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Tony Blythe and David Bloor
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Introduction

1.1 Overview

Although unified by direct concern with the effects produced by electric fields, the subject of the electrical properties of polymers covers a diverse range of molecular phenomena. Until the latter part of the twentieth century, known polymers generally displayed a much less striking electrical response than inorganic materials. While inorganic solids behave as semiconductors and metals (where the electrical response is overwhelmingly one of electronic conduction), or as insulators, the common polymers were distinctly confined to the latter category. From 1950 onwards this situation changed with the emergence of polymers displaying semiconducting properties and the discovery in the 1970s of polymers that even had metallic levels of conductivity. Since then there has been an explosion in fundamental and applied research and numerous conductive polymers have been produced and studied. While the macroscopic properties of these materials resemble those of their inorganic counterparts, their microscopic behaviour is markedly different and reflects fundamental differences between the rigid crystal lattices of inorganic materials and the deformable, molecular structure of polymers.

The absence of conduction in insulating polymers allows a whole set of more subtle electrical effects to be readily observed. For instance, polarisation resulting from distortion and alignment of molecules under the influence of an applied field becomes apparent. Examination of such polarisation not only gives valuable insight into the nature of the electrical response itself, but it also provides a powerful means of probing molecular dynamics. In conductive polymers the presence of charge carriers produces pronounced local deformation of the molecular framework, significantly larger than that found in inorganic semiconductors. The Coulomb interaction of charge carriers is less effectively screened in conductive polymers. Hence electron–phonon and

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electron–electron interactions have more profound effects in conductive polymers. It should also be noted that single crystal polymers are rare and the complex morphology of partially crystalline polymers has an impact on their electrical properties. For all these reasons electrical studies form a desirable supplement to studies of mechanical and thermal properties aimed at reaching an understanding of the behaviour of polymers on a molecular basis.

In the remainder of this chapter we outline the main features of polymer structure and its relation to electrical properties, as a basis for the subsequent more detailed explanation and discussion of electrical behaviour.

1.2 Structure of polymers

Most of the synthetic high polymers with which this book is concerned are organic compounds consisting of long, chain-like molecules where repeated molecular units are linked by covalent bonds. A single molecular chain can contain a thousand or more repeat units and reach a total length in excess of 1 μm. Such large molecules have complex shapes and form solids that may be either amorphous or crystalline, but are commonly partially crystalline. The atoms, which form the *backbone* of organic polymers, are predominantly carbon atoms, sometimes in combination with oxygen and/or nitrogen. The nature of the chemical bonding in the polymer directly influences the electrical properties.

1.2.1 Chemical structure – saturated polymers

The carbon atoms in a polymer are primarily bound together by *covalent bonds* formed by the interaction of two electrons, one from each of the atoms linked by the bond. We illustrate this process with the simpler example of bond formation between two hydrogen atoms. As the atoms are brought together their 1s-electron orbitals overlap forming two new σ-orbitals around the atoms, which are symmetric and have zero angular momentum with respect to the interatomic axis. One orbital, the bonding orbital, is formed by the linear superposition of the two s-orbitals, shown by the solid curves in Fig. 1.1(a). This gives a high electron density between the hydrogen nuclei, the dashed line in Fig. 1.1(a), which reduces their electrostatic repulsion. Thus the nuclei are drawn together and an electron in the bonding orbital has a lower energy than one in the isolated atom orbital. The other, the antibonding orbital, is formed by the superposition of s-orbitals with opposite sign, see solid curves in Fig. 1.1(b), giving a lower electron density between the nuclei, shown by the dashed curve in Fig. 1.1(b). The electrostatic repulsion between

