THE SCIENCE OF POLYMER MOLECULES

An introduction concerning the synthesis, structure and properties of the individual molecules that constitute polymeric materials

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Polymerization: an overview

Polymers are large molecules made up of many atoms linked together by covalent bonds. They usually contain carbon and often other atoms such as hydrogen, oxygen, nitrogen, halogens and so forth. Thus they are typically molecules considered to be in the province of organic chemistry. Implicit in the definition of a polymer is the presumption that it was synthesized by linking together in some systematic way groups of simpler building block molecules or monomers. Although the final molecular topology need not be entirely linear, it is usually the case that the linking process results in linear segments or imparts a chain-like character to the polymer molecule.

Most of the synthetic methods for linking together the building block molecules can be placed into one of two general classifications. The first of these results when the starting monomers react in such a way that groups of them that have already joined can react with other already joined groups. The linked groups have almost the same reactivity towards further reaction and linking together as the original monomers. This general class of reactions is called *step* polymerization. In the other general method, an especially reactive center is created and that center can react only with the original monomer molecules. Upon reaction and incorporating a monomer, the reactive center is maintained and can keep reacting with monomers, linking them together, until some other process interferes. This mechanism is *chain* polymerization.

1.1 Step polymerization

Aliphatic polyesters are interesting examples of step polymerization as historically they were the first such polymerizations to be carried out and studied in a systematic way (by W. H. Carothers, see Mark and Whitby,

1940). One might start with a dibasic acid such as adipic acid and a diol such as ethylene glycol. They can react to form an ester linkage and eliminate a water molecule (1.1). After linking, however, carboxyl groups

$$
\text{HO–CH}_2\text{–CH}_2\text{–...–C(=O)–OH} \;+\; \text{HO–CH}_2\text{–CH}_2\text{–OH} \longrightarrow
$$

$$
\text{HO–...–C(=O)–...–O–CH}_2\text{–...–OH} \;+\; H_2O
$$
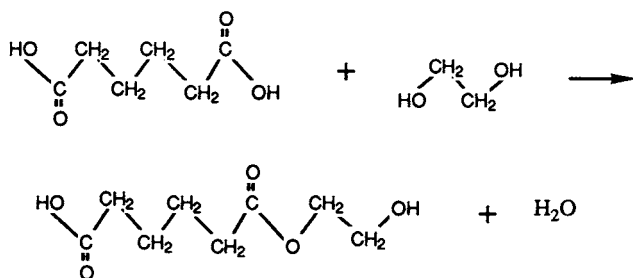
1.1

and hydroxyl groups remain for further reaction and in fact the reaction can continue until very long sequences of ester linkages are built up (1.2).

$$
\text{HO}\!\left[\;\text{...–C(=O)–...–CH}_2\text{–O–...}\;\right]_n\!\text{H} \;+\; 2n\,H_2O
$$
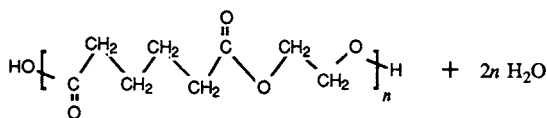
1.2

Molecular length builds up gradually through the course of polymerization (Figure 1.1). Accomplishing the building of long sequences requires that the numbers of carboxyl and hydroxyl groups be closely balanced, that the reaction proceed at a reasonable rate and that the by-product water be efficiently removed. These questions will be expanded on later in discussing molecular weight and the kinetics of polymerization (Chapters 2, 4).

The aliphatic polyesters of the type illustrated form crystalline solids and, as indicated above, they were seminal in demonstrating the viability of the concept of step polymerization and indeed of the concept that very large chain molecules held together by primary covalent bonds could be synthesized by conventional well-known chemical reactions. As a practical matter it turned out that the melting points of such polymers, only about 60 °C, were too low for significant applications. However, by replacing the diol in the reaction with a diamine, similar condensation takes place

A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B
A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B
A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B
A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B
A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B	A-A	B-B
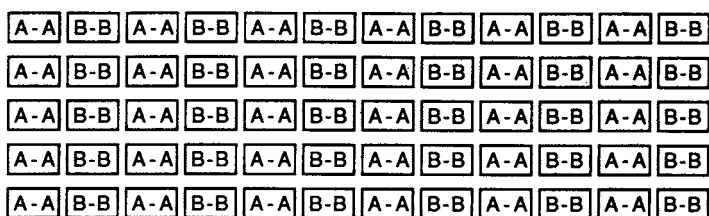
a group of unpolymerized monomers

