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DEFECT GENERATION AND MOTION IN POLYETHYLENE-LIKE CRYSTALS,

ANALYZED BY SIMULATION WITH SUPERCOMPUTERS*

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ABSTRACT

Defects in polymers were observed by high resolution electron microscopy and inferred from their mechanical and dielectrical behavior. The details of their generation was not known, however, in the past. During the last few years we have been able to extend the molecular dynamics simulation of polyethylene to crystals containing up to 6100 atoms and to times as long as 100 ps. The major observation was that single bond rotations of more than 90° become possible already more than 100 K below the melting temperature. These defects have lifetimes of only a few ps. By coupling to kinks (2g1) they can extend their lifetime considerably. Addition of a thermal, mechanical or dielectric free energy gradient to the thermally created defects seems to be able to account for the microscopic motion needed to explain the macroscopically observed annealing, deformations and relaxation effects. Key to the mechanical and dielectric properties is thus the existence of conformational disorder (condis crystal).

INTRODUCTION

Polymer molecules are, by definition, more than 1,000 atoms in size. More typically 10,000 to 100,000 atoms are linked to form a flexible, linear macromolecule. Polyethylene of 280,000 molecular mass for example, consists of about 60,000 atoms. In the melt this molecule, which has a contour length of 3080 nm, is randomly coiled to an end-to-end distance of about 53 nm and has a mass density of approximately 0.001 g/cm^3 , close to that of a gas at STP. To make up the overall density of the melt of 0.854 g/cm^3 , many molecules are statistically entangled. Crystallization under such conditions is kinetically hindered because of the coiling of the molecule and the entanglements. The initial crystals thus usually have dimensions of only 5 to 20 nm in the chain direction. The much longer molecules fold within the crystal and may remain partially amorphous, i.e. they cross the phase boundary. A final metastable, semicrystalline structure is obtained after additional secondary crystallization, annealing of the primary crystals, and reorganization within the remaining amorphous phase. A detailed summary of the structure of macromolecular crystals, their morphology and defects is given in Ref. [1], the process of nucleation, crystallization, and annealing is reviewed in Ref. [2], and the melting behavior of such metastable crystals is discussed in Ref. [3]. These references and the first part of the following text give a survey of the state of knowledge up to about 1980. This is followed in Part I with a summary of the defect types in polymer crystals. In Part II a description of the experimental and computational effort which was made to identify point defects in polymer crystals is reviewed. In Part III the molecular dynamics method and its applications are summarized. Part IV, finally, gives a description of the defects observed by the computer simulations.

*The contents of this paper were presented as paper K2.8 and poster K7.53 and expanded with a literature survey by A. X.

I. THE DEFECT CRYSTALS OF POLYMERS

Although the conditions of initial crystallization seem not conducive to the formation of perfect crystals, X-ray diffraction experiments have permitted the derivation of hundreds of ideal polymer crystal structures [4]. The initial ideas about defects in polymer crystals were based on the knowledge accumulated on crystals of small molecules, metals and salts [5]. Very quickly, however, the special conditions of molecular nature of polymers became obvious. While in nonpolymeric crystals structure-insensitive properties like density, heat content, modulus etc. could be approximated by the ideal crystal structure, this was not possible for polymer crystals. An added level of imperfection needs to be recognized, that of the "crystallinity". Structure-insensitive properties vary approximately linearly with the weight or volume fraction of crystallinity. Typically polymers may show crystallinities from 5 to 95%. This led to the model of a two-phase structure; one phase being represented by rather perfect crystals, the other by a fully amorphous phase. Since such a two-phase structure in a one-component system can, according to the phase rule, not be in equilibrium, there must be constraints hindering further crystallization of the amorphous phase. These may be called "amorphous defects" and provide the bridge from well-defined crystal defects to the well-defined amorphous phase [6]. Typical for the amorphous phase surrounding a crystalline area is its increased glass transition temperature when compared to noncrystalline samples. Often one can detect close to the crystal surface a less mobile layer than the unrestrained amorphous polymer, the "rigid amorphous fraction" [7].

