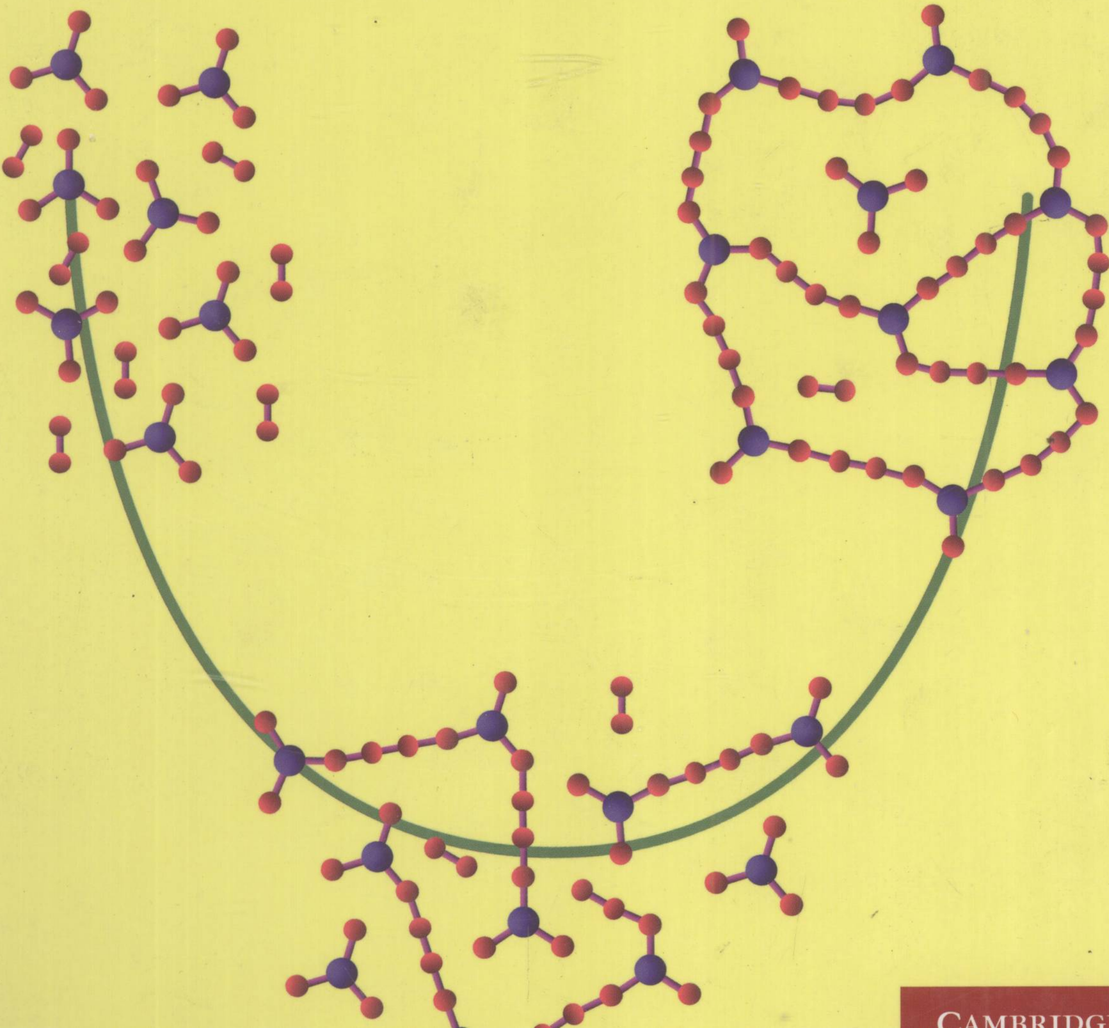
Chemorheology of Polymers

From Fundamental Principles to Reactive Processing

Peter J. Halley and **Graeme A. George**



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PETER J. HALLEY
University of Queensland

