present book, the polymerization processes are here reported in a form and in a detail aimed to provide appropriate information about the possible macromolecular structures formed when submitting a specific monomer to one of the applicable polymerization processes (Tobita 2015). Then, the following pages provide the reader with a basic knowledge about the synthetic possibility offered by the different monomers in reference to the related polymerization processes (Jenkins et al. 1996).

It is well known that polymerization processes were discovered and developed to convert monomers, which are usually in gas o liquid form, into macromolecules, which are the sub-, micro-constituents of solid polymers including plastics. These monomers are derived from feedstocks of fossil origin and were made available in huge amounts by man-developed process, which until now covered all human society requests. The type of polymerization process may be different depending on monomer general structure determining its chemical reactivity. Polymerization processes can be clearly used to produce polymers of monomers derived from renewable sources, but having the same structure as those from oil, such as ethylene from fermentation ethanol. In addition, the new bio-derived monomers, which were not obtained before in pure petrochemical production, are converted into the corresponding polymers through the mentioned polymerization processes here below described.

The polymerization is a typical man-made industrial process and its understanding, combined with the information connected to the monomer structure, is important to be fully aware of the molecular characteristics of the macromolecule constituting the derived polymeric materials.

It is fundamental to note that as the polymerization reaction consists of repeated covalent bond formation between successive monomer molecules that change their structure to that of the repeating unit either by internal electronic rearrangement in polyaddition or by eliminating small molecules in polycondensation. In case of plastic materials, the macromolecules are long linear chains derived from bi-functional monomers (see the previous section).

The final polymer product obtained from a single monomer, which originates only one type of monomeric unit, is a homopolymer but the macromolecular chains are in general not identical as they may differ in length that is in number of inserted monomeric units, as the initiation and termination reactions may not necessarily occur at the same time for all chains. The resultant molecular weight is then an average value and the dispersion (MWD) of these values is described by a curve with the maximum value corresponding to the most probable number of units per macromolecule that is equal to the number average molecular weight $\overline{M_n}$ (Eq. 4.1).

Basic definitions of the number average molecular weight $\overline{M_n}$ is reported below in Eq. (4.1):

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i} = \sum n_i M_i \tag{4.1}$$

were N_i is the number of macromolecules of the i-th fraction all having molecular weight M_i and n_i is the molar fraction of the same macromolecules having molecular weight M_i The weighted average molecular weight is given by Eq. (4.2):

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \sum w_i M_i \tag{4.2}$$

where w_i is the weight fraction of macromolecules having molecular weight $M_{i.}$

Note that the latter is usually higher than the former one.

An evaluation of the inhomogeneity of the molecular weight of the different length macromolecules is indicated by the ratio between the two above average and is named molecular weight dispersion MWD Eq. (4.3):

$$MWD = \frac{\overline{M_w}}{\overline{M_n}} \tag{4.3}$$

In polymerization processes giving chain with different length, $\overline{M_w}$ is always greater than $\overline{M_n}$ indicating a polydispersed material; only in the case of a monodispersed material, when all chains have the same length, $\overline{M_w} = \overline{M_n}$ and MWD = 1. Indeed, MWD accounts for the molecular weight heterogeneity of a polymer.

A more complex situation arises when the monomer is not single, and a mixture of two (copolymerization) or more (multi-polymerization) is submitted to the polymerization process. In this case, two different monomeric units are generated in a relative amount depending on starting feed composition and comparative monomers reactivity towards the polymer growth reaction. The macromolecules forming the polymer can then be different also for composition (ratio between the two monomer units) and distribution of these two units along the chain. Sometimes this type of structural complexity may be encountered even starting with a single monomer, as observed for 1,3-dienes, which can originate chemically distinct monomeric units (as 1,2 or 1,4 reaction) or stereochemically distinct units (1,4 trans or 1,4 cis-diene units). The stereochemical complexity is also observed for the polymerization of prochiral monomers, monosubstituted olefins (propylene, etc.) or racemic monomers (D- and L-lactic acid).

The average length of the chain, its dispersion, as well as the content and sequence along the chain of chemically or stereochemically distinct units can be modulated by the features of the used polymerization process and related reaction conditions.

It is out of the limits of this book to discuss in detail the mechanism and the many peculiar features of all available polymerization processes. Rather here one can find a synthetic description of the polymerization reactions industrially used to produce plastic polymers and the structural features that can be achieved depending on monomer and process mechanism.

The average number of monomeric units per chain provides the number average polymerization degree, which is equal to the number average molecular weight divided by the weight of the monomeric unit. The weight fraction of monomer converted into polymer provides the polymerization yield. The two values can be independent of each other as a high average molecular weight clearly does not imply a high yield. This latter can also be reached by converting all the monomer into low molecular weight polymer. The two aspects are schematized below:

$$n\,M = m\,M_x + (n - mx)\,M \tag{4.4}$$

where m = number of formed macromolecules;

x = average polymerization degree (number of monomer units per macromolecule) defined as

$$x = \frac{\overline{M_n}}{M} \tag{4.5}$$

and $\overline{M_n}$ the number average molecular weight;

Y = percent polymerization yield is given by

$$Y = (m\,x\,M/n\,M)\,100 \;=\; (m\,x/n)\,100 \tag{4.6}$$

The polymerization reactions follow two distinct kinetic mechanisms, namely, chain polymerization and stepwise polymerization.

The chain polymerization interests unsaturated monomers, such as olefin or cyclic compounds, and must be initiated by an appropriate compound, the initiator, which by reactions with the monomer produces activated species further reacting with the available monomer. The formation of a polymer from an unsaturated monomer is an example of a chain reaction, which once started is able to keep itself going if monomer is provided, while the reaction stops when the monomer is finished. Some processes can stop even in the presence of unconverted monomer; if the active species are consumed in undesired reactions. Therefore, chain polymerization reaches the maximum molecular weight allowed under the selected polymerization condition already when the monomer conversion is low. The successive progress of the reaction then is necessary to increase the polymer yield but it has very limited effect on the average chain length.

In the stepwise polymerization, the monomers combine in longer molecules one by one in successive steps. While many steps are necessary for a long chain, the monomer can disappear much earlier. In a borderline case of dimer, all the monomer would be fully converted but the polymerization degree would be only 2. We can then conclude that in the stepwise polymerization, the conversion reaches a high value when the molecular weight is low. Longer time is than necessary to reach a desired value of molecular weight, opposite to what happen in chain polymerization.

4.3.2 Chain Polymerization Processes

4.3.2.1 Free Radical Chain Polymerization

During the free radical polymerization process, it is suggested that four reactions occur and control the polymer yield and the molecular weight. The three first reactions are the initiation producing activated monomer species, the propagation responsible for the successive addition of monomer molecules to the initiated monomer and then of the chain growing, and the termination responsible for the disappearance of active species then giving termination of the growing chain and of the polymerization. These three reactions are clearly effective on the amount of polymer formed (polymerization yield), which is indicated also by the fraction of monomer converted into polymer. The molecular weight of the formed macromolecules and the average length of the chains depend on the occurrence of the additional fourth reaction, the chain transfer, which stops the macromolecule growth by transferring the activated species to a new macromolecule. This reaction has the effect of reducing the chain length and then the molecular weight but has no effect on the polymer yield. Indeed, this reaction does not reduce the number of active species and then does not affect the polymerization rate and the polymer yield, but stopping the growth of the single chain limit is molecular weight.

