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The Physics of Polymers

Concepts for Understanding Their Structures and Behavior

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Single Chain Conformations

Condensed matter is composed of strongly interacting molecules, and discussions of the bulk properties of low molar mass compounds therefore focus from the beginning on the role of the interaction forces between different molecules in establishing thermal equilibrium. In dealing with polymeric systems, one encounters a different situation. As each macromolecule possesses a huge number of internal degrees of freedom, the analysis of the properties of the individual polymer becomes an important first point of concern. It is obvious that the understanding of single chain behavior is a necessary prerequisite for treatments of aggregate properties, but in fact, it implies even more and in many cases leads to a major step forward. There are, of course, phenomena that are dominated by intermolecular forces, such as the phase behavior of binary polymer mixtures, the structures in polyelectrolyte solutions, or the flow properties of polymer melts. However, other important phenomena, in particular essential parts of the viscoelasticity, are much under the control of the dynamic properties of the individual molecules. It is therefore quite natural and also necessary to start an introduction into polymer physics with a discussion of the conformational states of single chains.

2.1 Rotational Isomeric States

Let us choose polyethylene as an example and consider its full steric structure. The latter is shown in Fig. 2.1. A polymer chain like polyethylene possesses a great internal flexibility and is able to change its conformation totally. Basically, the number of degrees of freedom of the chain is given by three times the number of atoms, but it is convenient to split them up into two different groups. A first group concerns changes in valence angles and bond lengths, because they occur during molecular vibrations with frequencies in the infrared range. These movements are limited and do not affect the overall form of the chain. The second group of motions is of a different character, in that they have the potential to alter the form. These are the rotations about the

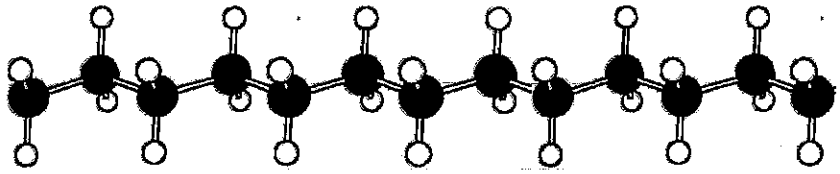

Fig. 2.1. The steric structure of PE. Rotations about the C–C bonds result in a change in the conformation

C–C bonds, which can convert the stretched chain of Fig. 2.1 into a coil and accomplish the transitions between all the different conformational states.

Clearly, in dealing with the conformational properties of a given polymer, only the latter group of degrees of freedom has to be considered. A discussion of the conformational states of a given macromolecule therefore first of all requires an analysis of the **bond rotation potentials**.

To begin with, we first go back to a related low molar mass molecule and consider the rotational potential of ethane. Here a rotation about the central C–C bond is possible, and one can anticipate the general form of the rotational potential. Interaction energies may be described as a superposition of a part that directly relates to the **rotational state** of the C–C bond and **non-bonded interactions** between the hydrogen atoms. The latter are for the given distances of repulsive nature. Figure 2.2 will help us to describe the situation. The staggered conformation of ethane, shown at the bottom on the right, corresponds to the minimum in the potential energy since it is associated with the largest distances between the hydrogens. Owing to the three-fold symmetry of the two methyl groups, the rotational potential $\tilde{u}(\varphi)$ (φ denotes the rotation angle) exhibits a 120°-periodicity. Therefore, in a first approximation, employing only the lowest order Fourier contribution, it can be described by

$$\tilde{u} = \tilde{u}_0(1 - \cos(3\varphi)) \ . \tag{2.1}$$

This rotational potential is indicated in the figure by the broken line and shows three energy minima with equal potential energies.

Next, we consider the rotational potential of butane. The replacement of one hydrogen atom by a methyl group for both carbon atoms removes the three-fold symmetry. As a consequence, the potential energy function $\tilde{u}(\varphi)$ gets a shape like that indicated by the continuous curve in Fig. 2.2. The minimum occurs for the staggered conformation depicted in the upper part on the right, where the distance between the two methyl groups is at the maximum. There still exist local minima in the potential energy at 120° and 240°, but now at an elevated level. The maximum of $\tilde{u}(\varphi)$ is expected for 180°, when the two methyl groups closely approach each other.