GRAEME A. GEORGE
Queensland University of Technology

华南理工大学
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Chemorheology of Polymers: From Fundamental Principles to Reactive Processing

Understanding the dynamics of reactive polymer processes allows scientists to create new, high value, high performance polymers. *Chemorheology of Polymers* provides an indispensable resource for researchers and practitioners working in this area, describing theoretical and industrial approaches to characterizing the flow and gelation of reactive polymers. Beginning with an in-depth treatment of the chemistry and physics of thermoplastics, thermosets and reactive polymers, the core of the book focuses on fundamental characterization of reactive polymers, rheological (flow characterization) techniques and the kinetic and chemorheological models of these systems. Uniquely, the coverage extends to a complete review of the practical industrial processes used for these polymers and provides an insight into the current chemorheological models and tools used to describe and control each process. This book will appeal to polymer scientists working on reactive polymers within materials science, chemistry and chemical engineering departments as well as polymer process engineers in industry.

Peter J. Halley is a Professor in the School of Engineering and a Group Leader in the Australian Institute for Bioengineering and Nanotechnology (AIBN) at the University of Queensland. He is a Fellow of the Institute of Chemical Engineering (FIChemE) and a Fellow of the Royal Australian Chemical Institute (FRACI).

Graeme A. George is Professor of Polymer Science in the School of Physical and Chemical Sciences, Queensland University of Technology. He is a Fellow and Past-president of the Royal Australian Chemical Institute and a Member of the Order of Australia. He has received several awards recognizing his contribution to international polymer science.

Preface

Plastics are the most diverse materials in use in our society and the way that they are processed controls their structure and properties. The increasing reliance on plastics for high-value and high-performance applications necessitates the investment in new ways of manufacturing polymers. One way of achieving this is through reactive processing. However, the dynamics of reactive processes places new demands on characterization, monitoring the systems and controlling the complete manufacturing process.

This book provides an in-depth examination of reactive polymers and processing, firstly by examining the necessary fundamentals of polymer chemistry and physics. Polymer characterization tools related to reactive polymer systems are then presented in detail with emphasis on techniques that can be adapted to real-time process monitoring. The core of the book then focuses on understanding and modelling of the flow behaviour of reactive polymers (chemorheology). Chemorheology is complex because it involves the changing chemistry, rheology and physical properties of reactive polymers and the complex interplay among these properties. The final chapter then examines a range of industrial reactive polymer processes, and gives an insight into current chemorheological models and tools used to describe and control each process.

This book differs from many other texts on reactive polymers due to its

breadth across thermoset and reactive polymers
in-depth consideration of fundamentals of polymer chemistry and physics
focus on chemorheological characterization and modelling
extension to practical industrial processes

The book has been aimed at chemists, chemical engineers and polymer process engineers at the advanced-undergraduate, post-graduate coursework and research levels as well as industrial practitioners wishing to move into reactive polymer systems.

The authors are particularly indebted to students, researchers and colleagues both in the Polymer Materials Research Group at Queensland University of Technology (QUT) and at the Centre for High Performance Polymers (CHPP) at The University of Queensland (UQ). Special thanks are due to those former students who have kindly permitted us to use their original material. We would also like to thank Meir Bar for his countless hours of redrawing, editing and proof reading during his sabbatical at UQ. Thanks are extended also to Vicki Thompson and Amanda Lee from Chemical Engineering, UQ, for their tireless printing work. Thanks also go to the Australian Research Council, the Cooperative Research Centre scheme, UQ, QUT and individual industrial partners for their funding of reactive polymer research work.

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Contents

1 Chemistry and structure of reactive polymers

The purpose of this chapter is to provide the background principles from polymer physics and chemistry which are essential to understanding the role which chemorheology plays in guiding the design and production of novel thermoplastic polymers as well as the complex changes which occur during processing. The focus is on high-molar-mass synthetic polymers and their modification through chemical reaction and blending, as well as degradation reactions. While some consideration is given to the chemistry of multifunctional systems, Chapter 2 focuses on the physical changes and time–temperature-transformation properties of network polymers and thermosets that are formed by reactions during processing.