From these just described three-dimensional defects, characteristic for polymeric materials one can move to two dimensions. External surfaces are always the prime defect of a polymer single crystal because of their usually small size and the need to accommodate long molecules. Because of the high regularity of the surface of solution-grown crystals, optical and electron microscopy gave much information about chain folding, tie molecules, fold sector boundaries, stacking faults, twin boundaries, kink bands, etc. [8]. Although more difficult, much could also be learned about surfaces and interconnections between amorphous and crystalline phases created by melt crystallization. The research involved the study of fracture surfaces, microtomed sections, etched samples, and decorated interfaces [8].

The next step down in dimensionality of defects leads to dislocations. The classical edge and screw dislocations of crystals of small molecules could also be documented in crystals of macromolecules. Particularly obvious are growth spirals with a Burgers vector of the size of the lamellar thickness, i.e. 5–50 nm, which are linked to the crystal growth mechanism [2]. Such large screw dislocations were already observed earlier for paraffins [9]. Dislocations with a Burgers vector of the unit-cell dimension were seen somewhat later by electron microscopy with the help of moiré patterns and were also linked to the accommodation of chain ends in the crystals [10]. Their link to deformation processes in polymers was, however, not successful. Most of these dislocations seemed to be formed by terminated growth planes and were not free to glide. The glide planes for motion of dislocations are limited to planes parallel to the chain direction because of the strong anisotropy of the crystal and interfere often with fold geometry and tie molecules [11]. The most important deformation in polymer crystals is that observed on drawing to fibers and films. These processes seem to involve, however, a much more chaotic deformation process leading perhaps to a "pseudomelting" [12].

The ultimate, zero-dimensional or point defects are again special in polymers. They must provide the ultimate element in the understanding of structure-sensitive properties, such as annealing, strength, mass transport, and chemical reactivity. While in small-molecular crystals vacant lattice sites, interstitial atoms, and foreign motifs on interstitial and substitutional positions form the basic point defects, in macromolecular crystals

differences arise from the overriding presence of the permanent covalent bonds of the backbone chain. Vacancies can only arise in connection with other defects such as kinks, chain ends, or wrong substituents in the chain (copolymers). Interstitial atoms must be linked with chain disorder, copolymerization or monomeric impurities. Similarly, substitutional positions can only be filled by prior copolymerization or by cocrystallization with small molecules (rare) [1]. Chain disorder, as described by kinks, folds, jogs, torsions (twists) etc., are thus the basic point defects in macromolecular crystals [13]. Their existence has been deduced initially from relaxation properties. The macromolecular crystals of interest to the present discussion are polyethylene-like, so that electronic defects need not be considered.

Two more comprehensive defect models were developed for the description of the defect state of macromolecules. One is the kink model of Pechhold, which represents an integrated approach to the description of the condensed state of polymers [14], the other is the paracrystalline model of Hosemann [15], which was recently shown to correspond to a crystal with a statistical dislocation distribution [16].

A starting point of defect evaluation can be based on the rotational isomer model [17]. It makes use of the three-fold minimum in rotational energy [see also Eq. (3), below] and describes the defect conformation as a sequence of *gauche* (g^+ , g^- ; $\tau = 300^\circ$, 60° , respectively) and *trans* (t ; $\tau = 180^\circ$) conformations. The simplest defect in polyethylene is a 2g1 kink that is represented by the sequence of g^+tg^- . The symbol 2g represents the number of *gauche* conformations, and the second numeral, the amount of shortening of the chain in multiples of $c/2$. A 2g1 kink displaces the chain in addition by about 0.2 nm in the directions at right angles to the zig-zag plane. The latter displacements were proposed to be removed by distortion of the chain, as shown by the more detailed models, below. In case the displacements in bigger defects (i.e. 2g2) are sufficient to occupy a neighboring zig-zag plane, the kinks are called jogs. The intermolecular energy of a 2g1 kink was then estimated from the increased volume multiplied with the cohesive energy density. Overall it was estimated that an equilibrium concentration of 1 kink per 250 carbon atoms may be possible at 400 K [14].