A-A-B-B-A-A	B-B-A-A	B-B-A-A-B-B-A-A-B-B-A-A	B-B
A-A-B-B	A-A-B-B-A-A-B-B	A-A	B-B-A-A-B-B-A-A-B-B
A-A-B-B-A-A-B-B-A-A-B-B-A-A	B-B-A-A-B-B-A-A-B-B
A-A-B-B-A-A-B-B	A-A-B-B-A-A	B-B	A-A-B-B-A-A-B-B
A-A	B-B	A-A-B-B-A-A	B-B	A-A-B-B	A-A	B-B-A-A-B-B
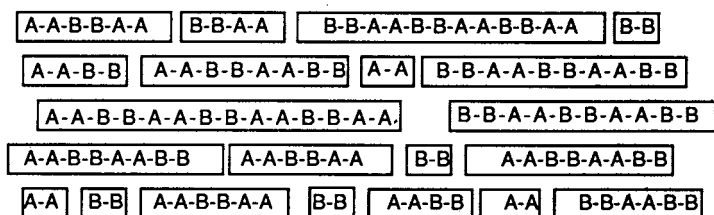
same group in an intermediate stage of polymerization

| A-A-B-B-A-A-B-B-A-A | B-B-A-A-B-B-A-A-B-B-A-A-B-B |
| A-A-B-B-A-A-B-B-A-A-B-B-A-A-B-B-A-A-B-B-A-A-B-B |
A-A-B-B-A-A-B-B-A-A-B-B-A-A	B-B-A-A-B-B-A-A-B-B
A-A-B-B-A-A-B-B-A-A-B-B-A-A-B-B	A-A-B-B-A-A-B-B
A-A	B-B-A-A-B-B-A-A	B-B	A-A-B-B-A-A	B-B-A-A-B-B
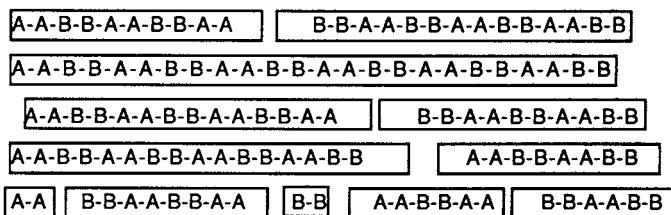
same group in a later stage of polymerization

Fig. 1.1 Molecular weight build-up in a step polymerization.

with the formation of amide linkages and elimination of water molecules (Mark and Whitby, 1940). Examples are items 6 and 7 in Appendix 1.1. Linear aliphatic polyamides were found to be crystalline solids also but the melting points were much higher, in the neighborhood of 260 °C. These materials could be drawn into strong fibers and thus immediately found important applications in this context, i.e., as 'nylon' and later as moulding resins and to some extent as films. There are now also a number of examples of polyesters as useful materials. For example, polymerization of terephthalic acid with ethylene glycol, item 10, Appendix 1.1, gives a high melting polymer useful as a fiber, as film and as a moulding resin.

1.2 Chain polymerization

As stated above, in this mechanism a reactive center is created that will react with the monomeric building blocks in such a way that the center is maintained and can continue to react with monomers. The reactive moiety can involve a free radical center, an anionic or a cationic species. Another type of chain polymerization can take place at active centers on a catalyst that might involve metal ions acting as a coordination catalyst rather than an initiator.

1.2.1 Radical initiation

Some organic molecules that contain especially unstable bonds can thermally dissociate into appreciable numbers of free radicals. Peroxides are an important class of examples. For example, tertiary butyl peroxide partially decomposes (**1.3**) and the ensuing radicals can attack a monomer
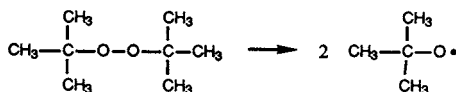
initiator decomposition

1.3

such as styrene (**1.4**). The unpaired electron is now centered on the
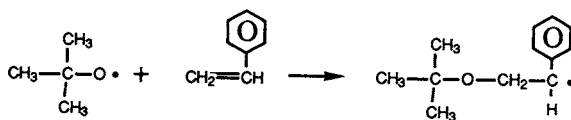
initiation

1.4

carbon containing the phenyl ring because this radical is more stable than the alternative position on the methylene carbon ($\bullet CH_2$—) of the styrene. The free radical center can continue to add styrene units to build up long sequences (**1.5**). The unpaired electron will continue to reside on the phenyl-ring-containing carbon as it is still the more stable position. Thus the polymerization is very selective with respect to head-to-tail linking and the resulting polymer has the pendant phenyl rings on alternating chain carbon atoms.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_2-\underset{H}{\overset{\phi}{C}}\cdot \;+\; CH_2{=}CH \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_2-\underset{H}{\overset{\phi}{C}}-CH_2-\underset{H}{\overset{\phi}{C}}\cdot$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O{-}{\Big[}CH_2{-}\underset{H}{\overset{\phi}{C}}{\Big]}_n{-}CH_2{-}\underset{H}{\overset{\phi}{C}}\cdot \;+\; CH_2{=}CH \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O{-}{\Big[}CH_2{-}\underset{H}{\overset{\phi}{C}}{\Big]}_{n+1}{-}CH_2{-}\underset{H}{\overset{\phi}{C}}\cdot$$