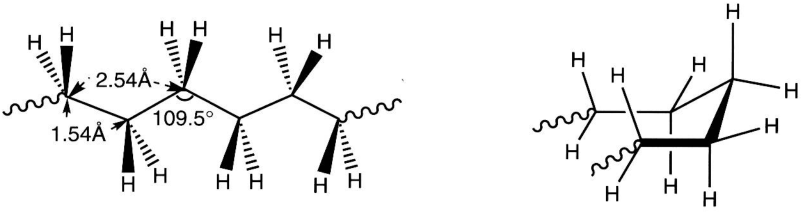
The attention paid to the polymer solid state is minimized in favour of the melt and in this chapter the static properties of the polymer are considered, i.e. properties in the absence of an external stress as is required for a consideration of the rheological properties. This is addressed in detail in Chapter 3. The treatment of the melt as the basic system for processing introduces a simplification both in the physics and in the chemistry of the system. In the treatment of melts, the polymer chain experiences a mean field of other nearby chains. This is not the situation in dilute or semi-dilute solutions, where density fluctuations in expanded chains must be addressed. In a similar way the chemical reactions which occur on processing in the melt may be treated through a set of homogeneous reactions, unlike the highly heterogeneous and diffusion-controlled chemical reactions in the solid state.

Where detailed analyses of statistical mechanics and stochastic processes assist in the understanding of the underlying principles, reference is made to appropriate treatises, since the purpose here is to connect the chemistry with the processing physics and engineering of the system for a practical outcome rather than provide a rigorous discourse.

1.1 The physical structure of polymers

The theory of polymers has been developed from the concept of linear chains consisting of a single repeat unit, but it must be recognized that there are many different architectures that we will be discussing, viz. linear copolymers, cyclic polymers, branched polymers, rigid-rod polymers, spherical dendrimers, hyperbranched polymers, crosslinked networks etc., all of which have important chemorheological properties. Initially we will consider the theory for linear homopolymers (i.e. only a single repeat unit) in solution and the melt. This will then be extended to determine the factors controlling the formation of the polymer solid state.

The starting point for an analysis of the structure of linear polymers is the C–C backbone of an extended hydrocarbon chain, the simplest member of which is polyethylene. The



(a) All trans conformation (extended chain)

(b) Cis conformation (chain kink)

Figure 1.1. The carbon–carbon backbone of a polyethylene chain in its extended planar (all-*trans*) conformation (a) and its kinked, out-of-plane (*cis*) conformation (b).

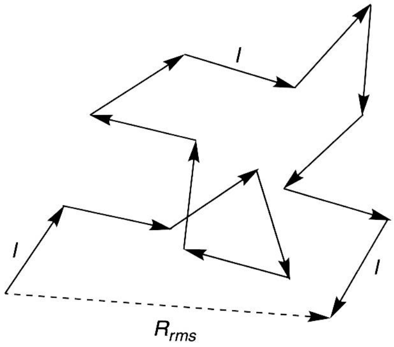


Figure 1.2. A schematic diagram of a freely jointed polymer chain with n segments of length l (in this case $n = 14$) showing the end-to-end distance, R_{rms}.

sp^3-hybridized tetravalent site of carbon that defines the angles and distances between the atoms along the backbone is shown in Figure 1.1 in

(a) an all-*trans* conformation with a planar C–C backbone and
(b) with the introduction of a *cis* conformation (as occurs in a cyclic six-membered hydrocarbon, cyclohexane), which allows the chain to kink out of the plane and change direction.

In the following we will initially consider the simpler concept of a freely jointed chain in which none of these constraints are present.

1.1.1 Linear polymers as freely jointed chains

The concept of polymer chains consisting of a freely jointed backbone which could occupy space as a random coil dated from 1933 when Kuhn defined a polymer chain as having n links of length l and the properties defined by a random flight in three-dimensions (Strobl, 1996). This is shown schematically in Figure 1.2.