The combination of these reactions is described in the commonly accepted mechanism of the free radical initiated polymerization that is summarized below with reference to the above fourth reactions.

I. Initiation (the polymerization get started)

Under the impact of energy supply, the initiator is converted into reactive free radicals. Light, heat or an appropriate redox reaction can provide the energy needed for this process. Figure 4.5 describes how this can happen in case the initiator is a peroxide.

The real initiation occurs when the free radical ties a monomer molecule with formation of a new free radical, called the activated monomer (Fig. 4.6).

II. Propagation (polymerization continues with chain length growing)

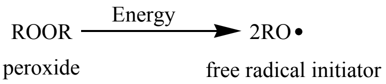
The initiation reaction is normally instantaneous, while the chain propagation reaction needs more time to allow the polymer chain to grow. In the propagation the newly formed activated monomer attacks and attaches to the double bond of another monomer molecule, which generates the new activated monomeric unit. This addition occurs again and again to make the long polymer chain (Fig. 4.7).

The '*n*' stands for any number of monomer molecules, typically in the thousands.

III. Termination (active species are stopped)

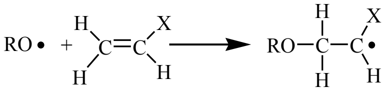
The free radical initiated chain reaction terminates as the free radical are cancelled by side reactions. Each termination reaction stops the addition of other monomers

Fig. 4.5 Formation of primary radicals



$$\underset{\text{peroxide}}{\mathrm{ROOR}} \xrightarrow{\text{Energy}} \underset{\text{free radical initiator}}{2\mathrm{RO}\bullet}$$

Fig. 4.6 Initiation reaction



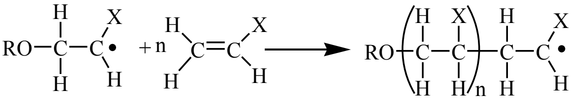


Fig. 4.7 Propagation reaction

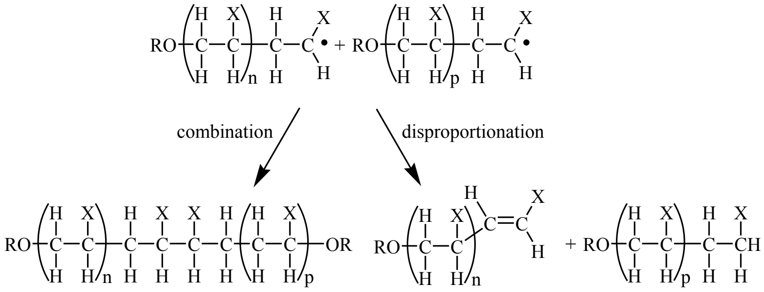


Fig. 4.8 Termination reactions

to a single chain that thus ends growing. The single termination results also in a reduction of the total concentration of free radicals and the reaction stops when these are consumed. If at this point monomer molecules are still present, the polymer yield is not complete. There are two termination mechanisms related to the encounter of free radicals at the end of two growing chains. Disproportionation occurs if the two free radicals give rise to the transfer of a hydrogen atom with formation of a saturated and one unsaturated macromolecules end group. On the other side, they may react to give a stable carbon–carbon bond between the two chain ends according to a combination process. In the former case, the length of the two terminated chains remains the same reached during the polymerization reaction, whereas in the latter case the length is the sum of the two terminated chains. The occurrence of these two processes, in addition to the termination of the reaction, affects the dispersion of the molecular weight.

The molecular description of the two termination reactions is schematically reported in Fig. 4.8.

The free radical undergoing the termination reaction can be of different origin and can be located either at the end of growing polymer chains, or in a low molecular weight molecule including the primary free radicals from the initiator. The reactants, the reaction times and the reaction conditions are important parameters determining the limitation of the termination or its direction towards preferred routes according to the various possibilities described above.

IV. Transfer (single chain stops while polymerization continues)

The transfer reaction is defined as a reaction in which a growing chain carrying the free radical end reacts with another molecule and transfers the free radical to this latter. The growth of the chain is stopped and the active specie, the free radical is

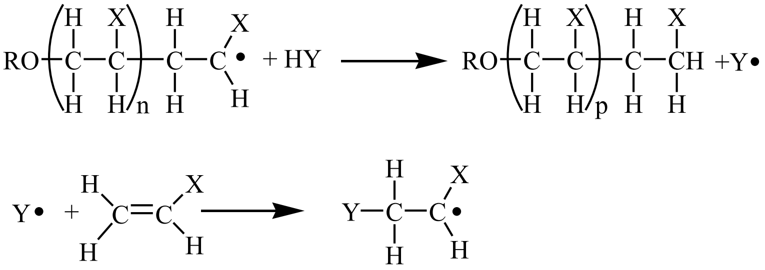


Fig. 4.9 Transfer reaction

transferred to the other molecule that can start the growth of a new chain. As the results, the chain is terminated and the macromolecule does not grow anymore. On the other side, the new free radical formed interacts with the remaining monomer and the polymerization reaction continues (Fig. 4.9).

The transfer reaction limits the polymer molecular weight but has small or no effect on the polymerization rate. In addition to the effect on the chain length, the transfer may be also responsible for branching of different length.

The occurrence of the transfer reaction in addition to the termination reactions is responsible for the formation of chains with different number of monomer units. Then the macromolecules formed by free radical chain polymerization have not all the same molecular weight and the resulting polymer has a broad distribution of the molecular weight with $MWD =$ up to 2.

For the above reasons, the physical properties of polymeric materials from a particular monomer can be varied depending on the polymer's average length, the molecular weight dispersion and the amount and type of branching.

The monomers suitable for the free radical polymerization must give rise, through the reaction with the primary radical, to an activated monomer unit bearing a relatively stable free radical. To act in this way the substituent on the monomer double bond should be capable to provide the radical stabilization while inducing on the double bond a modest or none electrons excess or deficiency to avoid the formation of charged species. These last giving electrostatic repulsion between activated monomer and incoming monomer would hinder the propagation reaction. Indeed, the activated monomer and the incoming monomer would bear a charge of the same sign as having the same substituent.