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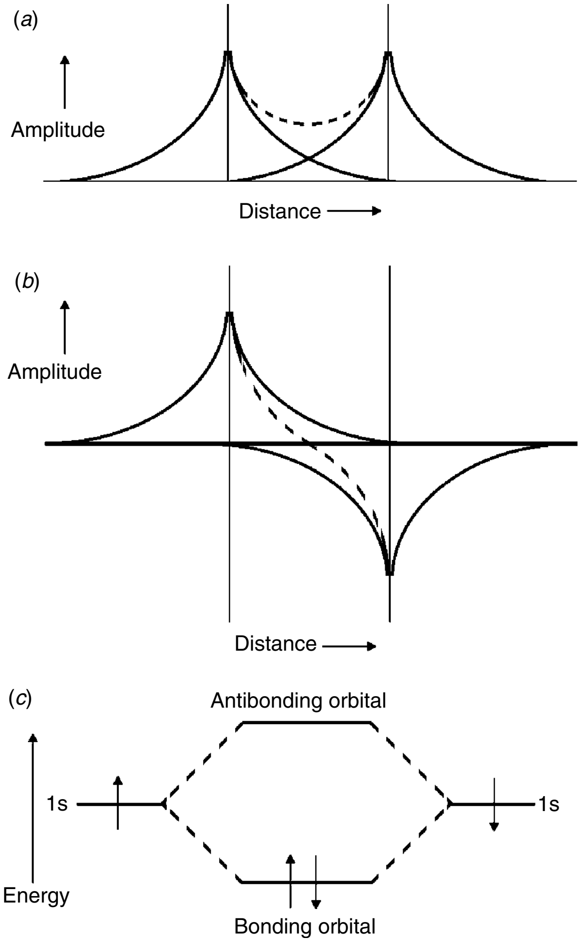


Fig. 1.1 Overlap of hydrogen atom orbitals to form (a) a bonding orbital, and (b) an antibonding orbital, with energies as shown in (c).

the nuclei is not screened and the energy of an electron in this orbital is increased, as indicated in Fig.1.1(c). The Pauli exclusion principle allows the two electrons from the hydrogen atoms to *pair* in the bonding orbital, if they are of opposite spin, to give a stable molecule with total energy less than that of the two isolated hydrogen atoms.

A neutral carbon atom has six electrons, which occupy the 1*s*, 2*s* and 2*p* orbitals giving an electronic configuration of $1s^2 2s^2 2p^2$. When a carbon atom forms a bond with another atom, an *s*-electron is promoted to the vacant *p*-orbital to give an sp^3 configuration (s, p_x, p_y, p_z) in the outer valence shell. These electronic orbitals do not bond separately but hybridise, i.e. mix in linear combinations, to produce a set of orbitals oriented towards the corners of

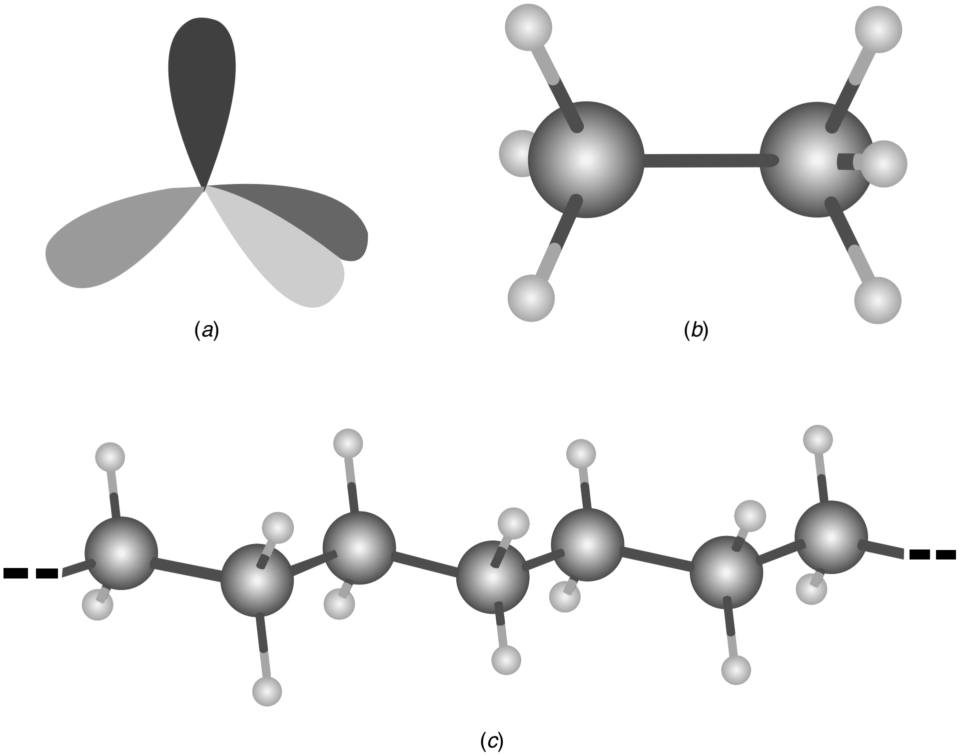


Fig. 1.2 (a) sp^3 hybrid orbitals, and the molecular structure of (b) ethane and (c) polyethylene. H atoms have light shading.