This gave the coil the following properties: root mean separation of ends

$$R_{\mathrm{rms}} = n^{1/2} l \tag{1.1}$$

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and radius of gyration

$$R_g = (n/6)^{1/2} l. \tag{1.2}$$

Thus,

$$R_{\mathrm{rms}}^2 = 6{R_g}^2. \tag{1.3}$$

From mechanics, the radius of gyration, R_g, is the average value of the first moment of all segments of the chain with respect to the centre of mass of the chain. If the chain is fully extended with no constraints regarding bond angles, i.e. a fully jointed chain as defined by Kuhn, then the maximum value of R_{rms} becomes

$$R_{\max} = nl. \tag{1.4}$$

The ratio $(R_{\mathrm{rms}}^2/R_{\max})$ is a measure of the stiffness of the chain and is termed the Kuhn length. Thus, if there is a hypothetical freely jointed polyethylene that has 1000 carbon atoms separated by 1.54 Å then $R_{\max} = 1540$ Å, $R_{\mathrm{rms}} = 49$ Å and $R_g = 20$ Å.

The limitations of the random-flight model when applied to real polymer chains arise from

- the fixed bond angles
- steric interactions, which restrict the angles of rotation about the backbone.

This is apparent for polyethylene as shown in Figure 1.1. The restriction from a freely jointed chain to one with an angle of 109.5° between links increases R_{rms}^2 by a factor of two (namely the value of $(1 - \cos\theta)/(1 + \cos\theta)$). Other effects that must be taken into account are the restricted conformations of the chain due to hindered internal rotation and the excluded-volume effect, both of which may be theoretically analysed (Strobl, 1996). The excluded-volume effect was recognized by Kuhn as the limitation of real chains that the segments have a finite volume and also that each segment cannot occupy the same position in space as another segment. This effect increases with the number of segments in the chain as the power 1.2, again increasing the value of R_{rms} (Doi and Edwards, 1986).

When all of these effects are taken into account, a characteristic ratio C may be introduced as a measure of the expansion of the actual end-to-end distance of the polymer chain, R_0, from that calculated from a Kuhn model:

$$C = R_0^2/(nl^2). \tag{1.5}$$

Experimental values of this parameter are given in Table 1.1 and it may be seen that the actual end-to-end distance of a polyethylene molecule with 1000 carbon atoms (degree of polymerization DP of 500) is 126 Å from Equation (1.5) (i.e. $C^{1/2}n^{1/2}l$) rather than 49 Å from the Kuhn model, Equation (1.1). Data for several polymers in addition to polyethylene are given, including a rigid-rod aromatic nylon polymer, poly(*p*-phenylene terephthalamide) (Kevlar®), as well as the aliphatic nylon polymer poly(hexamethylene adipamide) (nylon-6,6).

Comparison of the values of C for the polymers with a flexible C–C or Si–O–Si backbone (as occurs in siloxane polymers) of about 6–10 with the value for the rigid-rod polymer of 125 demonstrates the fundamental difference in the solution properties of the latter polymer which has a highly extended conformation characteristic of liquid-crystal polymers. Equation (1.5) also shows that for a real chain the value of R_0 would be expected to increase as the half power of the number of repeat units, i.e. the degree of polymerization, $\mathrm{DP}^{1/2}$.

Table 1.1. Experimental values of the characteristic ratio, C, for Equation (1.5)

Polymer	Characteristic ratio, C
Poly(ethylene)	6.7
Poly(styrene)	10.2
Poly(hexamethylene adipamide), Nylon-6,6	5.9
Poly(*p*-phenylene terephthalamide), Kevlar®	125