4.3.2.2 Ionic Chain Polymerization

While in the free radical chain polymerization the reaction starts when a non-electrically charged free radical interacts with the monomer to give rise to an activated free radical, in the ionic polymerization the monomer is activated under the action of a charged species that converts the monomer into a cation or an anion. This situation

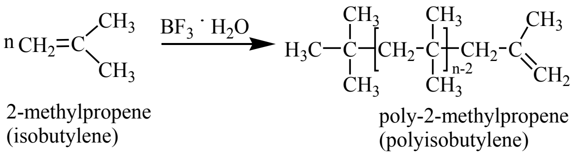


Fig. 4.10 Isobutylene polymerization

can be exemplified with reference to the X substituted ethylene monomers of Fig. 4.1. In this molecule, if X is an electron withdrawing substituent, an excess of positive charge is localized on the double bond and the polymerization can be initiated by an anion which converts the monomer in an activated monomer anion that will successively react with other monomer molecules to give a macromolecule. With an electron releasing X substituent, a negative charge excess is localized on the double bond. This monomer is then activated to a cationic monomer by the attack of a cation thus starting a cationic polymerization reaction. Cationic and anionic polymerization can also be applied to cyclic monomer bearing a site that can be subjected to cationic or anionic attack. These sites are in general related to the presence of heteroatoms either a member of the cycle or bond to a carbon atom of the cycle.

The ionic polymerization has no termination reaction as the electrostatic repulsion does not allow two growing chain ends to encounter for giving deactivated species. Therefore the whole kinetic mechanism of the ionic polymerization has only three reactions, namely, initiation, propagation and chain transfer. Clearly, the presence of transfer reactions means that one growing chain can be stopped as the active ion is removed by the transfer to another species, which can start a new chain. Therefore while the conversion monomer to polymer does not stop until there is monomer available, the molecular weight is limited by the transfer reaction. The average value of the molecular weight results at the end by the ratio between the polymerization rate and the transfer reaction rate.

Hydrogen atoms are not effective electrons donating substituent; methyl is better but still relatively weak. The simplest olefin that can be polymerized by cationic initiators is 2-methylpropene (isobutylene). Indeed, the double methyl substitution on the same carbon atom induces enough negative charging on the double bond.

The cationic polymerization of 2-methylpropene or isobutene can be performed by protic or Lewis acids such as sulfuric acid, hydrogen fluoride, or a complex of boron trifluoride and water or aluminium chloride. Anhydrous conditions are necessary to avoid initiator deactivation and low temperature to limit transfer reactions. If these conditions are fulfilled a long chain polyisobutylene is formed (Fig. 4.10).

As mentioned before, ionic polymerization can also be effective for the conversion of cyclic monomers with nucleophilic character as epoxide, where the oxygen atom of the epoxy ring is subjected to the attack of cations (Fig. 4.11). Other cyclic nucleophilic monomers are cyclic sulphides, cyclic amines, small ring cycloalkanes, cyclic carbonates and also lactones and lactams.

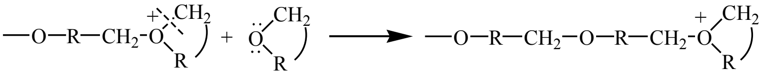


Fig. 4.11 Schematic representation of ring-opening polymerization mechanism

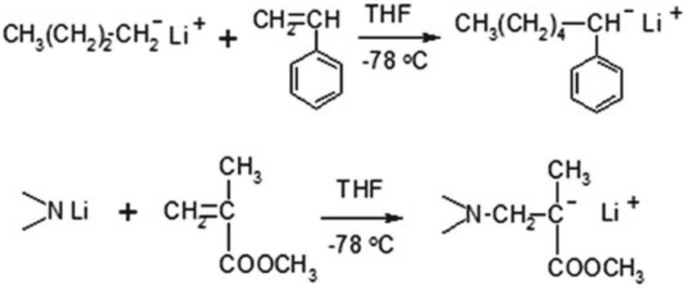


Fig. 4.12 Examples of anionic polymerization mechanisms

On the other side, if a monomer contains an electron deficient moiety, it can be subjected to nucleophilic attack by an anion to start anionic polymerization. Anionic polymerization can be efficient for unsaturated monomers having an electron deficiency on the double bond or with cyclic monomers containing an electrophilic site, such as acrylates, methacrylates, styrene and cyclic monomers such as lactams, lactones and epoxides. In these last cyclic monomers, the attack by the anion occurs on a different site in respect to what happens in the cationic initiate process (Fig. 4.12).

An important parameter in anionic polymerization is the polarity of the solvent promoting the dissociation of the active anionic growing chain end from the counterion. In polar solvents the dissociation is complete and each anion starts a chain.

In case any transfer reactions do not occur, the final number of chains is equal to the number of initiator molecules and therefore, in case of complete monomer conversion the degree of polymerization is given by Eq. (4.7):

$$\overline{x_n} = \frac{[M]_0}{[I]_0} \tag{4.7}$$

where $[M]_0$ and $[I]_0$ indicate the monomer and anionic initiator concentrations, respectively, at the zero reaction time.

4.3.2.3 Catalytic Polymerization

The most available and cheap potential monomers are the smallest olefins ethylene and propylene produced during the refining of oil and related simple processes. However, these monomers cannot polymerize by free radical or ionic polymerization under ambient conditions as the molecular structure does not allow the monomer activation and the propagation reaction to give high polymers. Ethylene polymers could be firstly obtained by ICI (Imperial Chemical Industries) in 1933 using a free radical initiator but working at relatively high temperature (200–300 °C) and extremely high monomer pressure (1.000–3.000 bar). Because of the high frequency of the transfer reaction under the drastic reaction conditions, the polyethylene formed was consisting of chains with many long and short branching. This polymer is today named low-density polyethylene (LDPE) as the branching does not allow a dense packing as expected for the linear chains.

About 20 years later, Karl Ziegler and Giulio Natta developed new catalytic processes to polymerize ethylene and propylene under extremely mild conditions, as example at room temperature and pressure. The inventive polymerization process is made possible thanks to a two components heterogeneous catalyst formed from the reaction of a transition metal derivative with an organometallic alkylating compound. The first-generation systems were prepared using $TiCl_4$ (or $TiCl_3$) with alkyl aluminium derivatives consisting of heterogeneous polymerization catalysts. A variety of transition metals as such or supported on various materials were successively employed and improved performances were obtained capable to provide very high polymer yield and to control molecular structure up to the stereochemical level. From the 80s also homogeneous catalysts were developed based on transition metal complexes bearing ligands capable to stabilize the transition metal- alkyl bond and with a spatial geometry controlling the monomer insertion stereochemistry and then the macromolecules microstructure.

The process allows the polymerization of all available 1-alkenes to obtain their copolymers. A variety of new polymers with paraffinic basic structure but with very different macromolecular structures and material properties were and are obtained. Polyolefins are today, indeed, the largest class of plastic polymers. The processes have allowed obtaining new ethylene polymers such as the very linear polymers HDPE, and many copolymers of ethylene with various 1-alkene with a good control of the density and thermomechanical properties. It is scientifically trivial, but in some way interesting to the objective of this book to remember that the application of the catalytic polymerization to the ethylene monomer obtained from renewable natural sources allows producing all the various ethylene polymers with exactly the same structures and properties as those originally obtained starting with ethylene from fossil origin.

The control of the primary structure of the formed macromolecules exerted by this catalyst class extends to stereochemistry. Thus the polymerization of the prochiral monomer propene, which gives a monomeric unit containing an asymmetric carbon atom (Fig. 4.13), is characterized by the possibility to have chains where the mentioned asymmetric carbon atom can have the same chirality (isotactic polymer) or alternate opposite chirality (syndiotactic polymer).

