

Computer Simulation

Molecular Dynamic Simulation of Motion in Solid Polymers. Rotator Phase of n-Alkane

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Abstract

The method of molecular dynamic computer simulation is applied for the investigation of structure and dynamics of C₁₀-n-alkane in the solid state. Analyzed is the behaviour of individual molecules as well as of a whole crystal. The investigated system consists of 31 molecules of C₁₀-n-alkane at the temperature 150-275 K. The influence of chemical defects, such as methylene group or chlorine atom, on the dynamics of the system is considered.

Introduction

The structure and the properties of amorphous polymers in the glassy state attract an ever increasing attention of investigators /1/. Emphasis is placed on the nature of chain mobility in a solid phase, on the geometry and the energy of moving entities and on the relation between mobility and concentration of different defects. Successful application of the method of molecular dynamic (MD) simulation to polymeric systems /2,3/ seems to make it promising for the investigation of solid polymers.

To ascertain what part various types of defects play in the formation of amorphous polymeric structures, we attempted earlier to investigate this problem from a model of the internal region of a polyethylene single crystal into which various physical and chemical defects could be introduced /4,5/. It turned out that in the temperature range 155-275 K the model corresponded to the "rotator" or "hexagonal" phase of n-alkanes which was subjected to intensive study last years /6-11/. It has been recently found that along with the rotational mobility of molecules this phase exhibits intensive dynamics of backbone torsional angles /6,8/. This fact makes it difficult to interpret some experimental data and requires more careful investigation of the behaviour of the n-alkane rotator phase /12-14/.

In this paper we present some results of the MD simulation of structure and dynamics of C₁₀-n-alkane based on the previously reported structural cell /4,5/. We believe this analysis is the first step in the MD investigation of amorphous polymers in the solid state.

Description of the model

For the computer simulation (Fig.1) we have taken a cell in the form of rectangular parallelepiped with 31 molecules of $C_{10}H_{20}R_2$. The long axes of molecules were aligned along the z -axis. 14 molecules were arranged at the boundaries of the cell (black molecules in Fig.1). During simulation experiments all the boundary molecules were motionless and preserved the form of a planar zigzag, their arrangement corresponding to an ideal orthorhombic lattice. The residual 17 molecules moved during the simulation to agree with their intra- and interatomic potentials.

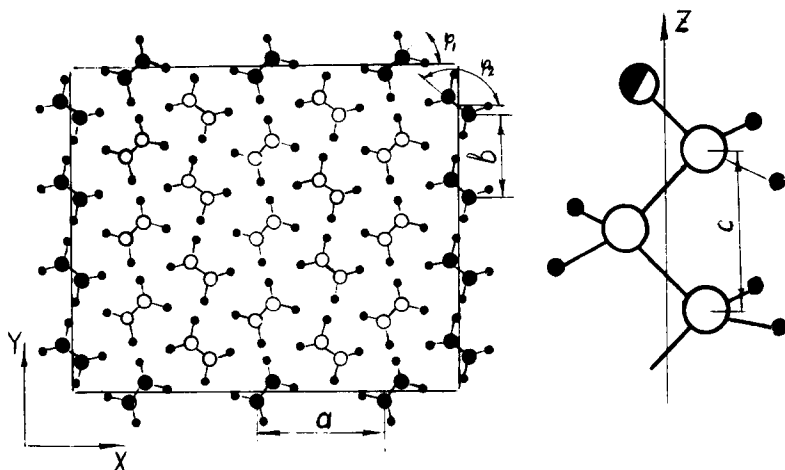


Figure 1: the structural cell for the computer simulation. \circ , \bullet - C-atoms, \cdot - H-atoms, \bullet - end group R. Chains with \bullet - marked C-atoms were kept immobile during the simulation (boundary chains). Their location corresponds to the orthorhombic lattice. Chains with \circ - marked C-atoms were mobile. Their positions shown in Fig. are regular, whereas in the simulation they usually vary.

The atoms of each molecule were represented by material points, and lengths of all chemical bonds were fixed. The valence angles could vary and were preset by potential

$$U(r) = D \cdot (r^2 - r_0^2)^2, \quad (1)$$

where r is the distance between the non-bonded atoms in the valence angle, and $D = 2 \cdot \text{kcal} \cdot \text{mol}^{-1} \text{Å}^{-4}$. All non-bonded atom-atom interactions were introduced by Lennard-Jones potential

$$U_{LD}(r) = 4 \cdot \epsilon \cdot \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

Parameters ϵ and σ of the potential (2) were chosen from the coincidence of the position and the depth of the potential minima with those of Williams /15/.

In most of simulations chain-end atoms R of mobile chains were bonded with the boundary planes (z-planes) by potential:

$$U_b(z) = C_b(Z_b - z)^2, \quad (3)$$

where z is z-coordinate of atoms R, Z_b is the coordinate of Z-plane and $C_b = 1 \text{ kcal} \cdot \text{Å}^{-2}$.

Chemical defects were introduced into the system by the substitution of $-\text{CH}_3$ (Me) or $-\text{Cl}$ for H-atom in the centre of the cell. The group $-\text{CH}_3$ was the material point with the corresponding parameters. The values of the parameters used are given in Table 1.

TABLE 1

The values of the parameters for calculations.