Conditions for observing the unperturbed chain

The data shown in Table 1.1 were experimentally determined from solutions under θ-temperature conditions. This involves measuring the properties when a solution has the characteristic properties which allow the polymer chain to approach ideality most closely. When a polymer chain is in solution the coil will expand due to polymer–solvent interactions and an expansion coefficient, α, is defined so that the actual mean square end-to-end distance $[R_{\mathrm{rms}}]_{\mathrm{act}}$ becomes

$$[R_{\mathrm{rms}}]_{\mathrm{act}} = aR_0. \tag{1.6}$$

The magnitude of α depends on the forces of interaction between the solvent and the polymer chain. Thus, if the polymer is polar, when it dissolves in a polar 'good' solvent, it will expand and α is large. The converse is true for 'poor' (eg. non-polar) solvents and the chain will contract to lower than the unperturbed dimensions and, in the limit, the polymer may precipitate from solution. When a combination of solvent and temperature is found that is neither 'good' nor 'poor', i.e. $\alpha = 1$, then the chain–solvent and polymer–polymer interactions balance and R_0 is the unperturbed dimension of the chain. For a particular solvent, the temperature at which this occurs is the θ-temperature.

An interesting calculation is that of the volume occupied by the segments themselves compared with the total volume that the chain occupies. The diameter of a sphere within which the chain spends 95% of the time is about $5R_0$. Since the chain segments occupy only about 0.02% of this volume, the remaining space must be occupied by other chains of different molecules both when the polymer is under θ-conditions and in the presence of solvent molecules when it is expanded. Thus, except in very dilute solutions, polymer molecules interpenetrate one another's domains so that intermolecular forces between chains are significant.

Polymer chains in the melt

Polymer chains, in the melt, behave as if they are in the θ-condition, so the dimensions are those in the unperturbed state. This argument was put forward by Flory on energetic grounds and has been confirmed by neutron scattering (Strobl, 1996). The consideration begins with an analysis of the excluded-volume forces on an ideal chain. These arise from non-uniform density distributions in the system of an ideal chain in solution as shown in Figure 1.3.

This shows the way that the local monomer concentration, c_{m}, varies from the centre of the chain ($x = 0$) to either end. The excluded-volume forces on the chain create a potential energy ψ_{m} sensed by each repeat unit, which depends on c_{m} and on a volume parameter v_{e} that controls their magnitude:

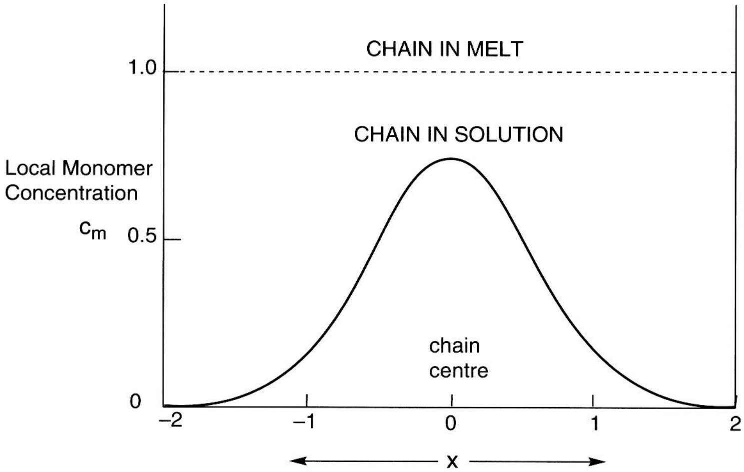

Figure 1.3. Comparison of the change in local monomer concentration with distance from the chain centre for a random chain in solution and in the melt. Adapted from Strobl (1996).

$$\psi_{\mathrm{m}} = v_{\mathrm{e}} c_{\mathrm{m}} kT. \tag{1.7}$$

This produces a net force for all non-uniform density distributions so that for the bell-shaped distribution in Figure 1.3 there will be a net force of expansion of the chain. When the melt is considered, every chain is surrounded by a chain of the same type, so the concentration c_{m} is constant in all directions (the dotted line in Figure 1.3). No distinction is drawn between repeat units on the same or different chains. (As noted above, there will be interpenetration of chains in all but dilute solutions.) The result is that there is no gradient in potential and there are no forces of expansion. In effect, the polymer chain in the melt behaves as if the forces of expansion due to excluded volume were screened from each chain and the dimensions are those for the unperturbed chain.