a regular tetrahedron. Figure 1.2(a) shows the form of the wavefunctions that describe the hybridised orbitals. The sp^3 hybrids allow a much greater degree of overlap in bond formation with another atom, and this, in turn, produces extra bond strength and stability in the molecules. The arrangement of bonds resulting from overlap with sp^3 hybrid orbitals on adjacent atoms gives rise to the tetrahedral structure that is found in the lattice of diamond and in molecules such as ethane, C_2H_6, as depicted in Fig. 1.2(b). In these structures all the available electrons are tied up in strong covalent bonds, *σ-bonds*. Carbon compounds containing σ-bonds formed from sp^3 hybrid orbitals are termed *saturated* molecules. Polyethylene, $\mathrm{-\!\!(CH_2)\!\!-}_n$, is a typical saturated polymer where the σ-bonds between adjacent carbon atoms form the zigzag of the polymer backbone and the two remaining bonds are to the pendent hydrogen atoms, as in Fig. 1.2(c). The strong σ-bonding gives rise to chemically stable compounds and localises the electrons in the molecular structure rendering saturated compounds electrically insulating.

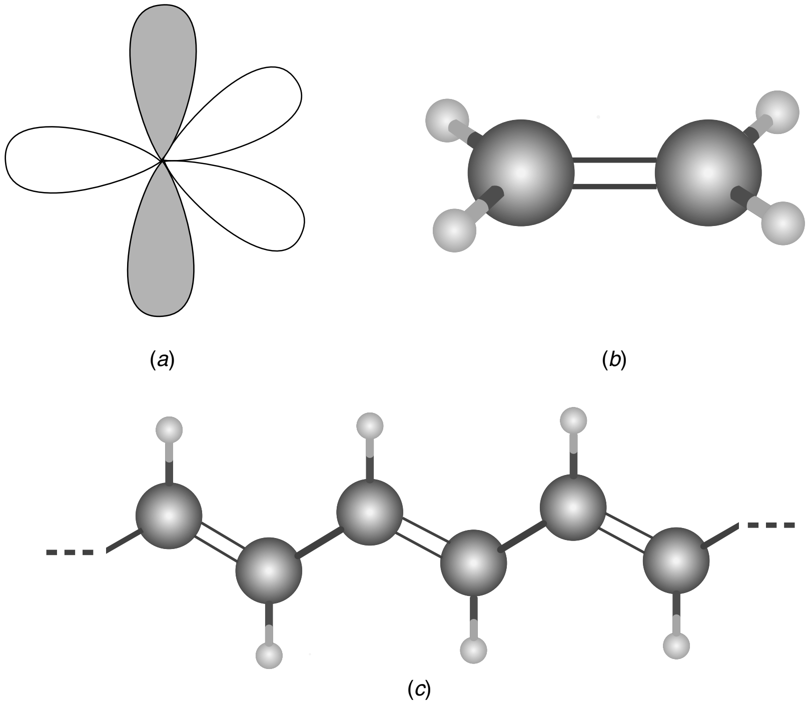


Fig. 1.3 (a) sp^2 hybrid orbitals, and the molecular structure of (b) ethylene and (c) polyacetylene.

1.2.2 Chemical structure – unsaturated polymers

While tetrahedral bonding is common in carbon compounds, it is not the only possibility. A planar σ-bond structure occurs if the hybrid orbitals are formed from one *s*- and two *p*-orbitals. sp^2 hybrid orbitals, which lie in a plane with angles of 120° between them, are shown by the unshaded lobes in Fig. 1.3(a), whilst the remaining *p*-orbital (p_z), which lies orthogonal to the plane of the σ-bonds, is shown by the shaded lobes. This p_z electron is then available to form additional π-orbitals, with unit angular momentum about the bond axis, with p_z electrons in adjacent atoms. The resulting π-*bond* will form parallel to the underlying σ-bond, resulting in a multiple (double) bond, as in ethylene, C_2H_4, as shown in Fig. 1.3(b). Compounds where orbitals are used in this way to form double bonds between carbon atoms, rather than to form single bonds with other atoms, e.g. hydrogen, are said to be *unsaturated*. Where successive carbon atoms in a chain engage in π-bonding, the structure is said to be *conjugated*, and may be represented as a sequence of alternating single and double bonds, as shown in Fig. 1.3(c), which illustrates the bonding in polyacetylene, $-\!\!(\mathrm{CH}=\mathrm{CH})\!\!-_n$.