propagation
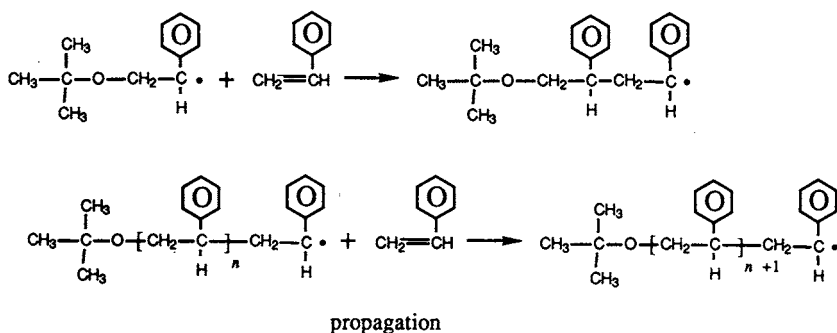
1.5

Notice that the peroxide, although it causes an otherwise unreactive system to proceed to polymerize, is chemically combined with the polymer chains and is thus consumed. It is therefore called an *initiator* rather than a catalyst. The polymerization step could continue, in principle, until all the monomers are consumed. However, an interfering reaction usually takes place. The free radical centers on two growing chains can react with each other to stop the polymerization. One way this can happen is readily apparent; two radical ends can simply combine directly to form a bond joining the two growing chains into one and stopping further polymerization. A less obvious but competitive reaction results from a radical end abstracting a hydrogen alpha to the center on another chain and forming *two* stable non-growing chains (**1.6**). The direct structural differences between the two termination reactions are minimal since there is only one

$$\sim\!\!\sim\!\!\sim CH_2{-}\underset{H}{\overset{\phi}{C}}\cdot \;+\; \cdot\underset{H}{\overset{\phi}{C}}{-}CH_2 \sim\!\!\sim\!\!\sim$$

recombination
$$\longrightarrow \sim\!\!\sim\!\!\sim CH_2{-}\underset{H}{\overset{\phi}{C}}{-}\underset{H}{\overset{\phi}{C}}{-}CH_2\sim\!\!\sim\!\!\sim$$

disproportionation
$$\longrightarrow \sim\!\!\sim\!\!\sim CH{=}\overset{\phi}{CH} \;+\; H{-}\underset{H}{\overset{\phi}{C}}{-}CH_2\sim\!\!\sim\!\!\sim$$
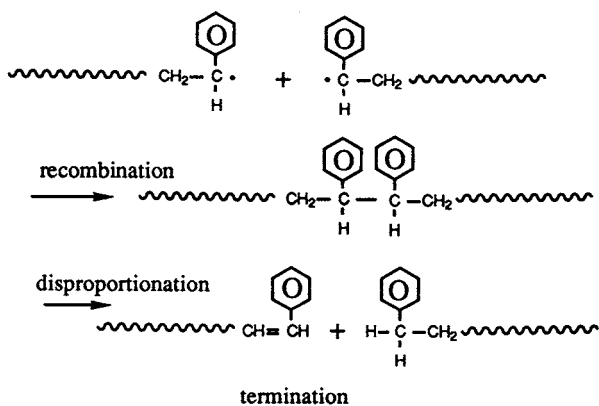
termination

1.6

termination event connected with very long chains. However, the two termination reactions do result in different distributions of molecular lengths. This will be developed later in the treatment of polymerization kinetics (Chapter 4). Very often it is not known which type of termination prevails. In polystyrene polymerization, both are known and the ratio depends on temperature.

In a chain polymerization, due to the high reactivity of the reactive centers, there are relatively few polymerizing chains compared to unreacted free monomer or finished terminated chains. Thus the reaction vessel throughout the polymerization contains largely only these latter entities, monomer and rather long completed chains, until all monomer is consumed (Figure 1.2). This is in contrast with step polymerization where the chain lengths increase through the course of polymerization.

1.2.2 Anionic initiation

Some monomers are capable of forming relatively stable anions and are thus susceptible to anionic initiation. For example, an acetate ion, Ac^-, introduced as a salt, C^+Ac^-, of a generic cation C^+, can attack formaldehyde (**1.7**), and the anionic center created can continue to

$$C^+ Ac^- + CH_2O \longrightarrow Ac\text{-}CH_2\text{-}O^- \ C^+$$
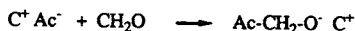
initiation

1.7

polymerize to form polyoxymethylene (**1.8**). In contrast to the radical case,

$$Ac\text{-}CH_2\text{-}O^- \ C^+ + CH_2O \longrightarrow Ac\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O^- \ C^+$$

$$Ac\text{-}[CH_2\text{-}O]_n\text{-}CH_2\text{-}O^- \ C^+ + CH_2O \longrightarrow Ac\text{-}[CH_2\text{-}O]_{n+1}\text{-}CH_2\text{-}O^- \ C^+$$
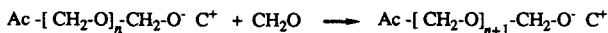
propagation