This result may, by a similar argument, be extended to the interpenetration of chains as random coils in the amorphous solid state. These results will be of importance when the rheological properties of the melt through to the developing solid are considered in Chapters 2 and 3.

1.1.2 Conformations of linear hydrocarbon polymers

Figure 1.1 showed the planar zigzag (a) and the kinked chain (b) as two possible ways of viewing the chain of polyethylene. The conformation that the chain will adopt will be controlled by the energy of the possible conformers subject to the steric and energetic constraints dictated by the structure. The main feature of transforming from the stretched chain (a) to the coil through structures such as the *cis* conformation (b) depends on the rotation about the C–C backbone. The remaining degrees of translational and vibrational freedom will affect only the centre of mass and the bond angles and bond lengths, not the molecular architecture.

The possible rotational conformations possible for the chain can be envisioned by focussing on a sequence of four carbon atoms as shown in Figure 1.4(a).

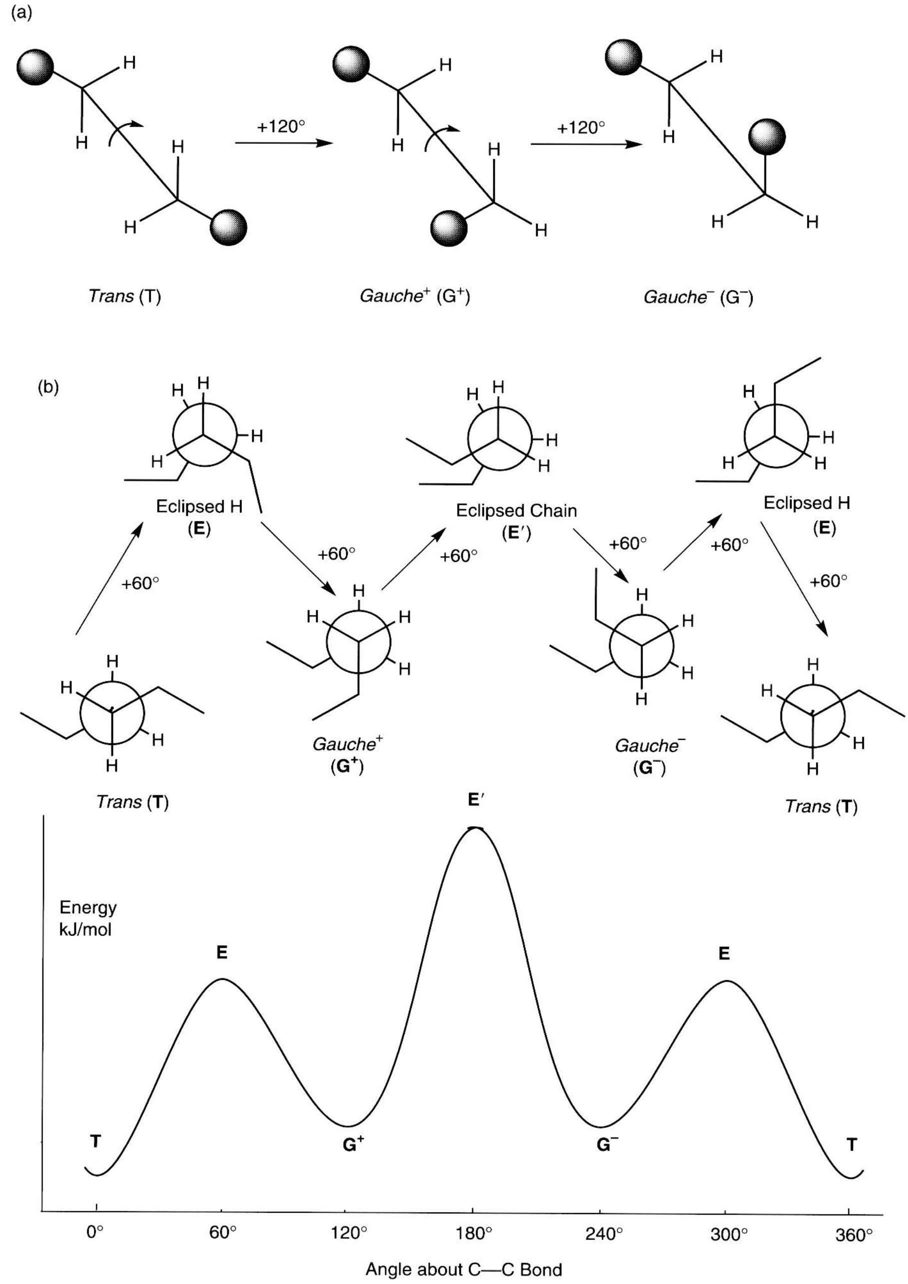

Figure 1.4. (a) Conformations adopted by a segment of a polymer chain by successive rotation about a C–C bond. The balls represent the carbon atoms from the continuing chain (initially in an all-*trans* extended-chain conformation). (b) Changes in conformational energy on successive rotation of an all-*trans* extended-chain conformation by 60° about a C–C axis.

This shows the successive rotation by 120° about the central C–C bond of the adjacent methylene group. Initially all carbon bonds lie in a plane and then after each rotation a hydrogen atom lies in the initial plane. A detailed analysis may be made of the rotational isomeric states of model compounds progressively from ethane, butane and pentane to determine the energy states of the conformers and, from the Boltzmann distribution, their populations (Boyd and Phillips, 1993).

The depiction of the conformers is facilitated by a simple schematic approach in which the atoms in Figure 1.4(a) are viewed along the central C–C bond initially in the *trans* (T) conformation and then rotation of the groups clockwise by 60° occurs in succession about this axis (Figure 1.4(b)). Analysis of these conformations identifies the energy maxima (eclipsed, E, conformations) and the energy minima (*trans* and *gauche* conformations) separated by up to 21 and 18 kJ/mol, respectively, as shown in the energy profile in Figure 1.4(b).