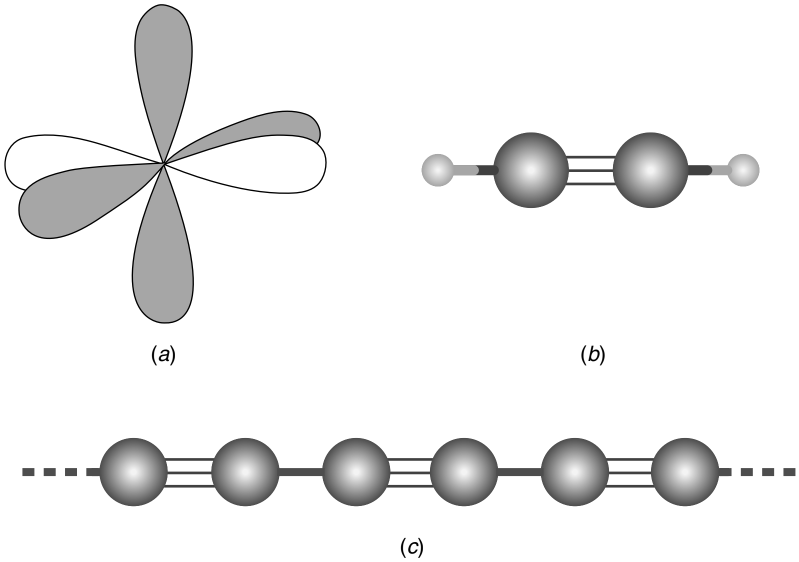


Fig. 1.4 (a) *sp* hybrid orbitals, and the molecular structure of (b) acetylene and (c) polyyne.

Furthermore, compounds containing triple bonds can be obtained from *sp* hybrid orbitals. *sp* hybridisation produces two orbitals oriented at 180° to each other, as shown by the filled lobes in Fig. 1.4(a), which can form co-linear σ-bonds. This leaves two *p*-electrons, shown by the shaded lobes in Fig. 1.4(a), which are free to form π-bonds aligned with the σ-bond, as in acetylene, C_2H_2, shown in Fig. 1.4(b).

The polymer polyyne, $-\!(\mathrm{C}{\equiv}\mathrm{C})\!-_n$, also known as polycarbene, and shown in Fig. 1.4(c), is formed with *sp* hybrids in this way. Its structure may be either an alternation of single and triple bonds or a sequence of double bonds, depending on the terminal groups – see Fig. 1.5.

The formation of multiple bonds leads to a reduction in the separation of the carbon atoms involved. Thus a triple bond is shorter than a double bond, which is shorter than a single bond. This gives rise to an alternation of bond length in conjugated polymers such as polyacetylene and polyyne, Figs. 1.3(c) and 1.4(c). The electrons in the π-bonds are less strongly bound than the electrons in the σ-bonds. Hence the π-electrons can be more easily removed from the bonds than can the σ-electrons. In consequence unsaturated compounds are less chemically stable than saturated compounds. The multiple bonds are subject to chemical attack, being reduced to saturated (single) bonds in the process. The weaker binding of the π-electrons also means that