A third polymer of propene can also be obtained where the two configurations are randomly distributed (atactic polypropylene). The first two polymers are ordered and can crystallize to give a semicrystalline plastic material. The last is irregular and then results in an amorphous polymer. The three different chains are schematically represented in the planar zig-zag conformation just to show the stereochemical cor-

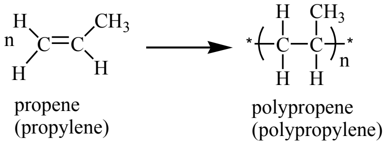


Fig. 4.13 Propene polymerization

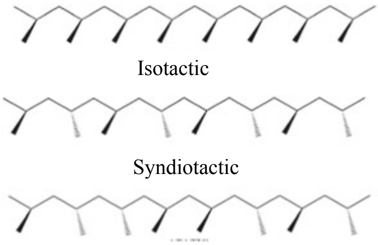


Fig. 4.14 Steric order and disorder of polypropylene macromolecules

relations along the chain (Fig. 4.14). The sketched conformation is not possible in the isotactic polymer due to the steric interaction among methyl side chain, but is observed in the syndiotactic stereoisomer where the above interaction is removed as the methyl groups are located on opposite sides of the planar zig-zag chain. Also, the atactic polymer cannot assume the indicated conformation and must rotate out of the plane when isotactic dyads are present.

From the industrial viewpoint, only the isotactic polypropylene is interesting having a range of plasticity from just below zero centigrade degree up to 160 °C with remarkable mechanical properties allowing applications as commodity but also in more advanced uses. For the industrial production heterogeneous new generation catalysts are the most used with some relevant examples reported in Table 4.3. These new catalytic systems have a very high sustainability thanks to the remarkable productivity and high stereospecificity avoiding catalyst purification and atactic polymer removal.

A large number of unsaturated monomers were indeed polymerized according to differently initiated chain mechanism. Several of them have plastic properties but differences performances thus being of interested in various applications and uses. The most successful that are produced on a large scale and are used constantly in everyday life in addition to the polyolefins are reported in Table 4.4.

4.3.3 Stepwise Polymerization

In this process different from the chain reaction one, the chains increase their length by stepwise binding of any two molecules present in the reaction mixture independent of the respective molecular weight. Indeed, the monomer and longer molecules, dimers, trimers and so on can link together at any time having two reactive terminal

Table 4.3 Typical formulations and performance of $MgCl_2$-supported Ti-based Ziegler–Natta catalyst for propylene isotactic polymerization

Internal donor	External donor	Productivity[a]	Index of isotacticity[b]	$MWD = \frac{\overline{M_w}}{\overline{M_n}}$
Aromatic monoester (e.g. ethyl benzoate)	Aromatic monoester (e.g. methyl-*p*-toluate)	0.5	>95	5–6
Aromatic diester (e.g. dibutyl-*o*-phtalate)	Alkoxysilane (e.g. $R^1R^2Si(OMe_2)$)	1–2	>97	5–6
2,2'-dialkyl-1,3-dimethoxypropane	Alkoxysilane (e.g. $R^1R^2Si(OMe_2)$)	>2	>97	3–4
Aliphatic diester (e.g. dialkyl succinate)	Alkoxysilane (e.g. $R^1R^2Si(OMe_2)$)	1–2	>98	>7

[a] 10^3 kg (PP) g $(Ti)^{-1}$
[b] wt% of highly isotactic PP

complementary groups. Both condensation and addition reactions can be involved in the linking between the two molecules. The former mechanism proceeds through a condensation reaction, in which a small molecule is eliminated in each step as happens in the formation of Nylon 66 from adipic acid and hexamethylene diamine (Fig. 4.15).

As all molecules have an amino and a carboxylic acid end groups, the condensation reaction can involve two molecules containing any number of monomer units. The different lengths are all present, and the average length of the macromolecules can be described by a typical Gaussian distribution whose maximum value indicates the numerically most represented chain length that is $\overline{M_n}$.This value depends on the fraction P of reacted functional groups of the monomer, which rapidly reaches values higher than 0.9. However, this is no sufficient for a useful molecular weight, which increases with time while increasing P. Values of P near to 1 are necessary to provide polymer with molecular weight enough high to have a plastic response. In case the molar ratio between the two different reacting groups is equal to 1 (this is always the cases for hetero-functional monomers as amino acids and hydroxycaboxylic acids) (Fig. 4.15), the average polymerization degree is given by (4.8):

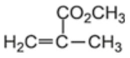
$$x = \frac{1}{(1-P)} \tag{4.8}$$

Therefore for having $x = 50$ one needs P = 0.98.

In this case the molecular weight distribution ($\overline{M_w}$ /$\overline{M_n}$) is also controlled by P and increases with increasing P to reach the maximum value near 2.0 when P is very close to 1.

The polymerization rate is determined by the nature of the reacting groups present on the monomer and also on the molecular structure of the organic residue to which

Table 4.4 Non-hydrocarbon monomers for chain polymerization

Monomer	Formula	Polymerization	Trade name	Uses
Chloroethene (vinyl chloride)	$H_2C{=}CHCl$	Coordination Radical	Polyvinylchloride (PVC)	Piping Film, insulation Piping leatherette
Chlorotrifluoroethene	$FClC{=}CF_2$	Radical	Kel-F	Gaskets, insulation
Tetrafluoroethene	$F_2C{=}CF_2$	Radical	Teflon	Gaskets, valves Insulation, coatings
Propenenitrile (acrylonitrile)	$H_2C{=}CHCN$	Radical	Orlon Acrilan	Acrylic fibres
Methyl 2-methylpropenoate (methyl methacrylate)	 $H_2C{=}\overset{\overset{\displaystyle CO_2CH_3}{\vert}}{C}{-}CH_3$	Radical Anionic	Lucite Plexiglas	Coatings Moulded articles

(a) $H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow H_2N(CH_2)_6NHOC(CH_2)_4COOH + H_2O$

(b) $H_2N(CH_2)_6NH\text{-}[\text{-}OC(CH_2)_4CO\ HN(CH_2)_6NH\text{-}]_{x-1}\text{-}OC(CH_2)_4COOH$

Fig. 4.15 **a** Condensation reaction between hexamethylene diamine and adipic acid and **b** typical Nylon 66 macromolecule with x degree of polymerization (number of units per chain)

$zM_1 + pM_2 \longrightarrow$ -M1M2M2M1M2M2M2M1M1M2M2M1M1M2M1M1M1M2M2M1M1-

Fig. 4.16 Schematic representation of copolymerization reaction and the corresponding copolymer macromolecule (the reaction is not balanced, and z and p are initial numbers of M_1 and M_2, respectively)

these groups are bound. Clearly, the reaction can be accelerated by the presence of catalysts. These effects are summarized in Table 4.5 for a few selected examples.