For polyethylene, the actual bond rotation from the *trans* (T) position to the other stable conformers (the *gauche* positions, G^+ and G^-, respectively) is slightly less than 120° due to unsymmetrical repulsions (Flory *et al.*, 1982). There are situations in which the repulsion due to steric crowding results in further deviations. For example, the sequence TG^+G^- will produce a structure with a sharp fold where the steric repulsion between methylene groups no longer allows an energy minimum. This is accommodated by a change in the angle of rotation giving an angle closer to that for the *trans* position (the so-called pentane effect) (Boyd and Phillips, 1993, Strobl, 1996).

When other groups are introduced into the polymer chain, such as oxygen in poly(oxy methylene) $[-CH_2-O-]_n$, the most stable conformation is no longer the all-*trans* chain but the all-*gauche* conformation $G^+G^+G^+$, etc. This means that the chain is no longer planar but instead is helical. The stability of the *gauche* conformation over *trans* is linked in part to the electrostatic interactions due to the polar oxygen atom in the chain (Boyd and Phillips, 1993). These conformations translate to the most stable structure expected at low temperatures. However, the low energy barriers between isomeric states mean that in the melt a large number of conformations is possible, as indicated in the previous section where the melt is seen to reproduce the properties of an ensemble of ideal random interpenetrating coils.

Asymmetric centres and tacticity

The structures considered above have been concerned with the behaviour of the backbone of the polymer. On proceeding from polyethylene to the next member in the series of olefin polymers, polypropylene, $[-CH_2-CH(CH_3)-]_n$, an asymmetric centre has been introduced into the backbone, in this case the carbon bearing the methyl group. An asymmetric centre is one where it is possible to recognize two isomeric forms that are mirror images and not superimposable. These are often described as optical isomers and the terms *d* and *l* are introduced for *dextro* (right-) and *laevo* (left-) handed forms. For small molecules these isomers may be resolved optically since they will rotate the plane of polarization in opposite directions.