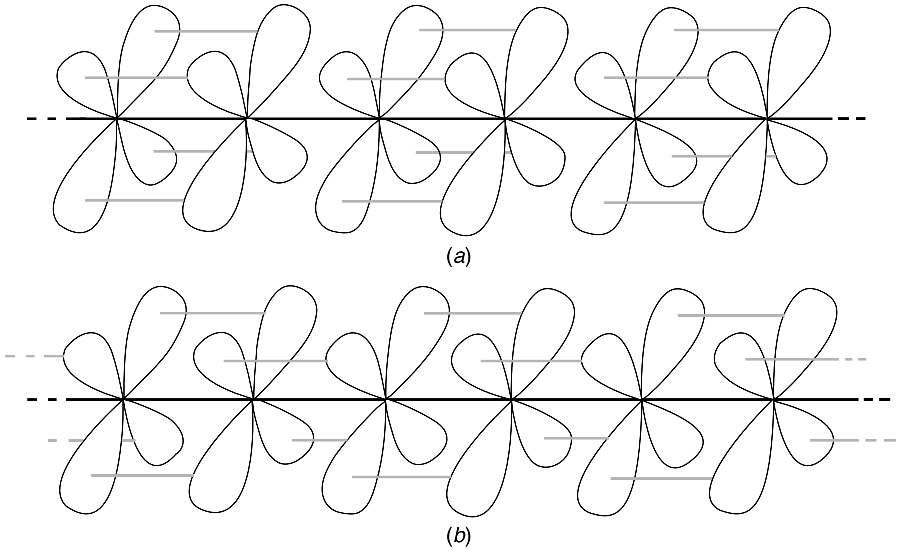


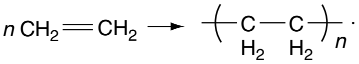
Fig. 1.5 The alternative structures of polymers formed with *sp*-hybridised orbitals, (a) polyyne and (b) polycarbene. Overlap of the π-electron orbitals, shown by the off-axis lines, gives an interatomic π-bond. The σ-bonds are shown by on-axis lines.

unsaturated compounds have the potential to display either semiconducting or metallic behaviour.

1.2.3 *Preparation of polymers*

The process of polymerisation in which small molecules of the starting material, the monomer, undergo chemical reaction together to form long chains, may proceed in a variety of ways. These may be divided into two principal categories, addition and condensation polymerisation, which have major structural implications for the final product.

Addition polymerisation is typified by the conversion of ethylene to polyethylene according to the following equation:

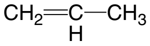
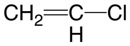
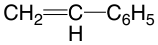
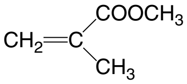


$$n\,\mathrm{CH_2{=}CH_2} \longrightarrow \left(\underset{\mathrm{H_2}}{\mathrm{C}}-\underset{\mathrm{H_2}}{\mathrm{C}}\right)_n .$$

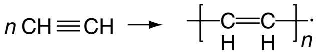
In this joining together of molecules of ethylene the necessary linking bonds are obtained by breaking the original double bonds, which are relatively unstable.

The chain reaction may be initiated with the aid of a catalyst, often a peroxide, which provides a chemically reactive species to attack a limited

Table 1.1 *Examples of vinyl and related polymers*

Monomer formula	Polymer name	Polymer structure
$CH_2{=}CH_2$	Polyethylene	$-\!(CH_2)\!-_n$
 $CH_2{=}\underset{H}{C}{-}CH_3$	Polypropylene	$-\!(CH_2{-}CH(CH_3))\!-_n$
 $CH_2{=}\underset{H}{C}{-}Cl$	Poly(vinylchloride)	$-\!(CH_2{-}CHCl)\!-_n$
 $CH_2{=}\underset{H}{C}{-}C_6H_5$	Polystyrene	$-\!(CH_2{-}CH(C_6H_5))\!-_n$
	Poly(methylmethacrylate)	$-\!(CH_2{-}C(CH_3)(COOCH_2))\!-_n$
$CF_2{=}CF_2$	Polytetrafluoroethylene	$-\!(CF_2)\!-_n$

number of double bonds. Sequential addition of ethylene molecules then proceeds until all the ethylene is used up. None of the atoms of the original monomer, ethylene in this case, is excluded from the final polymer, the addition process only involving rearrangement of bonds. The polymer chains produced are of finite length because of the presence of termination reactions, which compete with the monomer addition reaction. Similarly, polymerisation of acetylene leads to the conjugated polymer polyacetylene:

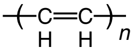
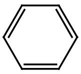
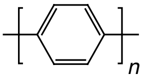
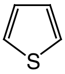
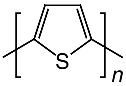
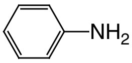
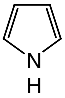
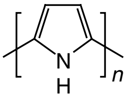


$$n\,CH{\equiv}CH \rightarrow \left[\underset{H}{C}{=}\underset{H}{C} \right]_n .$$

Addition polymers include the important class derived from vinyl monomers, general formula $CH_2{=}CHX$, having a backbone consisting entirely of carbon atoms. Some examples of vinyl polymers and closely related ones are given in Table 1.1.