4.3.4 Copolymerization

Copolymerization indicates a polymerization reaction starting with two different monomers giving macromolecules where two different units are incorporated in a random or controlled sequence mode and in a different molar ratio. The process then provides a useful tool for modulating material properties from the structural and functional viewpoints. Clearly similar structures can be also produced by partial post-polymerization modification of a fraction of units in a homopolymer macromolecule.

Here the possibilities are only discussed regarding the structural possibility offered by the copolymerization of two monomers, even one can easily understand that the process can be also applied, if convenient, to even complex mixtures of three or more different monomers. A typical example in this last contest is evidently offered by natural proteins.

While the term homopolymerization is used to identify the polymerization of a single monomer, the term copolymerization usually refers to the polymerization by any mechanism of a mixture of two monomers

In order to obtain a copolymer through chain polymerization is normally necessary that the process is carried out with mixture of two monomers to form polymeric products with two different structures in the polymer chain with possibly different sequential distributions. Then the product can be called copolymer if it is not a mixture of two homopolymers, but contains units of both monomers incorporated into each copolymer molecule as depicted in Fig. 4.16. Where M1 and M2 are the monomeric units formed from the two different monomers M_1 and M_2.

The composition of the copolymer is determined by the respective copolymerization rates of the two monomers in relation to their relative concentration and reactivity. The sequential distribution of the two different units along the chain can be casual (random copolymer, Fig. 4.16) as in the case reported before, in form of

Table 4.5 Kinetic constant of selected stepwise polymerizations

	Monomer 1	Monomer 2	T (°C)	Kinetic constant × 10^3 (L mol^{-1} s^{-1})
Polyester	$HO(CH_2)_{10}OH$	$HOOC(CH_2)_4COOH$	161	7.5×10^{-2}
	$HO(CH_2)_{10}OH$	$HOOC(CH_2)_4COOH$ [acid catalyst]	161	1.6
	$HO(CH_2)_6OH$	$ClOC(CH_2)_8COCl$	59	2.9
Polyamide	$H_2N(CH_2)_6NH_2$	$HOOC(CH2)_8COOH$	185	1.0
Polyurethane	m-OCN-R-NCO	$HOCH_2CH_2OCO(CH_2)_4COOCH_2CH_2OH$	60	0.40

Block copolymer: -M1M1M1M1M1M1M1-M2M2M2M2M2M2M2M2-

Fig. 4.17 Schematic representation of a block copolymer macromolecule

Alternating Copolymer: -M1M2M1M2M1M2M1M2M1M2M1M2-

Fig. 4.18 Schematic representation of an alternating copolymer macromolecule

$$x\ H_2N(CH_2)_5COOH \longrightarrow H_2N(CH_2)_5CO\text{-}[\text{-}HN(CH_2)_5CO\text{-}]\text{-}OH + (x\text{-}1)\ H_2O$$

Fig. 4.19 Polymerization reactions producing and Nylon 6

blocks (Fig. 4.17) or alternate (Fig. 4.18). These different sequences depend on the two monomer reactivity in relation to the polymerization mechanism selected. The effective formation of copolymer macromolecules is attained if the two monomers are both polymerizable with the selected type of initiator and catalyst.

The simultaneous chain polymerization of different monomers can also be carried out with mixtures of three or more monomers, referred to as multicomponent copolymerization, yielding more complex macromolecular structures, but it is not very common in plastic material.

The copolymerization reaction is important from the technological viewpoint as a sustainable tool to tailor-made plastic polymers with specifically desired properties combined in a single structural and functional material. An outstanding example is offered by the copolymers of ethylene with higher alkenes in the presence of transition metal catalyst to give the linear copolymer LLDPE with increased flexibility and lower melting point and density than the homopolymer HDPE. Also, the free radical initiated copolymerization of ethylene (E) with vinyl acetate (VA) provides the copolymer EVA combining the properties of ethylene blocks with those of the polar ester side chains.

The stepwise copolymerization needs some consideration to be well understood in relation to the concepts developed for the chain copolymerization summarized above.

Indeed the stepwise polymerization requests two complementary reactive groups that either by polycondensation or by polyaddition form links between shorter molecules present in the reaction vessel. As mentioned the two groups forming the link may be at starting present on two different molecules or on the same molecule. In the former case as for example, in the synthesis of poly(hexamethylene adipamide) [Nylon 66] the reaction is started with two distinct reactants, the diamine and the diacid, but the polymer obtained contains along the chain only one type of monomer unit derived from the alternate condensation of the two original reactants. And is therefore a homopolymer. Accordingly, Nylon 66 obtained from two reactants (Fig. 4.15b) and Nylon 6 from a single reactant (Fig. 4.19) give rise to very similar homopolymer chains.

A real copolymer with polyamide structure (Nylon) is obtained by using two heterobifunctional monomers, two amino acids, or a second diammine or diacid must be used when having the situation of homobifunctional reactants.

The particular mechanism of stepwise polymerization where reactivity towards incorporation of shorter chains into longer ones depends on the reactivity of the two linking groups and, in general, very moderately on the overall monomer structure, leads frequently to random copolymers. A segmental short block structure can be obtained by the use of macromers, which are low molecular weight polymers with two terminal reactive groups as for examples ethylene oxide oligomers. These approaches can allow the insertion in the macromolecules of part from renewable sources without substantially changes the final properties. This is the case of several diacids and diols that can replace at least in part the corresponding ones from fossil origin in the synthesis of polyamide and polyesters, respectively.

4.4 Processing to Materials

The product of the polymerization is in most cases an apparently solid material which needs fluidification to be shaped into forms useful for man activity. This fluidification process is performed with low energy consumption thanks to the relatively low melting points of organic polymers used as plastics (generally below 300 °C, which is a very low temperature as compared with the processing temperature of metals and alloys up to 550 °C and more) (Tadmor et al. 2006).

The processing of plastic material to form an object is facilitated by the remarkable reduction of the viscosity that a thermoplastic polymer shows with increasing the temperature. The original viscosity value is promptly recovered during the process of cooling (Fig. 4.20).

Once converted into a low viscosity fluid, the plastics material can be shaped in many different items by one of the following mechanical processing, the method selected being determined by the desired production (Agassant et al. 2016).

- *Extrusion*

Extrusion is a continuous industrial process for converting plastic materials from row shape (powder, pellets, and eventually milled scrap) to finished components. It consists in bringing the material in the fluid state (by heating) and in forcing it to pass continuously through a shaped profile, called extrusion head (or die), where it takes the form, and then cooling it to definitely stabilize the mould (Fig. 4.21).

First, plastic pellets are gravity fed from a hopper into a heated screw or into two co-rotating screws (Fig. 4.21). As the screw turns about its axis, it transports, melts, and pressurizes the plastic (through the degassing section). After complete melting and, in some cases, additives mixing (see the following section), the molten material is forced through a die that shapes it into a specified cross section, producing parts with a potentially wide range of lengths. The product assumes its final shape inside the die and, as a function of its different design, the final object assumes a final geometry; by considering that the extrusion is a continuous process, generally it is adopted to obtain films, profiles, laminates, tubes, pipes.