1.8

no direct termination step is possible since two anionic centers would not react. However, there are still competitive processes that will limit the length of the chains produced. For example, the presence of a small amount of water in the system can result in reactions that stop the *physical* chain from growing but allow the reactive center to persist and keep the

o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o
o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o
o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o
o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o o
o o o o o o o o o o o o o o o o o o o o o o o

monomers before polymerization

intermediate stage of polymerization

polymerization complete
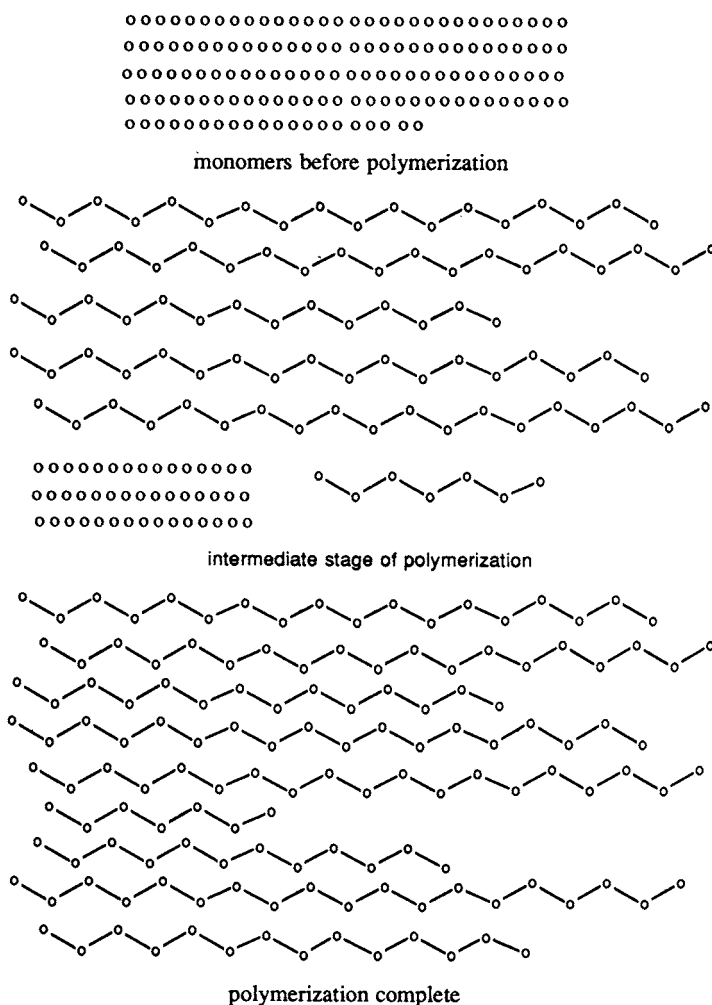
Fig. 1.2 Molecular weight build-up in a chain polymerization.

kinetic chain alive and growing (see **1.9**). This phenomenon is known as *chain transfer*. In one form or another it is common in chain polymerizations, see Chapter 4.

$$Ac\text{-}[CH_2\text{-}O]_n CH_2\text{-}O^- \ C^+ \ + \ H_2O \longrightarrow Ac\text{-}[CH_2\text{-}O]_n CH_2\text{-}OH \ + \ C^+ OH^-$$

$$C^+ OH^- \ + \ CH_2O \longrightarrow HO\text{-}CH_2\text{-}O^- \ C^+$$

chain transfer

1.9
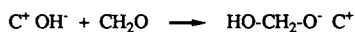
1.2.3 Cationic initiation

The reactive center can be cationic as well. As an example, the carbon–carbon double bond can be protonated by a very strong acid and a cationic center created. The Lewis acid BF_3 forms a very strong acid with halogen acids HX, $BF_3X^-H^+$. This acid can protonate isobutene (or 'isobutylene') to create a reactive cationic center at the tertiary carbon (**1.10**) and polymerization ensues (**1.11**). As in the case of an anionic

$$BF_3X^- H^+ \; + \; CH_2\!::\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \; \longrightarrow \; CH_3\!:\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \quad BF_3X^-$$

initiation

1.10

$$CH_3\!:\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \quad BF_3X^- \; + \; CH_2\!::\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \; \longrightarrow \; CH_3\!:\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!:\!CH_2\!:\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \quad BF_3X^-$$

$$H\!\!-\!\!\left[\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\right]_n\!\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \; BF_3X^- \; + \; CH_2\!=\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \; \longrightarrow \; H\!\!-\!\!\left[\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\right]_{n+1}\!\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \; BF_3X^-$$
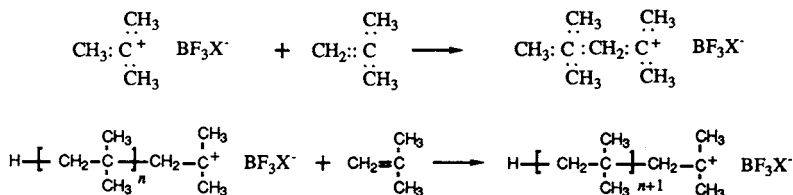
propagation

1.11

center, direct termination is not possible but physical chain length limiting reactions can take place. A chain transfer reaction occasioned by the reversibility of the initiation reaction to regenerate the initiator is shown in **1.12**.