Particular terms are used to address the three energy minima. The conformational state with the lowest energy at $\varphi = 0°$ is called the **trans**-conformation. The other two minima at 120° and 240° are called **gauche** and

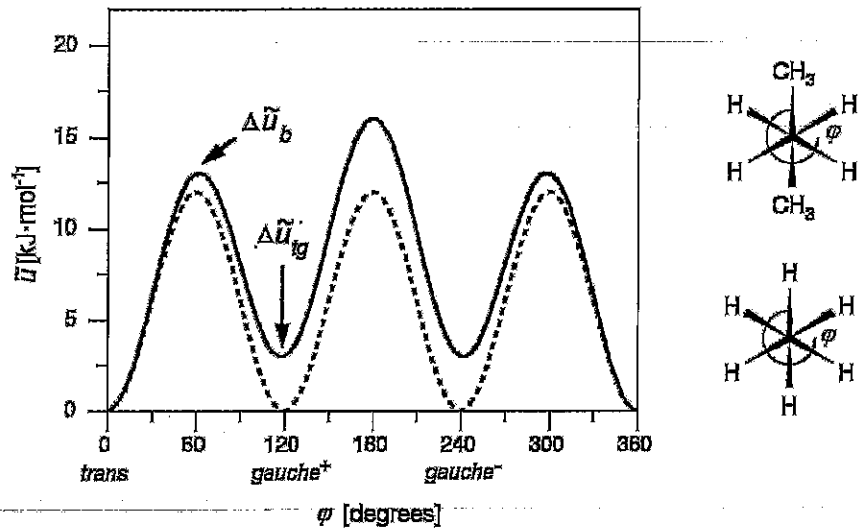

Fig. 2.2. Potential energies associated with the rotation of the central C–C bond for ethane (*broken line*) and butane (*continuous line*). The *sketches* show the two molecules in views along the C–C bond

are distinguished by adding a plus or minus sign. Note that in the trans-state the three C–C bonds of butane lie in one plane; the gauche-states are non-planar.

The internal dynamics of butane depends on the energy difference $\Delta\tilde{u}_{\mathrm{tg}}$ between the trans-state and the gauche-state and the height of the barriers, $\Delta\tilde{u}_{\mathrm{b}}$, between the local minima. One can envisage two limiting cases. For $\tilde{R}T \gg \Delta\tilde{u}_{\mathrm{b}}$ (the symbol $\tilde{R}$ stands for the perfect gas constant) rotations about the C–C bonds are quasi-free, and the details of $\tilde{u}(\varphi)$ with its minima and maxima become irrelevant. In the opposite case, $\tilde{R}T \ll \Delta\tilde{u}_{\mathrm{tg}}$, the molecules settle down in the lowest energy state, i.e., in the trans-conformation, and only librate about the equilibrium position.

The prerequisite in order to be able to judge the actual situation, say at ambient temperature, is therefore a knowledge of the two energy differences $\Delta\tilde{u}_{\mathrm{tg}}$ and $\Delta\tilde{u}_{\mathrm{b}}$. These can be determined by spectroscopic and calorimetric experiments. $\Delta\tilde{u}_{\mathrm{tg}}$ can be derived from temperature-dependent Raman scattering experiments, due to the vibrational spectra for the trans-state and the gauche-state being different. One selects two bands associated with the gauche-conformation or the trans-conformation, respectively, and measures their intensities, I_{g} and I_{t}, as a function of temperature. The ratio $I_{\mathrm{g}}/I_{\mathrm{t}}$ changes with the populations of the two states, according to

$$\frac{I_{\mathrm{g}}}{I_{\mathrm{t}}} \propto \exp -\frac{\Delta\tilde{u}_{\mathrm{tg}}}{\tilde{R}T} \,. \tag{2.2}$$

An Arrhenius plot of $\ln(I_g/I_t)$ versus $1/T$ thus yields $\Delta\tilde{u}_{tg}$. Experiments were performed on different n-alkanes and gave values in the range

$$\Delta\tilde{u}_{tg} \simeq 2-3\,\mathrm{kJ\,mol^{-1}}.$$

The fraction ϕ_g of molecules in the two gauche-states follows from

$$\phi_g = \frac{2\exp(-\Delta\tilde{u}_{tg}/\tilde{R}T)}{1+2\exp(-\Delta\tilde{u}_{tg}/\tilde{R}T)}\,, \tag{2.3}$$

which leads to

$$\phi_g \simeq 0.5\,.$$

Hence, trans-states and gauche-states are populated with similar probabilities.