By using a slit die films with different thickness may be produced, but the most common method to extrude films is the blowing process. This process is basically the same extrusion with suitable die to provide pipe or profile apart from the die orientation which is generally vertical.

During extrusion processes, plastics are transformed from solid to liquid and back again without loss of the main properties (at least for several cycles). This is particularly effective when proper conditions to minimize degradation are adopted. Based on this feature, scrap parts can be ground and re-extruded, making the extrusion the most popular method for reducing or recycling plastic waste.

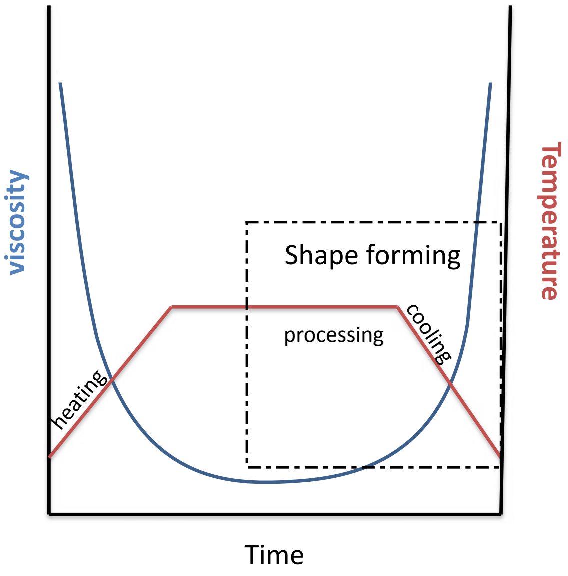
– *Injection moulding*

It is a cyclical and discontinuous process that consists in heating the material fed from a hopper of the extruder and plasticizing it; the mould is then periodically injected in a die (or mould) with the desired shape, which is then cooled to obtain the desired issue (Fig. 4.22).

The resin, in the form of granules (powders or pellets), is at first fluidized under heating, and then forced through a nozzle into the die, while kept under pressure, so as to fill the cavities and comply in a desired manner. A cooling cycle reports the material in the solid state and the formed item is expelled from the machine by an automatic extraction mechanism.

A moulding cycle lasts from several seconds to few minutes and includes the closing of the mould, the injection, the cooling of the material in the mould, opening the

Fig. 4.20 Viscosity and temperature profile vs. time during the processing of a thermoplastic polymer (dashed zone roughly indicates the range where the material is processed and assumes the desired shape)



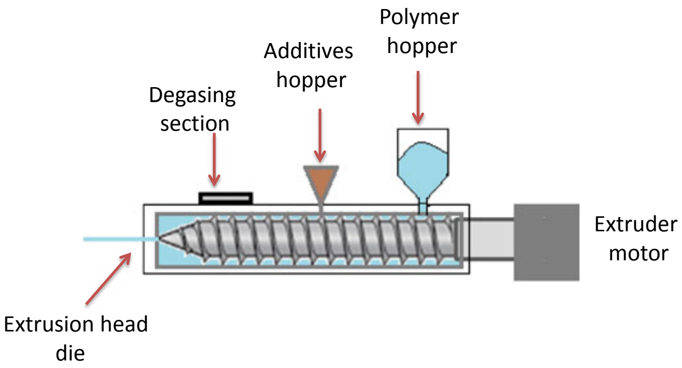


Fig. 4.21 Schematic extruder profile

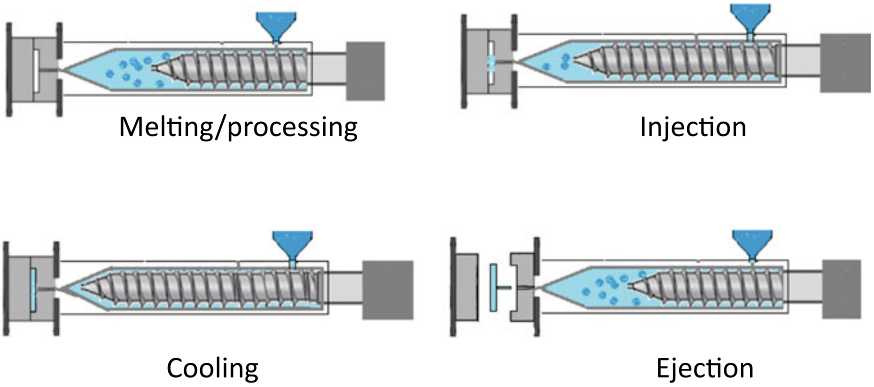


Fig. 4.22 Schematic representation of the injection moulding cycle of plastic materials to provide the desired piece by means of a mould with especially geometry

mould and the extraction of the moulded piece. The pieces unsuccessfully designed or scraps are ground and the material thus obtained is mixed with fresh polymers and additives and can be reused. A very large number of different objects are moulded with this processing methodology (ranging from parts of appliances, tools for the house, bottles and containers of various kinds) and by considering that the automatic system allows the cylinder filling a second mould during the cooling of the first, the modern machinery can be considered to work in semi-continuous cycle.

– *Blow moulding*

It is a moulding process of polymers used for manufacture opaque flasks and bottles (milk bottles, detergent bottles, containers, etc.). The most common system combines extrusion and blow moulding technologies (Fig. 4.23). Step one is the extrusion of a tube of plastic material that goes through an open mould divided in half (a); then, the

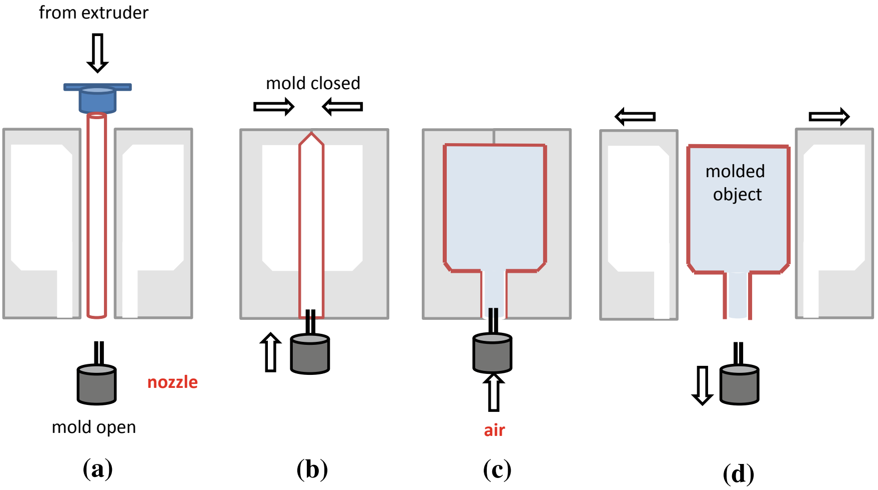
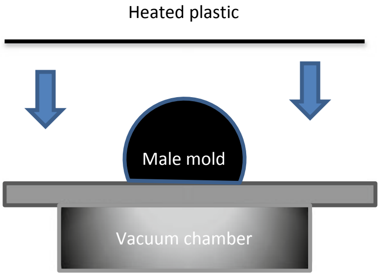


Fig. 4.23 Schematic representation of blow moulding processing of plastic materials

Fig. 4.24 Schematic representation of vacuum thermoforming technology



two cavities are closed and the polymer mould cuts the tube in one of the sections (b).