For macromolecules it is useful to consider the structure of the polymer resulting from monomer sequences that contain the asymmetric centre. Figure 1.5 shows the two possibilities for the addition of the repeat unit as sequences of *d* units or *l* units to give meso (*m*) diads (*dd* or *ll*) when adjacent groups have the same configuration or racemic (*r*) diads (*dl* or *ld*) when they are opposite. If these sequences are repeated for a significant portion of the chain then we can define the tacticity of the polymer as being principally

isotactic if they are . . . mmmmmmmmm . . .
syndiotactic if they are . . . rrrrrrrrrrrrrr . . .
atactic if they are random . . . mmrmrrrmrmr . . .

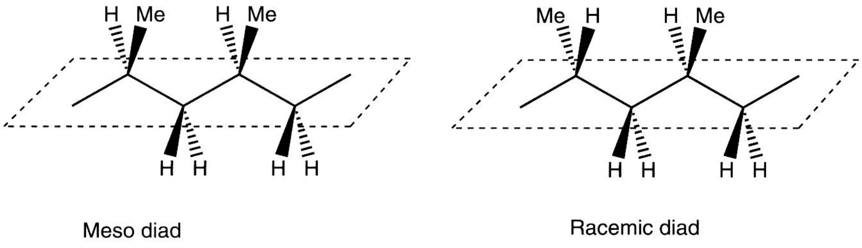

Figure 1.5. A schematic diagram illustrating meso (m) and racemic (r) diads.

As will be discussed later, special synthetic techniques are required to achieve isotactic and syndiotactic structures, and polypropylene, the example above, achieved commercial success only through the discovery of stereoregular polymerization to achieve the isotactic structure. The measurement of the degree of tacticity of a polymer is achieved through ^{13}C NMR studies of the polymer in solution (Koenig, 1999).

Isotactic polypropylene will adopt a conformation very different from the extended chain of polyethylene. In the early part of Section 1.1.2 it was noted that the minimum-energy conformations were considered to be attained by rotation about the C–C backbone and this introduced the possibility of *gauche* conformers as alternative energy minima. This can now be performed on the meso dyad in isotactic polypropylene by considering rotations about the two C–C bonds that will minimize the interactions between the pendant methyl groups. The starting point in this analysis is the nine near *trans* and *gauche* conformers since these define the local minima in energy of the backbone in the absence of the methyl groups. Introduction of the steric repulsion by the methyl groups in a TT conformation (Figure 1.5) suggests that this is not going to be a likely conformation and the conformers which are able to minimize the repulsion due to methyl groups in a meso dyad are limited to TG^- and G^+T. Just as a helix was generated when *gauche* conformers were accessible minima in poly(oxymethylene), so too we have two possible helices if the chain consists of m-dyads as in isotactic polypropylene. For TG^- it will be right-handed and for G^+T it will be left-handed. This helix will have three repeat units in one turn of the helix, i.e. a 3/1 helix, and this is the form which crystallizes.

In syndiotactic polypropylene, the methyl groups are well separated and the TT form is favoured, but there are other energy minima among the *gauche* conformations and TT/G^+G^+ and TT/G^-G^- sequences can generate left- and right-handed helices, respectively, where the repulsions are minimized (Boyd and Phillips, 1993). The chains may crystallize both in the TT and in the TTG^+G^+ form, so syndiotactic polypropylene is polymorphic.

1.1.3 Molar mass and molar-mass distribution

The length of the polymer chain or the degree of polymerization, DP, will have a major effect on the properties of the polymer since this will control the extent to which the polymer chain may entangle. The changes in this degree of polymerization that may occur on processing, resulting in either an increase (crosslinking) or a decrease (degradation) in DP, will have a profound effect on the properties both of the melt (e.g. viscosity) and of the resulting solid polymer (strength and stiffness). A formal definition of DP and thus the **molar mass** (or, less rigorously speaking, **molecular weight**) of a polymer is required in order to investigate the effect on properties as well as the changes on processing.

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