II. POINT DEFECTS IN POLYMER CRYSTALS

A more recent review of point defects was given by Zerbi [18]. Stable, highly conformationally *disordered* states which usually have hexagonal symmetry about the chain axis have been termed *condis* crystals [19]. They can be looked upon as crystals with high, mobile defect-concentrations. A review of over 100 *condis* crystals, ranging from macromolecules such as the high-pressure polymorph of polyethylene, polytetrafluoroethylene, 1,4-*trans*-polybutadiene, and nylon 6.6 to small molecules such as cycloparaffins, lipids and soaps, has been published recently [20].

Estimates of the energies required to produce a defect have usually been made by finding the intramolecular conformational energy needed to rotate the backbone out of its equilibrium conformation in the crystal (i.e. the *trans*-conformation for polyethylene), and the changed intermolecular interactions caused by the deformation of the crystal structure. In the past, most of the energetics calculations were based on the molecular mechanics formalism, seeking the potential minimum of a given defect. Typical semiempirical potential energy functions that can be used for such calculations are given below for polyethylene in the Eqs. (3)–(6). Various combinations and simplifications of these equations have been used to compute energy and geometry of defects and also crystal structures. A typical, simple molecular mechanics result for an effective potential energy surface of polyparaxylylene from our laboratory is shown in Fig. 1 [21]. In this calculation only the internal rotation and the nonbonded potentials of a single chain were used. The

condis phases of polyparaxylylene are the β_1 and β_2 polymorphs. The rigid α -crystal is largely restricted to torsional oscillations in the given region of θ of $\pm 10^\circ$. The condis phases populate the other rotational isomers.

Reneker and Mazur [22] calculated defect energies in a polyethylene crystal of chains of 60 CH_2 -units each, arranged as shown in Fig. 2. The to-be-analyzed defect was placed in the center chain, surrounded by one mobile layer of 6 such CH_2 -chains and

fixed with an outer layer of 12 additional chains, the latter being solidly anchored on their respective orthorhombic lattice positions. A Newton-Raphson energy minimization algorithm was then used to calculate the defect energy. Adding an extra CH_2 -unit to the center chain (interstitial-like dispiration) increased the crystal energy by an amount of 49.2 kJ/mol, removing one CH_2 -unit from the center chain (vacancy-like dispiration) by 88.4

Figure 2 View of $(\text{CH}_2-)_x$ in a crystal along the c -axis.

chain rotation needed for dielectric relaxation. The other defects have also been linked to structure-sensitive properties [22]. In particular a 180° chain twist with tensional or compressional matching of the lattice register far away from the twisted region was proposed and linked to the α -transition of polyethylene. Mansfield and Boyd [23] used harmonic intramolecular forces as an approximation and thus this defect could be described as a soliton [24]. A detailed summary of the experimental facts concerning the mechanical and dielectric relaxation processes and the microscopic mechanism proposed in semicrystalline polymers was given by Boyd [25]. Infrared analysis can possibly detect the existence of such defects [26]. The realistic mobile conformational defect was called a twiston.

Conformational Energy of Polyparaxylylene as a function of the rotation angle about the CH_2 -phenyl- CH_2 bonds

Figure 1 Molecular mechanics result for polyparaxylylene.

kJ/mol. In the same way the authors calculated the energies of disclinations (two chain twists at constant number of CH_2 -groups, 72.1 kJ/mol), interstitial-like dislocations (62 CH_2 -groups as center chain, 98.9 kJ/mol, 196.2 kJ/mol), and twist (180° , 62.1 kJ/mol 90° , 32.7 kJ/mol) and dislocation boundaries (interstitial-like, 31.8 kJ/mol).

The interstitial-like dispiration was suggested to provide the simplest and lowest energy process for mass transport along the chain and may also provide

A succession of kinks, as described in Part I, above, was also used to model the folding of chains at crystal surfaces [27]. For helical polymers helix reversals (ambidextrons) have been proposed as major defects [28].