$$H\!\!-\!\!\left[\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\right]_n\!\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \; BF_3X^- \; \longrightarrow \; H\!\!-\!\!\left[\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\right]_n\!\!CH\!=\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \; + \; BF_3X^- \; H^+$$
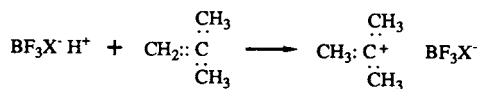
$$BF_3X^- \; H^+ \; + CH_2\!=\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \; \longrightarrow \; CH_3\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \; BF_3X^-$$
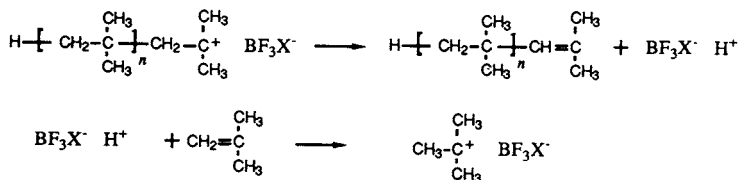
chain transfer via reversal of initiation reaction

1.12

1.2.4 Coordination catalysis

The preceding three types of chain polymerization all involve an initiator that creates a reactive center by attacking a monomer and becoming bonded chemically to it. There is a very important class of polymerizations where a true catalyst acts to create the active center. The most important of these involves coordination to a transition metal ion. The catalyst is usually heterogeneous in nature. Historically, important examples are the Ziegler–Natta catalysts. They usually consist of an organometallic compound in concert with the transition metal compound. The combination of triethyl aluminum, $(C_2H_5)_3Al$ ('TEA'), and titanium tetrachloride, $TiCl_4$, is a well-known example.

In an initiated polymerization, usually carried out homogeneously, the initiator itself plays little direct role after the initiation step. The addition of a new monomer in the propagation step depends on the structure and nature of the reactive center at the end of the growing chain and the monomer itself. In contrast, in the catalyzed polymerization the end of the growing chain, the entering monomer and the catalyst are all three bonded or coordinated together in the transition state. This three-party event gives rise to relatively severe and strong steric interactions or restrictions on the way in which the arriving monomer approaches the growing end of the chain. This is to be compared with the less restricted two-party environment of the monomer approaching the reactive center in an initiator induced polymerization. In turn, this restrictive environment gives rise to a phenomenon that tends to be less noticeable in initiated polymerizations. In the initiated polymerizations discussed above, attention was drawn to the strong tendency toward head-to-tail ordering in polymerizations at double bonds. That results from the reactive center having greater stability at one of the two possible positions than at the other. There is another type of ordering possible, in addition to head-to-tail. If the incoming monomer has different *substituents* about the polymerizing bonds there is a choice of orientation of the substituents. For example, in the free radical initiated polymerization of styrene the placement of the phenyl rings versus the hydrogen substituent on the same chain carbon tends to be random (Figure 1.3). However, in the Ziegler–Natta polymerization of propene (or 'propylene') the placement of the substituent methyl groups is very regular in the direction of the substituent methyl group in each monomer as it adds to the chain. Such polymerizations are very *stereoregular* (Figure 1.4). The consequences of this will be taken up in more detail in Chapter 5.
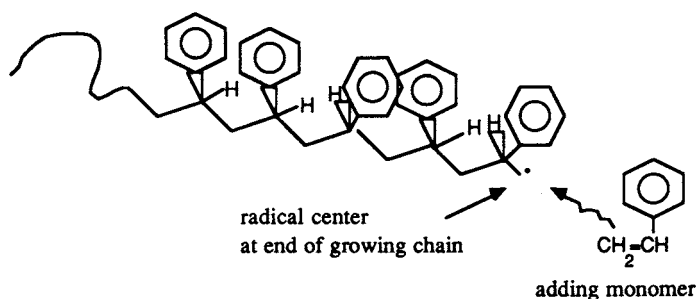
radical center
at end of growing chain

adding monomer

Fig. 1.3 Non-stereospecific radical polymerization of styrene.

end of growing chain
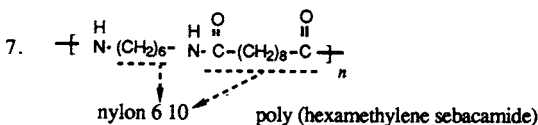
adding monomer

catalyst active site
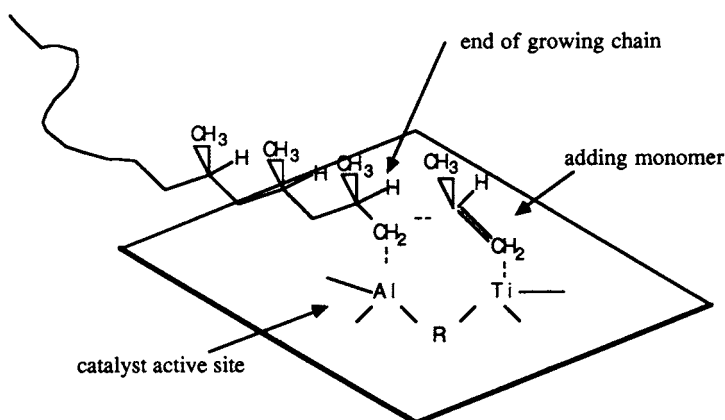
Fig. 1.4 Stereospecific Ziegler–Natta catalyzed polymerization of propene.