The barrier height $\Delta\tilde{u}_b$ can be deduced, for example, from measurements of the heat capacity of ethane. It turns out that data can only be described if the internal degree of freedom associated with the C–C bond rotation is accounted for, in addition to the translational and rotational degrees of freedom of the whole molecule. A fit of the data yields $\Delta\tilde{u}_b$, with the result

$$\Delta\tilde{u}_b \simeq 12\,\mathrm{kJ\,mol^{-1}}\,.$$

This is the barrier height for ethane. For butane, one expects somewhat larger values.

Looking at these results, we conclude that

$$\Delta\tilde{u}_b \gg \tilde{R}T \simeq \Delta\tilde{u}_{tg}\,.$$

Under these conditions, the internal dynamics of the butane molecule may be envisaged as follows. Most of the time, the molecule is in one of the three conformational states and just vibrates about the respective energy minimum. From time to time, the molecule collects sufficient thermal energy so that the barrier can be passed over and the conformation changes. As the transitions take place rapidly compared to the time of staying near a minimum, a sample of butane resembles a mixture of different rotational isomers. For each molecule there exist three **rotational isomeric states**. They are all accessible and populated according to the available thermal energy.

We now turn to polyethylene and discuss its case by starting from butane considering the effect of a replacement of the two methyl endgroups by longer chain sequences. The result is qualitatively clear. One expects modifications in the details of $\tilde{u}(\varphi)$, which also depend on the conformations of the two sequences. However, the overall form of the rotational potential energy of a given C–C bond will remain unchanged. There still exists an energy minimum for the trans-conformation and local minima for two gauche-states. Also the values of $\Delta\tilde{u}_{tg}$ and $\Delta\tilde{u}_b$ do not alter significantly. We may thus conclude that the conformation of polyethylene can again be described in terms

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of rotational isomeric states and that there are still three rotational isomeric states per bond, corresponding to trans, gauche$^+$ and gauche$^-$. A polyethylene chain with a degree of polymerization N therefore possesses 3^N different conformational states. In order to address one specific conformation, the rotational isomeric states for all bonds have to be given. This may be done, for example, in the form

$$(\varphi_1, \varphi_2, \ldots, \varphi_N)\,, \qquad (2.4)$$

whereby $\varphi_i \mathrel{\widehat{=}}$ trans, gauche$^+$ or gauche$^-$.

Two different situations are found in polymer systems and shall be dealt with separately. In the crystalline state, chains adopt unique conformations that represent helices with a straight axis. In the fluid state, on the other hand, all rotational isomeric states are populated, with probabilities determined by the temperature and the respective energies.

2.2 Helices

Polymers can form crystals, not like low molar mass substances under all circumstances, but for many species under the prerequisite that the cooling from the molten state occurs slowly enough to enable the necessary rearrangements of the chains. The building principle is obvious. As a basic requirement, chains must adopt a straight, perfectly ordered form. Then a lattice can be constructed by orienting the chains uniformly in one direction and packing them laterally in a regular manner. The thus-obtained lattice with three-dimensional order has the monomeric units as structure units. The specific property is the strong anisotropy in the binding forces, with valence forces in one direction and weak van der Waals forces in the two other directions.

Crystal lattices at low temperatures generally represent the structure with the minimum internal energy. For polymer crystals one expects that the main contribution be furnished by the intramolecular energies as determined by the bond rotations. Structure determinations in combination with energetic calculations, which have been carried out for several polymers, do indeed support this view. They indicate that the conformation adopted by a polymer in the crystalline phase equals, or comes very close to, the lowest energy rotational isomeric state of the single chain. Conditions are simple if the coupling between successive bonds is only weak. Then rotations take place independently and each bond settles down in the energy minimum.

To have equal conformations in all monomeric units is of course not a peculiarity of chains with independent bonds. In the general case, in the lowest energy state of a chain one also finds a uniform conformation of the monomers. What is the general structure that then emerges? It is important to recognize that this is of the helical type. To see and to illustrate this, we consider some examples.