A second important class of addition polymers is that derived from monomers containing triple bonds and aromatic groups, when the polymers possess conjugated backbones containing multiple bonds. This group includes polyacetylene, and some further examples are shown in Table 1.2. The conjugated backbones are inflexible and the polymers are insoluble in the solvents normally used for polymerisation reactions, which limits the length of the polymer chains that can be attained. This problem can be overcome by either the inclusion of long flexible pendent groups, which render the polymer soluble,

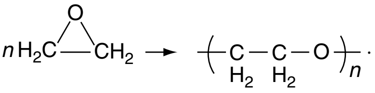
Table 1.2 *Examples of conjugated polymers*

Monomer formula	Polymer name	Polymer structure
$HC \equiv CH$	Polyacetylene	 $-\!\!\!\left(\underset{H}{C}=\underset{H}{C}\right)\!\!\!-_n$
	Poly(*p*-phenylene)	
	Polythiophene	
	Polyaniline	See Fig. 9.6 [a]
	Polypyrrole	

[a] Polyaniline has a complex structure dependent on the degree of oxidation and protonation.

or the preparation of a non-conjugated, soluble precursor polymer, which is subsequently converted into the desired, conjugated product.

Polyethers, which contain oxygen as well as carbon atoms in their backbones, are examples of addition polymers that are generally made by a ring-opening reaction. Thus the cyclic compound ethylene oxide polymerises to a polyether as follows:



$$n\,H_2C\overset{O}{\frown}CH_2 \rightarrow -\!\!\left(\underset{H_2}{C}-\underset{H_2}{C}-O\right)\!\!-_n .$$

Condensation polymerisation occurs when multifunctional monomers, which possess more than one chemically reactive group per molecule, react together with the elimination of small molecules, typically either water or HCl. With a bifunctional monomer the product is a linear polymer, e.g. the polyamide Nylon-6 is derived from ε-amino caproic acid as follows:

$$NH_2(CH_2)_5CO\boxed{OH + H}NH(CH_2)_5COOH \rightarrow$$
$$NH_2(CH_2)_5CO{\cdot}NH(CH_2)_5COOH + H_2O \text{ etc.}$$

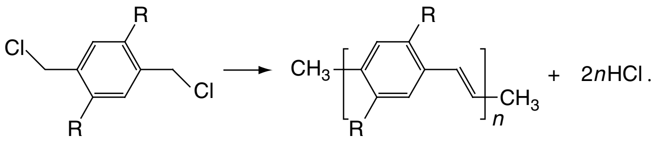
Quite often polymerisation proceeds by interaction of pairs of complementary monomers. Thus Nylon-6,6 is formed by reaction of adipic acid with hexamethylene diamine:

$$\begin{aligned}&HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2 \rightarrow\\&\quad HOOC(CH_2)CONH(CH_2)_6NH_2 + H_2O \text{ etc.}\end{aligned}$$

The formation of poly(ethyleneterephthalate) from ethylene glycol and terephthalic acid is another very well-known example:

$$\begin{aligned}&n HO(CH_2)_2OH + n HOOC{\cdot}C_6H_4{\cdot}COOH \rightarrow\\&\quad HO[(CH_2)_2OCO{\cdot}C_6H_4{\cdot}COO]_n H + n H_2O.\end{aligned}$$

Conjugated polymers can also be prepared by condensation polymerisation, usually from a dihalide with the elimination of the related acid. The dehalogenation reaction for the preparation of poly(*p*-phenylenevinylene) is a typical example:



Some common condensation polymers are given in Table 1.3.

The final product of polymerisation, be it of an addition or condensation type, will contain chains covering a range of lengths, and it is only possible to specify an average molar mass.[1] The number-average molar mass $(M_\mathrm{n})_\mathrm{av}$ is defined by

$$(M_\mathrm{n})_\mathrm{av} = \frac{\sum M_x n_x}{\sum n_x},$$

where M_x and n_x are the molar mass and relative number, respectively, of the species containing x repeat units.

Electrochemical polymerisation offers an alternative synthetic route in some cases. Initiation here proceeds by electrochemical oxidation or reduction of monomer molecules at an electrode to generate reactive ions, i.e. species with both an unsatisfied valency and a net charge, which are termed radical ions. This method is of limited applicability in saturated polymers that are electrically non-conducting, as an insulating barrier quickly builds up on the electrode where the radical ions are generated and the polymerisation is terminated. This does not occur with conjugated polymers, which generally possess some degree of electrical conductivity, and thick layers of conjugated

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[1] The molar mass M of a molecular compound is the mass per mole of the molecules (kg/mol). 1 mole is the amount of the compound that contains as many molecules as there are atoms in 12 g of C^{12}.