Compressed air blows from the other open section of the mould through a blow pin so that the softened polymer adheres to the wall of the mould taking the desired form and shape (c). Then the mould is cooled and the manufactured item, which is a hollow object (a bottle in Fig. 4.23), is ejected from the opened mould (d).

– *Thermoforming*

It is a fabricating process where sheet of plastics are heated up to the softening point and formed over a male or female mould. Vacuum forming and pressure forming can be used to make plastic assuming a broad and diverse shape. It is generally considered a sideline technology owing to processing taking place on materials previously extruded in the form of plates, sheets or films. The sheet, before processing, is heated in special furnaces/ovens or directly in the machine; then it is placed over a hollow mould and compressed or the vacuum allows the materials taking the form (Fig. 4.24).

Thermoformed plastics are ideally suited for automotive, consumer products, packaging, retail and display, sports and leisure, electronics, and industrial applications with particular reference to glasses, plates, interior of refrigerators, panels, small boats and even works of contemporary art.

Other less important plastic processing methodologies that deserve nomination are the calendaring, a finishing process used on cloth, paper, or plastic film/laminates; the rotational moulding a particular moulding technique dedicated almost exclusively to create hollow objects of large dimension and the sintering used in some cases for plastic powders.

– *Plastic limitations*

Plastic polymers are very convenient materials to be submitted to shaping, after thermo-conversion into the fluid state, to obtain items with features that can respond to the market demand. The shaping temperature depends on polymer melting and glass transition temperatures of the polymer as well as on the selected processing method. The selected temperature for the forming is in general higher than the polymer characteristic transition temperatures as a result of the fact that it is necessary to grant the appropriate fluidity, which should be low enough for the polymer to assume the model shape after its complete filling (see Fig. 4.20). Such requirement is particularly necessary in case of injection moulding where complicated mould has to be filled completely by the fluid materials to avoid defects in the produced item. On the other side, the temperature control is very important and must be kept well below the thermal stability limit of the polymer to avoid material degradation.

The polymer thermostability must be evaluated in advance when designing a production process. The aggressive environment by the mechanical treatment at relatively high temperature is in part released by using additives acting as plasticizer and fluidificants. Additional negative effect against the material stability during processing can derive by the chemical attack against the weakest chain sites. Molecules acting in this way should be removed before processing. A typical example is given by the water present in polymers having hydrolyzable bonds; indeed at melting temperature and over, water can hydrolyze the ester groups thus reducing the molecular weight of polyesters (Fig. 4.25) during the processing. Therefore, these polymers must be dried in advance at temperature over 100 °C to be processed.

The processing of polyesters after appropriate removal of adsorbed water allows maintaining the original chain length thus giving products with properties corresponding to those of the fed material. Practically, all organic plastics are also subjected to the free radical attack creating free radical on the chain, which can be responsible for the modification of the starting molecular structure by initiating side reactions such as degradation, branching and cross-linking. Free radical inhibitors must then be added before processing a polymer either from fossil or renewable origin.

– *Additives for processing*

Polymers need to become soft or fluids to be properly processed and this is attained by adequate increase of the working temperature.

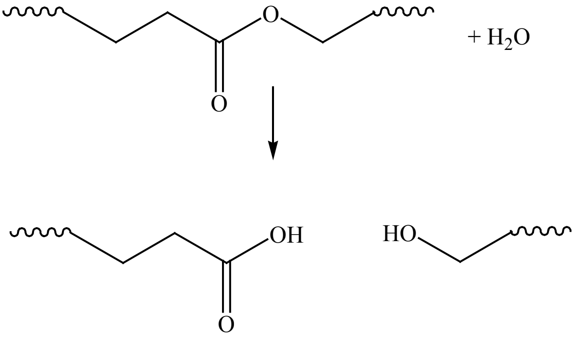


Fig. 4.25 Hydrolytic degradation of polyesters

For reaching this target it is at first necessary to operate above the glass transition temperature (T_g), in the case of amorphous polymers, and above the melting temperature (T_m) in the case of semicrystalline polymer. It is necessary that the polymer responds with a liquid behaviour in the region where the modulus exponentially decreases with small temperature variations and consequently the polymer viscosity resembling that of a viscous liquid, allowing the workability of the molten plastic. The polymer has to be structurally and chemically stable during the processing, granting the ultimate mechanical features necessary to the end products expected from those of the selected starting polymer. The bare requisite of a polymer to be used as the main material for a specific plastic object is that the degradation temperature is actually higher than the processing temperature, including attritions and shear stresses generally applied by machines. This aspect has first to take into account that plastic materials are organic molecules that are subjected to oxidation and degradation reactions with modification of the chemical structure responsible for lower quality of ultimate properties if compared to the expectation. The above undesired reactions are initiated generally by free radicals formed by thermal cracking of the weakest molecule bonds and facilitated then by the presence of substituted reactive groups that are more common in plastic materials from renewable resources than from fossil. Certainly, the best stability is observed in aromatic and paraffinic structures while the presence of functional groups acts as activator towards the degradation of the original structure.

The synthetic chemistry has developed a large number of additives to reduce the above degradative effects; listing of all of them and related efficiency is out of the aim of this book. To give the reader a first insight of the importance of the plastic industry of these polymer additives, Table 4.6 reports some information about the size of the related market of some processing additives whose use is growing.

These additives consist in different chemicals as they have to act as antioxidants, heat stabilizers, radical scavengers, plasticizers and lubricants and all these properties cannot be found in a single molecule and are more easily achieved by a mix of selected molecules. On the other side, the demand for commercial purpose considers important to extend the plastics service life by maintaining their properties. According to the relationship between the molecular structure and the degradation reactions

Table 4.6 Global market for plastic additives by type, 2010–2018 ($ Millions)[a]

Additives	2010[a]	2011[a]	2012[a]	2013[a]	2018[a]
Modifiers	21,000	22,000	23,000	24,000	30,000
Extenders	4,000	4,500	4,800	5,000	5,100
Stabilizers	10,000	11,000	11,500	12,500	15,000
Processing aids	2,000	2,100	2,200	2,200	2,500

$ Millions, roughly estimated

[a] Data from https://bccresearch.wordpress.com/category/plastics/page/2/

occurring when processing, it is evident that these man-made additives are necessary also for the good performances of bio-related polymers. The developments of eco-friendly additives also from natural resources is therefore of primary importance. Indeed these additives when the polymer is disposed and biodegraded are released in the environment.

Looking in more detail to structure and role of the above additives, it is of primary importance to correlate their structure to the stabilization against various degradative effects. Several types of phenols have been largely used for their efficient action as free radical scavengers. For outdoor applications, light and UV stabilizers which, in addition to the family based on benzotriazoles and benzophenones, includes hindered amine light stabilizers (HALS and their polymeric derivatives) and hydroxyphenyl triazines. Further specific protection requirements have promoted the preparation and addition to the main plastic materials of additives acting as biocides, flame retardants, and antimicrobial agents. Moreover, the need to modulate mechanical and physical properties was satisfied by organic and inorganic fillers, impact modifiers, antistatics, plasticizing and crystallization nucleating agents.