All these efforts are based on more or less simplified applications of Eqs. (1)–(4), below, and have led to what may be called the classical defect model of polymer crystals. The main draw-back of these descriptions are the uncertainties introduced by neglecting the coupling between the various degrees of freedom at conditions away from minimum energy. To gain insight into the dynamical behavior it is necessary to develop a full-scale simulation of the polymer crystal, as will be described in the last two parts of this paper.

III. MOLECULAR DYNAMICS SIMULATION OF THE POLYMER CRYSTAL

The molecular dynamics method (MD) is well known and has been recently reviewed [29]. Basically one needs to solve Hamilton's equation or any other formulation of the classical equation of motion starting from some initial positions and momenta of all atoms:

$$\dot{q} = \partial H / \partial p \quad \dot{p} = -\partial H / \partial q \quad (1)$$

In our MD simulations the integrations were carried out with an up to 12th order predictor/corrector routine [30] with a variable time step to gain sufficient accuracy. As a result, total energy, angular and linear momenta were conserved to at least four digits without the need of *ad hoc* scaling. A highly efficient program permitted simulations of up to 0.1 ns for up to 6100 atoms [31]. The Hamiltonian for Eq. (1) takes the form:

$$\begin{aligned} H = & \sum_{n=1}^m \left[\sum_{i=100(n-1)+1}^{100m} \frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2M} + \sum_{i=100(n-1)+1}^{100m-1} V_{\text{bond}}(r_{i,i+1}) \right. \\ & + \sum_{i=100(n-1)+1}^{100m-2} V_{\text{bend}}(\theta_{i,i+1,i+2}) + \sum_{i=100(n-1)+1}^{i=100m-3} V_{\text{introt}}(\tau_{i,i+1,i+2,i+3}) \left. \right] \\ & + \sum_{i=1}^{100m} \left[\sum_j V_{\text{nonbonded}}(R_{i,j}) + \sum_{k=1}^{100l} V_{\text{nonbonded}}(R_{i,k}) \right] \end{aligned} \quad (2)$$

where the first sum of nonbonded interactions runs over all pairs of mobile atoms; not treated in Eqs. (3)–(5), below, and the second sum of nonbonded interactions runs over all fixed atoms k which retain a constant volume on the outside of the dynamic part of the crystal (see Fig. 2). Equations (3)–(6) represent the various potential energies for a crystal of m mobile chains of 100 atoms each, given a crystal thickness of about 12.6 nm. All distances in the equations are in nm and the potential energies V are given in kJ/mol.

1. *Rotation about the backbone bond by the angle τ* : [32]

$$V_{\text{introt}}(\tau) = 8.3704 - 18.4096 \cos \tau + 26.78 \cos^3 \tau \quad (3)$$

This equation represents the molar energy change on rotation about one backbone bond, starting from the *trans* conformation ($V=0$, $\tau=180^\circ$). It does not include interactions beyond the next nearest chain atoms to the rotated bond (4-body interaction), and in its

application one assumes constant bond distances and bond angles, and treats only the isolated chain (no intermolecular interactions).

2. *Bending of the valence angle, θ :* [32]

$$V_{\text{bend}}(\theta) = 65.061(\cos 113^\circ - \cos \theta)^2 \quad (4)$$

In Eq. (4) one considers the change in potential on bending the valence angle between three successive chain atoms (3-body interaction). Again, all intermolecular interactions beyond the three involved atoms, as well as rotation about the backbone away from the all-*trans* conformation, changes in bond length, and intermolecular interactions are not considered in this equation.

3. *Bond-length change to the value r :* [33]

$$V_{\text{bond}}(r) = 334.72(1 - e^{-19.9(r-0.153)})^2 \quad (5)$$

The 2-body interaction along the backbone chain is expressed by Eq. (5). By using the Morse equation, the often used harmonic-oscillator approximation is avoided.

4. *Nonbonded interaction between atom pairs:* [32]

$$V_{\text{nonbonded}}(R) = 1.9748 \left[\left(\frac{0.4335}{R} \right)^{12} - \left(\frac{0.4335}{R} \right)^6 \right] \quad (6)$$

In this last equation one considers with a Lennard-Jones 6-12 potential the dispersion forces between any pair of atoms not involved with both atoms in Eqs. (3)-(6).