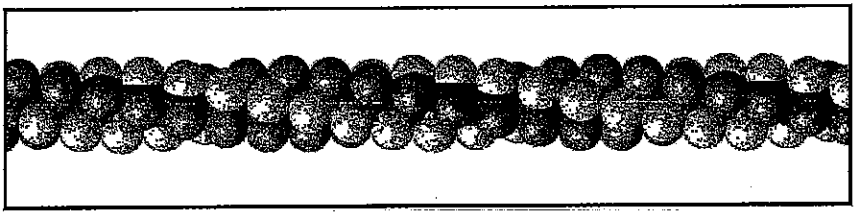

Fig. 2.3. PTFE in the crystalline state. The conformation corresponds to a 13/6-helix

We begin with polyethylene. Here, in order to have the energy minimum, all C–C bonds must be in the trans-state. Crystalline polyethylene thus adopts the **all-trans**-conformation, which is the structure shown in Fig. 2.1.

While polyethylene with its planar zig-zag structure is not a helix in the usual sense, poly(tetrafluoroethylene) (PTFE) in the crystalline state possesses the typical wound appearance. This chain is shown in Fig. 2.3. Poly(tetrafluoroethylene) is obtained from polyethylene by a replacement of all hydrogen atoms by fluorines. The reason for the resulting structure change is easy to see. The replacement of hydrogen atoms by the much larger fluorines increases the interaction energy between the CF_2 groups of second nearest neighbors. When we start off from an all-trans-form, a uniform twist of the chain diminishes the repulsive F–F interaction energies but, at the same time, the bond rotational energy increases. There exists an energy minimum at a finite torsion angle, $\varphi_{\min} = 16.5°$.

Figure 2.4a presents as a further example a helix of poly(oxymethylene) (POM). It corresponds to an **all-gauche**-conformation. Different from poly(tetrafluoroethylene), here a trans-rotational isomeric state also exists, but it does not represent the energy minimum.

For some polymers, one does not observe a unique helical form but two or three different ones that possess very similar energies. Poly(oxymethylene) actually gives an example for such a **polymorphism**. Here one can also find the helix shown in Fig. 2.4b. It also represents an all-gauche-conformation, but the torsion angle, which was near 60° for the first modification, has now increased to 77°. Which of the two helices is formed depends on the crystallization conditions. In principle, at a given temperature, only one of the modifications can be stable, the other one being metastable. Annealing can induce a transformation to the stable state, but often this transformation is kinetically hindered, and then it may become difficult to identify the stable modification.

For the description of a given helix, we have a natural basis. One refers to the screw symmetry and just specifies the screw operation that maps the molecule onto itself. Screw operations comprise a turn about a certain angle, say $\Delta\zeta$, together with a simultaneous longitudinal shift, say Δz. These two values that describe the move from one monomer unit to the adjacent one constitute the **external helix parameters**. For polyethylene we have $\Delta\zeta =$

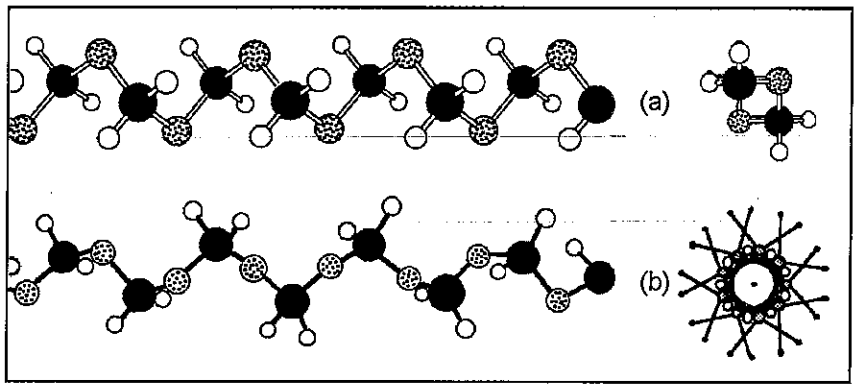

Fig. 2.4. Two different helices formed by POM: 2/1-helix (a) and 9/5-helix (b). Side views (*left*) and views along the helix axis (*right*)