1.3 Further reading

The history of the development of the concept of synthesis of high molecular weight chain molecules is quite interesting and in no small part because considerable controversy was involved. Two good accounts are Flory (1953) and Morawetz (1985).

General books on synthesis are Lenz (1967), Odian (1991) and Stevens (1990). The last work has extensive references to other books and reviews and also has a good compendium of continuing serial publications covering the subject. The multivolume series, *Comprehensive Polymer Science*, edited by Allen and Bevington (1989) deals largely with chemistry and synthesis.

Appendix A1.1 Some common polymers

1. $-\!\!\left[\!\!\text{ CH}_2\!-\!\text{CH}_2\right]\!\!_{\!n}$

polyethylene

2. $-\!\!\left[\text{CH}_2\!-\!\underset{\underset{\text{CH}_3}{|}}{\text{CH}}\right]\!\!_{\!n}$

polypropylene

3.

$-\!\!\left[\text{CH}_2\!-\!\underset{\underset{\text{H}}{|}}{\overset{\overset{\overset{\text{O}}{\|}}{\text{C}-\text{O}-\text{CH}_3}}{\text{C}}}\right]\!\!_{\!n}$ $-\!\!\left[\text{CH}_2\!-\!\underset{\underset{\text{H}}{|}}{\overset{\overset{\overset{\text{O}}{\|}}{\text{C}-\text{OH}_\epsilon}}{\text{C}}}\right]\!\!_{\!n}$

poly (methyl acrylate)   poly (acrylic acid)

4.

$-\!\!\left[\text{CH}_2\!-\!\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\overset{\text{O}}{\|}}{\text{C}-\text{O}-\text{CH}_3}}{\text{C}}}\right]\!\!_{\!n}$ $-\!\!\left[\text{CH}_2\!-\!\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\overset{\text{O}}{\|}}{\text{C}-\text{OH}}}{\text{C}}}\right]\!\!_{\!n}$

poly (methyl methacrylate) 'PMMA'   poly (methacrylic acid)

5. $-\!\!\left[\text{CH}_2\!-\!\text{O}\right]\!\!_{\!n}$
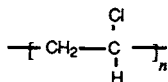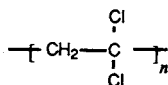
polyoxymethylene

6. $-\!\!\left[\underset{}{\overset{\text{H}}{\text{N}}}\!-\!(\text{CH}_2)_6\!-\!\underset{}{\overset{\text{H}}{\text{N}}}\!-\!\overset{\overset{\text{O}}{\|}}{\text{C}}\!-\!(\text{CH}_2)_4\!-\!\overset{\overset{\text{O}}{\|}}{\text{C}}\right]\!\!_{\!n}$

nylon 6 6   poly (hexamethylene adipamide)

7. $-\!\!\left[\underset{}{\overset{\text{H}}{\text{N}}}\!-\!(\text{CH}_2)_6\!-\!\underset{}{\overset{\text{H}}{\text{N}}}\!-\!\overset{\overset{\text{O}}{\|}}{\text{C}}\!-\!(\text{CH}_2)_8\!-\!\overset{\overset{\text{O}}{\|}}{\text{C}}\right]\!\!_{\!n}$

nylon 6 10   poly (hexamethylene sebacamide)

8. $-\!\!\left[\overset{\overset{\text{O}}{\|}}{\text{C}}\!-\!(\text{CH}_2)_5\!-\!\underset{}{\overset{\text{H}}{\text{N}}}\right]\!\!_{\!n}$

nylon 6   poly (caprolactam)

9.

$-\!\!\left[\text{CH}_2\!-\!\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_3}{}}{\text{C}}}\right]\!\!_{\!n}$

poly (vinyl acetate) 'PVAc'

10.

$$+ \overset{O}{\underset{}{C}} - \bigcirc - \overset{O}{\underset{}{C}} - O - CH_2 \cdot CH_2 \cdot O +_n$$

poly (ethylene terephthalate) 'PET'

11.

$$-\left[CH_2 - \overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}} \right]_n$$

poly (vinyl chloride) 'PVC'

12.

$$-\left[CH_2 - \overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}} \right]_n$$

poly (vinylidene chloride)

13.

$$-\left[O - \bigcirc - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - \bigcirc - O \cdot \overset{O}{\underset{}{C}} \right]_n$$

'polycarbonate' $\left(- O - \overset{O}{\underset{}{C}} - O - \text{ linkage} \right)$

14.

$$-\left[\bigcirc - \overset{O}{\underset{}{C}} - \bigcirc - O - \bigcirc - O \right]_n$$
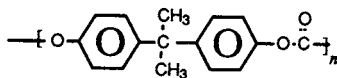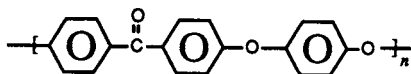
'poly ether ether ketone' , 'PEEK'

15.

$$-\left[\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}} - O \right]_n$$
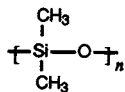
poly (dimethylsiloxane) 'silicone rubber'