The modification of properties in the desired directions and the recovery of partially degraded polymers have promoted the use of reactive processing to either change or restore the main polymer structure by favouring branching and chain extension of polycondensates, adjusting the molecular weight, all effect which can act on both rheology during processing and on ultimate application properties. More specialized additives have also been introduced for specific functional applications once granted the necessary structural properties. Examples in this last direction are UV light spectrum modifiers for greenhouse films, additives for oxygen barrier in flexible food packaging films, and additives for tuning the hydrophobic/hydrophilic character.

Certainly, this basic information points out the complex formulation of plastic polymers in order to make them suitable for a predesigned application. Therefore the role of the main plastic polymer either from fossil or renewable sources must be considered by looking to the above aspects as they can indeed have an important role in deciding the best sustainability of the final product.

- *Polymer blending*

Specific desired performances of plastic materials can be reached by changing monomer structure in homopolymers, type and ratio of two different monomers in copolymers, mixing with additives with various functionalities to both homo- and copolymers. The polymer blending methodology provides an additional and very sustainable tool for producing new plastic materials and expand application properties. For having plastic properties at least one of the two polymers, the matrix must be plastics and the two different polymers must be at least partially miscible or compatible (Utracki 1995).

Indeed, this processing technology to be successful requires the possibility of compatibilization of the two blended polymers often structurally and morphologically different from each other. The chemical structure of polymers, their molecular weight and distribution, presence and nature of ends groups, melt viscosity and rheological features at the temperature used for processing may affect the compatibility even of similar polymers.

In a very few words (Chap. 6 reports a more detailed discussion of the matter), the miscibility of two polymers corresponds to the thermodynamic solubility: the two polymers are miscible when the free energy of mixing ($\Delta\text{Gmix} = \Delta\text{Hmix} - \text{T}\Delta\text{Smix}$) is negative. The entropy of mixing (ΔSmix) approximates values very close to zero when the molecules have a high molecular weight (macromolecules). The enthalpy of mixing, (ΔHmix), depends mainly on the energy variations associated with the structural changes that occur as a result of interfacial contact during the mixing and its value is strongly influenced by the degree of interaction of the polymers constituting the mixture. It has therefore miscibility between the two polymers when the enthalpy of mixing is negative.

While the miscibility has a strictly thermodynamic meaning, the compatibility is defined experimentally or based on the determination of a characteristic property of the mixture and the degree of compatibility is defined indirectly on the basis of what has performance that property. It depends on the method of analysis and the scale with which the measured property relates to the structure of the mixture. Usually, the thermal properties, with particular reference to the evaluation of glass transition temperature (T_g), morphological analyses by microscopies, the rheological properties, the mechanical properties are determined and related to the degree of compatibility.

A mixture of two components is more or less compatible depending on how much it is near or far from the miscibility condition. Obviously in a system fully compatible the polymers are completely miscible.

The compatibilization concept is closely related to the development of an appropriate morphology. There are two extreme situations, the complete phase separation (for immiscible polymers) or the formation of a homogeneous mixture at the molecular level (for fully miscible polymers); however intermediate situations are generally obtained, ranging from the formation of co-continuous morphologies to the formation of heterophasic morphologies with dispersed particles of increasing (or decreasing) size (for compatible or compatibilized polymers). The formation of a heterophasic system should not necessarily be considered an unfavourable event since many interesting properties characteristic of a single phase may be retained in

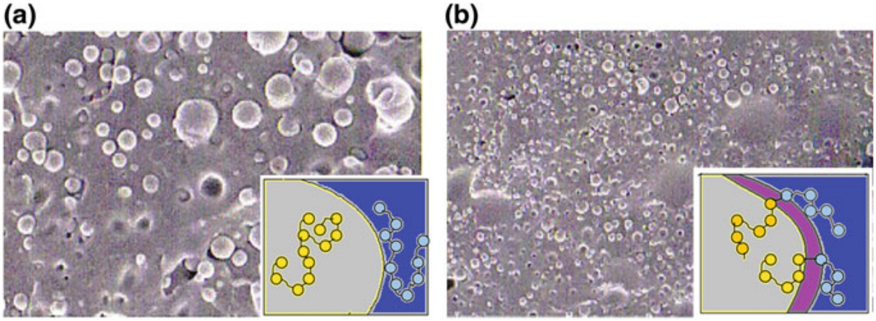


Fig. 4.26 Role of interactions at interface in the morphology development during the compatibilization procedure

the mixture while other properties are 'mediated' in accordance with the composition of the mixture. As for example by blending two amorphous polymers generating a heterophasic morphology with good adhesion at interface, the resulting polymer material is characterized by two different T_g, that are maintained (even if with different values with respect to the pristine polymers) but able to grant the plastic features at least in the temperature range between the two T_g.

There is no compatibility and thus interfacial adhesion between two polymers when they are not able to develop specific interactions whether weak or strong (Fig. 4.26a). The inter-macromolecular interactions are of two types and the total contribution comes from the energy balance of the two terms: the homo-association of two polymers AA and BB the hetero-association AB. For obtaining a morphology characterized by a stable and fine distribution of a polymer in the other, it is necessary that the interpolymer interactions of AB type are enough to form an interface, a real new polymeric phase constituted by macromolecules of A and B (Fig. 4.26b). The same effect is obtained by adding to the mixture an appropriate block copolymer or graft segments made up of identical or similar chains to the constituent polymers (A and B). In practice, it adopts the same approach used for the stabilization of emulsions and the copolymer acts as a surfactant or an emulsifier. The copolymer used is called compatibilizer or compatibilizing agent, and more rarely emulsifier or adhesion promoter.

The compatibilization of a mixture of immiscible polymers can, in principle, be obtained physically through the use of the mentioned compatibilizing agent, chemically synthesized prior to the blending/processing operations, and then added to the mixture as a non-reactive component (*physical blending*). Thanks to its chemical and molecular structure is able to be placed at the interface by reducing the interfacial tensions and promoting the adhesion between the polymer phases.

On the contrary, in the *reactive blending*, the compatibilization is achieved by chemical reactions that occur during the mixing process producing the blend. The reactions promote *in situ* formation of the real compatibilizing species, which is usually a block or graft copolymer, or the formation of cross-linked macromolecules, or also ionic associations. All these have to reduce the interfacial tension and to increase the adhesion between the phases of the two immiscible polymeric materials as in physical blending. This occurs by generally adding a polymer precursor miscible with one polymer and able to react with other macromolecules.

In the *physical blending*, it is critical that the compatibilizer exerts its action at the interface overcoming the diffusion problems associated with the different polymer viscosities. In addition, the suitable compatibilizer should be available in the market.

In the *reactive blending*, it is necessary, instead, that at least one of the two polymers has reactive functional groups capable to provide (directly at interface, in this case) the formation of the compatibilizer.

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