180° and $\Delta z = 1.27\,\text{Å}$, for poly(tetrafluoroethylene) $\Delta\zeta = 166°$ and $\Delta z = 1.31\,\text{Å}$, for the two polymorphic forms of poly(oxymethylene) $\Delta\zeta = 180°$, $\Delta z = 1.78\,\text{Å}$ and $\Delta\zeta = 200°$, $\Delta z = 1.93\,\text{Å}$, respectively. The external helix parameters are functions of the **internal helix parameters**, the latter being given by the bond rotational angles. The dependencies may be formulated on the basis of geometrical considerations, assuming constant values for both bond lengths and valence angles.

Several polymers form helices that are simple in the sense that $\Delta\zeta$ is a fraction of 360°, like 180°, 120° or 90°. These are called $m/1$-helices, m giving the number of monomeric units arranged along one 360°-turn. Examples are polypropylene, polystyrene or poly-1-butene, which all form 3/1-helices. The all-trans-conformation of polyethylene and the all-gauche-conformation of poly(oxymethylene) correspond to 2/1-helices. The next general helical form is given by the m/n-helices. The name is meant to indicate that m monomeric units are equally distributed over n turns.

Particularly interesting is the observation that polymers with $n > 1$ often cannot be described as an m/n-helix with m and n being small numbers. Poly(tetrafluoroethylene) and the second form of poly(oxymethylene) represent such examples. The helix of poly(tetrafluoroethylene) is usually called a 13/6-helix, thereby indicating that 13 CF_2 units are distributed over six turns. This results in the measured value of $\Delta\zeta$ as

$$360° \cdot 6 : 13 = 166° \,.$$

Likewise, the second modification of poly(oxymethylene) also requires a non-simple notation for the description of the conformation, namely that of a 9/5-helix. If we recall the reason for the winding of chains, these results are not surprising. The helix conformation represents the minimum of the intramolecular energy and this may arise as a result of competing forces. The internal

helix parameters thus determined do not always have to be associated with a simple external helical structure.

Interestingly enough, measurements with higher accuracy showed that even the descriptions of the poly(tetrafluoroethylene) chain as a 13/6-helix and of the poly(oxymethylene) chain as a 9/5-helix are only approximations. Refinements of data necessitated a change in the characteristic ratio m/n towards higher numbers. In the case of poly(tetrafluoroethylene), the evaluation of electron diffraction data indicated a 473/219-helix. What does this mean? Indeed, these observations can be understood as indicating a qualitative structural change. Rather than accepting helix descriptions with large numbers n and m as representing exact structures, it might be more appropriate to assume that these helices possess no strict periodicity at all. This would mean that poly(tetrafluoroethylene) and poly(oxymethylene), in the crystalline state, both form **irrational helices**. As a consequence, the lattice lacks periodicity in one direction. We rather find, in the chain direction, two independent length scales, as given by the height Δz per monomeric unit and the height of one 360°-turn, respectively. Structures like this are generally addressed as **incommensurate**. They are also found in non-polymeric materials such as, for example, certain anorganic ferromagnetic compounds, where the positional and the magnetic order show different periodicities.

2.3 Coils

The huge number of rotational isomeric states that a polymer chain may adopt becomes effective in fluid phases. Polymers in solution or the melt change between the different states, and these are populated according to the laws of Boltzmann statistics. Because the large majority of conformations are coil-like, it is said that polymers in the fluid state represent **random coils**.

At first, one might think that any treatment of the properties of a polymer has to emanate from its microscopic chemical structure, since this determines the rotational isomeric states. One would then have to consider in detail the effects of bond lengths, bond angles, rotational potentials, the presence and length of sidegroups, etc. Treatments of this kind are necessarily specific and vary between different compounds. It is now a most important fact that one can omit the consideration of all these structural details in many discussions. Indeed, the dependence on the chemical constitution vanishes if structural properties are discussed for a lowered resolution, corresponding to length scales in the order of some nanometers. In such a coarse-grained picture, polymer chains become equivalent to each other and then also exhibit a common behavior.

Figure 2.5 shows a polymer coil as it might look like at limited resolution. We would observe a bent chain with a continuous appearance.