16.

$$-\left[O - \bigcirc - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - \bigcirc - O - \bigcirc - \overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}} - \bigcirc \right]_n$$

'polysulfone' $\left(- \overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}} - \text{ linkage} \right)$

17.

$$-\left[CF_2 - CF_2 \right]_n$$
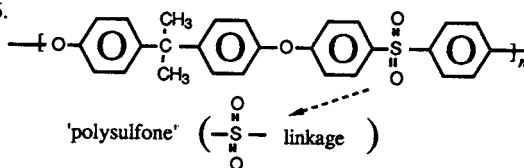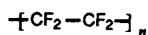
poly (tetrafluoroethylene) 'PTFE'

18.

poly (p-phenylene terephthalamide)   'Kevlar ® '

19.

a 'polyimide' $\left(\begin{array}{c} \text{linkage} \end{array}\right)$
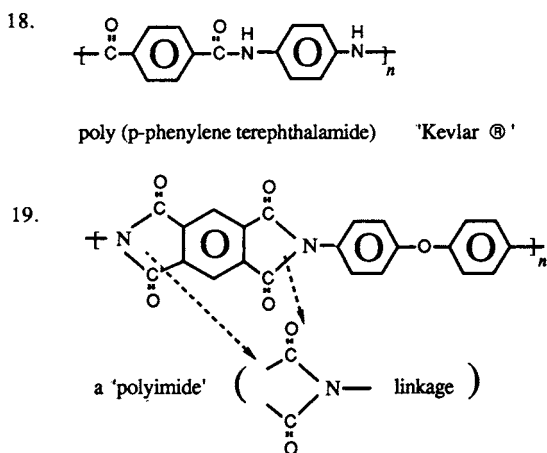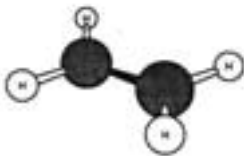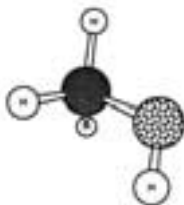
Appendix A1.2 Some common functional groups occurring in polymers
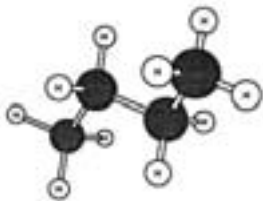
tetrahedral sp^3 carbons in CH_2 and CH_3 groups in butane

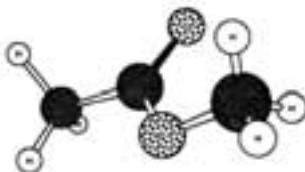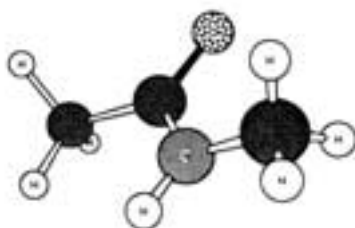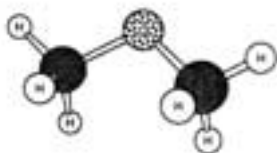planar sp^2 carbons in ethylene, $CH_2{=}CH_2$

hydroxyl group, OH, in methanol

planar carboxyl group (-C=O)-OH in acetic acid

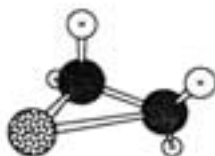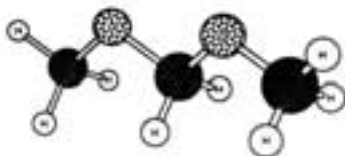planar ester group, (-C=O)-O-C, in methyl acetate

planar amide group, (-C=O)-NH-C, in methyl acetamide.

ether linkage -O- in dimethyl ether
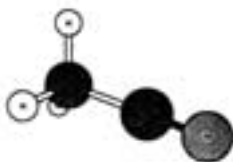

epoxy group, -CH-CH-, in ethylene oxide
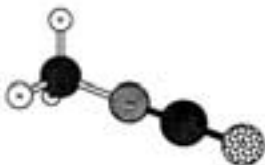\ /
O