An effective temperature T :

$$KE = \frac{3}{2}NkT = \sum_{i=1}^{100m-1} \frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2M} \quad (7)$$

could be computed after thermal equilibrium was reached (1-4 ps). For efficiency of computation the CH_2 -groups were collapsed to a single atom of mass 14 amu. The computation times needed for a single run on the CRAY XMP or IBM 3090 supercomputers were from 2 to 16 h. A typical result is shown in Fig. 3 as a time sequence of drawings of the lower third of a crystal of seven dynamic chains [34]. The total energy was initially added randomly as purely kinetic energy, subject to a zero center-of-mass velocity constraint. To estimate the effects of the potential coupling between stretching and bending, and stretching and torsion a number of runs were made including switching functions [35]. The effect of these was, however, small as long as the

Figure 3 Conformational disorder, seven-chain simulation.

temperatures were far from bond dissociation [34]. Much larger effect were observed on increasing the intermolecular forces, as experienced when going from constant-pressure simulations (no retaining ring of rigid chains) to constant-volume simulations (with 37, 19, and 7 mobile chains).

The surprising observation was that more than 100 K below the melting temperature significant conformational disorder is produced as shown in Fig. 3 [34, 36]. Many Isolated rotational isomers were created and quenched randomly. (Counted as soon as the rotation angle τ exceeded $\pm 90^\circ$ from the *trans* conformation). Their rate of formation is displayed in Fig. 4.

Figure 4 Rate of formation of conformational defects.

The population of rotated bonds for the constant-volume, 19 mobile chain model is shown in Fig. 5 as a function of temperature. The lifetimes of the defects range from a fraction of a picosecond to 10 or more picoseconds. The longer lifetimes are observed for the less restrictive intermolecular forces. Similarly a maximum in defects with τ closer to the *gauche* conformation seems to be favored by less restrictive molecular forces [34]. The increased potential energy due to the conformational defects was in qualitative agreement with the observed increase in heat capacity in the same temperature range [37].

Overall this MD crystal simulation showed [34] that random, uncorrelated conformational disorder was governed by three processes:

1. the intramolecular dynamics leading to local isomer transitions;
2. the number of intermolecular collisions; and
3. the restrictiveness of the crystal environment.

These initial conformational defects do not correspond to a potential energy minimum and can thus not be predicted by molecular mechanics calculations. They are more likely the result of the dynamic interaction of skeletal vibrations [Eqs. (4)–(6)] and internal rotations [Eq. (3)] [34].

In addition to forming the basis of the defect discussion in Part IV these MD simulations have also been used to calculate vibrational spectra without making use of the normal mode approximation [38]. Furthermore, high-power laser interaction with crystals

Figure 5 Population of conformational defects.

was simulated [39]; chemical reactions such as pyrolysis and reaction of atomic oxygen were analyzed [40]; initial progress was made to describe the melting and crystallization kinetics [41], and a project has been started to model the probing of polymer surfaces with an atomic force microscope [42].

IV. THE SIMULATION OF DEFECTS

Based on the MD simulation described in Part IV one can now look for possible point defects and a microscopic mechanism for structure-sensitive macroscopic processes. The crystals that were treated up to now are equilibrium crystals (extended-chain crystals) and the simulations usually did not exceed 30 ps. No correlated motion of the defects could be observed. Figure 6 shows a typical plot of defects in the central mobile chain of a very restrictive crystal of 7 dynamic chains, surrounded by 12 fixed chains (see Fig. 2). The defects are created and destroyed quickly. The high simulation temperature is chosen in order to display many defects. There exists also no correlation of the initial defect with the defects of neighboring chains [43]. The defects are largely isolated and show no diffusion to different locations. The lack of appearance of any stable progression of these defects may be a signature of chaotic motion [44] in these many-body systems.

Increasing the number of dynamic chains leads to the defect situation depicted in Fig. 7 [34]. The lifetime of the defects is increased, predominant sequences that could be characterized as $g^{\pm}tg^{\mp}$ appear. From the measured average chain-length at 440 K there is a shortening by about 1 nm, or an equivalent of four

2g1 defects, in approximate agreement with Fig. 7. Any introduction of geometric defects (by rotation of an initial two-bond sequence) or kinetic defects (by addition of kinetic energy pulse) has no lasting effect on the defects. The initially created defects disappear

Figure 6 Simulation with seven dynamic chains.