acetal linkage, -O-CH$_2$-O-, in dimethoxymethane
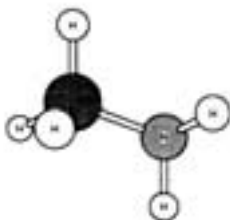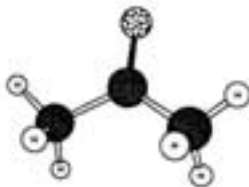
nitrile or cyano group, -C≡N, in acetonitrile
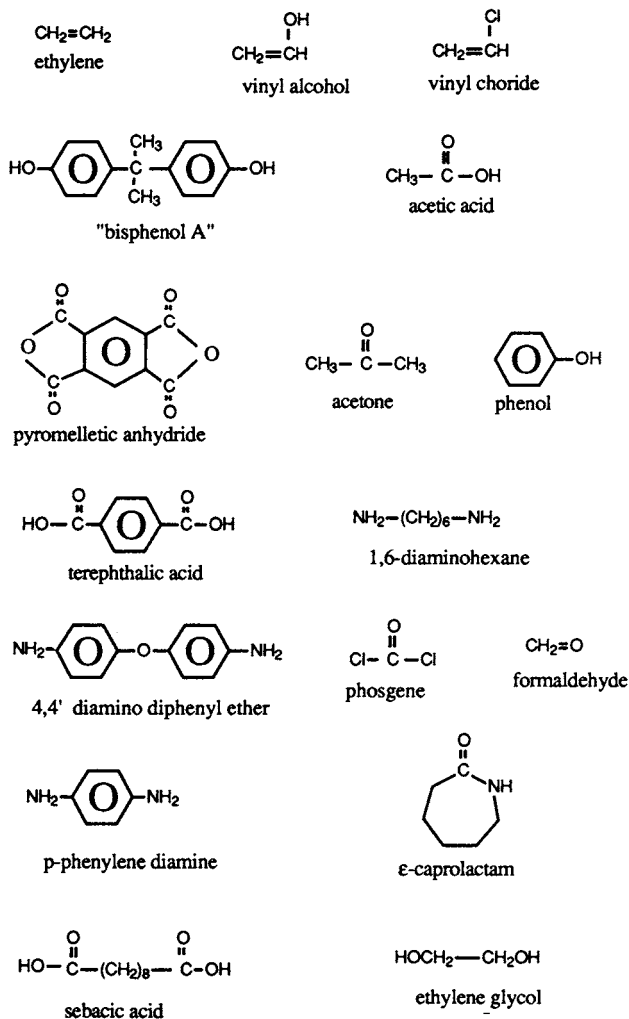
isocyanate group, -N=C=O , in methyl isocyanate

amine group, -NH$_2$, in methyl amine

ketone group, C-(C=O)-C, in acetone

Problems

1.1 Using monomers and other reagents shown in **1.13**, write chemical reactions for making as many of the polymers in Appendix A1.1 as possible. Classify each of the polymers you make as made by either *step* or *chain* polymerization.

$$CH_2=CH_2$$
ethylene

OH
|
$$CH_2=CH$$
vinyl alcohol

Cl
|
$$CH_2=CH$$
vinyl choride

HO—⟨O⟩—C(CH₃)(CH₃)—⟨O⟩—OH
"bisphenol A"

$$CH_3-\overset{O}{\overset{\|}{C}}-OH$$
acetic acid

pyromelletic anhydride

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$
acetone

⟨O⟩—OH
phenol

$$HO-\overset{O}{\overset{\|}{C}}-⟨O⟩-\overset{O}{\overset{\|}{C}}-OH$$
terephthalic acid

$$NH_2-(CH_2)_6-NH_2$$
1,6-diaminohexane

$$NH_2-⟨O⟩-O-⟨O⟩-NH_2$$
4,4' diamino diphenyl ether

$$Cl-\overset{O}{\overset{\|}{C}}-Cl$$
phosgene

$$CH_2=O$$
formaldehyde

$$NH_2-⟨O⟩-NH_2$$
p-phenylene diamine

ε-caprolactam

$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH$$
sebacic acid

$$HOCH_2-CH_2OH$$
ethylene glycol

1.13

1.2 As is shown in **1.14** formaldehyde can react (**1**) with phenol in either the *para* or *ortho* positions marked to form methylolphenols.
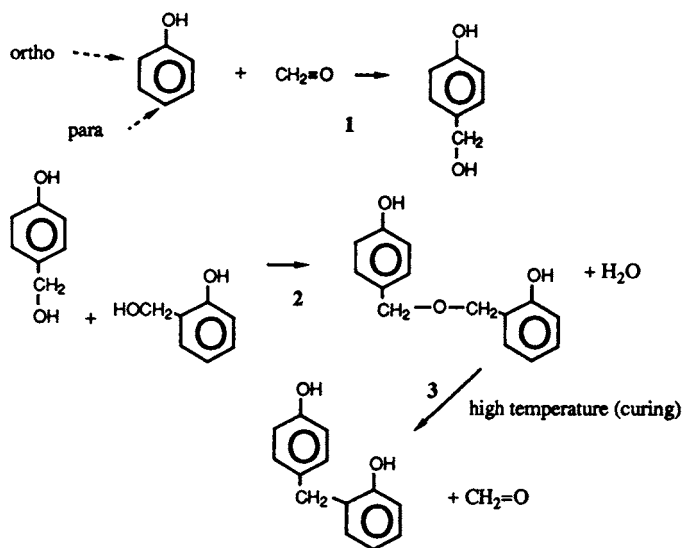
1.14

Then further reaction (**2**) of the methylolphenols with themselves or with phenol at either *para* or *ortho* positions leads to condensation to form polybenzyl ethers. The latter are thermally unstable and upon heating ('curing') decompose (**3**) leaving a methylene bridge and release formaldehyde for further reaction.

(*a*) By continuing these reactions, using all the ortho and para positions, draw a final structure that is an indefinite three dimensional network.

(*b*) How many moles of formaldehyde per mole of phenol are required to form the most dense network?