Figure 7 Simulation with 19 dynamic chains.

as quickly as the randomly generated thermal defects [43]. At lower temperature (135 K) these introduced point defects show also only lifetimes of less than one picosecond. Defects within single chains are thus unstable.

Figure 8 shows a sequence of perspective drawings of the lower half of a simulated seven dynamic chain crystal into which a twist defect, as discussed in Part III, has been introduced. The defect is

located in the center chain. The atom which is marked with a circle at the bottom of the crystal shows that below the defect, the chain is not in crystallographic register. The lifetime of the defect is less than 2 ps and the travel of the defect goes to the nearest crystal surface at the shown simulation of 320 K. Even at 50 K the defect was not frozen, but was destroyed within 2 ps [45]. Once any of the large defects described in Part II have been formed by overcoming the high energy of formation, their lifetime is very short. The thermal generation of these defects is such a rare event that they cannot be observed in the simulation time. The direction of travel is determined by the existing free energy gradient. In the thermally generated defects no gradient existed and no travel was observed. Application of an external force to simulate a free energy gradient does, however, lead to motion of the thermally generated defects [42]. The twist defects travel along the low free energy path towards the nearest crystal surface as is shown in Fig. 8.

Figure 8 Simulation with seven dynamic chains.

The next step of analysis is the introduction of an external force. Adding a constant mechanical pull on the center chain produces mass transport, as is needed for crystal thickening observed during annealing and permits to observe the simplest steps of crystal deformation.

Figure 9 shows an example of a pull with 7, 14, and 280 pN at 500 K on the central chain of a crystal of seven dynamic chains of 100 atoms each (see Fig. 1). These forces are of the order of magnitude of the torsional coordinate [Eq. (1)], but should not affect significantly the bending and stretching coordinates [Eqs. (2) and (3), respectively]. For comparison, typical forces for cold drawing of

Figure 9 Motion of a chain on application of a force.

polyethylene are smaller still by a factor of 1/10. This is perhaps not surprising since there is no stress concentration in the model, and the chosen crystal has a very restrictive intermolecular potential. Increasing the size of the simulated crystal, thereby reducing the restrictiveness of the intermolecular potential, causes a significant decrease in the activation energy for the motion of a polyethylene chain by one lattice step. For the model with 37 dynamic chains at constant pressure, for example, a 1.0 pN force resulted in the complete removal of a 100 polyethylene chain of CH_2 -groups in 0.25 ns [34]. At the lower forces a hopping mechanism is observed, while at the highest force a constant velocity is attained [46].

The next step involves the application of a constant force at a given position of the crystal, trying to twist the polymer chain, as is observed for an electric field operating on a dipole. The presently still preliminary observations show that twists of the chain can be observed, but that other than the expected full alignments reach stability for reasonable lengths of time [47]. It is hoped that movies of these simulations will reveal more of the intermediate steps of defect geometry, motion and energetics.

SUMMARY AND OUTLOOK

Considerable insight into the defects in polymer crystals had been gained by studying the geometrical structure and by molecular mechanics calculations. Although providing useful information, the rotational isomer model and the minimum energy calculations of molecular mechanics could, however, not resolve the detailed nature of the defect state, seemingly because of the coupling of skeletal vibrations and intramolecular rotation. The rotation of a single bond in a crystal by more than 90° was considered impossible because of the high energy when considering the stationary crystal. It turns out that this conformational defect seems to be the basic step in all defect formation and motion. The development of sufficiently powerful computers and more efficient programming has made the first inroads to a full defect crystal description and its link to macroscopic, structure-sensitive properties. With the present computation capability many of the problems of the solid state of macromolecular crystals can be tackled and we expect a substantial advance in the understanding of the solid state behavior on macromolecules. As usual, this new knowledge should also influence the other areas of solid state physics and materials science.

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