Masses of atoms, a.e.	Bond length, Å	r_0 in eq. (1), Å	ϵ in eq. (2) ⁻¹ , kcal·mol ⁻¹	σ in eq. (2), Å
$m_H=1$	$l_{CH}=1.090$	$r_{CC}=2.498$	$\epsilon_{HH}=0.013$	$\sigma_{HH}=2.25$
$m_C=12$	$l_{CC}=1.534$	$r_{CH}=2.161$	$\epsilon_{CC}=0.097$	$\sigma_{CC}=3.45$
$m_R=12$	$l_{CR}=1.090$	$r_{HH}=1.775$	$\epsilon_{CH}=0.043$	$\sigma_{CH}=2.85$
$m_{Me}=15$	$l_{CMe}=1.534$	$r_{CMe}=r_{CCl}$	$\epsilon_{CMe}=\epsilon_{CCl}$	$\sigma_{CMe}=\sigma_{CCl}$
$m_{Cl}=35.5$	$l_{CCl}=1.534$	$=2.509$	$=0.140$	$=3.45$
		$r_{HMe}=r_{HCl}$	$\epsilon_{HMe}=\epsilon_{HCl}$	$\sigma_{HMe}=\sigma_{HCl}$
		$=2.152$	$=0.080$	$=2.85$

Computational procedure

Equations of motions for the 17 mobile molecules were integrated known algorithm /16/. The time step for the integration was $2 \cdot 10^{-3}$ ps. The fluctuations of the total energy of the system over the whole run (about 10 ps) were smaller than 0.2%. The temperature of the system was determined from the average kinetic energy per degree of freedom.

Initially, all the molecules were arranged in the cell to make an ideal orthorhombic polyethylene crystal /17/. The parameters of this cell were: $a=7.25$ Å, $b=4.95$ Å, $c=2.53$ Å and setting angles $\psi_1=45^\circ$, $\psi_2=135^\circ$ (Fig.1). A special procedure was used to obtain the equilibrium parameters of the cell such that they agreed with the chosen interaction potentials (1-3), temperature and equalled zero external pressure. The atoms of the 17 mobile chains were given random momenta corresponding to 370 K, and the motions of all the atoms over the period of 10 ps. Then a special run of 10^4 time steps was performed. Unlike the other runs, the parameters a , b and c of the boundary chains varied slowly with the internal pressure. Over the run the total energy of the system slowly reduced.

At some moments the dimensions of the cell were fixed, and the obtained coordinates and velocities of atoms were taken

as initial for further simulation. The value of the parameters a, b and c, density of the system and temperature of the performed runs are given in the Table 2.

TABLE 2
Lattice parameters, density and temperature
over the MD runs.

The type of defect	Tempe- rature, °K	Lattice parameters, Å			a/b	Density, g·cm ⁻³
		a	b	c		
without defect	155	7.08	4.38	2.517	1.62	1.20
"-	200 ^a	7.21	4.45	2.485	1.62	1.17
"-	210	7.21	4.45	2.492	1.62	1.17
"-	235	7.22	4.46	2.491	1.62	1.16
"-	275	7.34	4.52	2.463	1.63	1.15
methyl	275	7.32	4.54	2.466	1.61	1.14
Cl	275	7.32	4.54	2.460	1.61	1.14

^aIn this case the potential U_0 was not used.

Results

1. Crystal structure. Configurations of 17 mobile chains in their positions inside the structural cell were determined by the total energy of the system and the boundary conditions. Therefore in the computer simulation it was necessary to check the arrangement of the molecules in the cell and to compare them with the ideal lattice parameters.

The analysis showed that the system was crystalline over all the runs. We have calculated the average projections of the centres of masses of molecules (c.m.) onto X,Y plane and their standart deviations. It has been revealed that the projections of c.m. of the chains fluctuate with small amplitudes (<0.2 Å) around the average positions of a regular lattice with parameters close to a and b values of Table 2. The values a, b, a/b and their temperature dependence are rather close to the X-ray experimental data for the rotator phase of n-alkanes /7/ (a and b for 17 mobile chains deviate from experimental values by 4% and 14%, respectively). The c-value is normal for n-alkane chains (1% of deviation from experiment).

Restricted mobility of molecules along their axes caused by the potential (3) does not practically influence the mean parameters of the crystalline cell at 200 K.

Chemical defects into the cell do not affect the average sizes of the cell due to their small concentration (4 defects per 1000 carbon atoms).

Thus in the above parameters the system is similar to n-alkanes in the rotator phase.

2. Molecular conformations. As is found, all the backbone

torsional angles (TA) fluctuate around the trans-positions with variable amplitudes. At the temperature higher than 210K one can observe fluctuations of TA from 60° to 120° with lifetime up to 3.5 ps at 275 K. This may be termed as gauche conformations in the chains.

The careful analysis of these gauche conformations existing at 275 K for a period longer than 0.5 ps has revealed single g^\pm conformations in 40% of all the cases. The conformations like g^+tg^- were observed in 22% of all the cases. We have also found the g^+g^+ (7%), $g^+g^+g^-$ (15%) and $g^+g^+g^+g^-$ (5%) conformations.

The chemical defects affect substantially the dynamic behaviour of the TA. The skeleton chemical bonds nearest to the defect appear only in trans-conformations and have TA amplitudes much smaller than the average value for the other TA.

3. Valence angles. The potential (1) is chosen such that the equilibrium value of the CCC-angles is identically 109.5° . But the average CCC-angles in all the mobile chains measured over each run were equal to $111.5 \pm 1^\circ$, which is in good agreement with experimental data /17/. The valence angles are independent of the chain position within the structural cell and of the temperature, though we can observe small systematic fluctuations ($\pm 0.3^\circ$) along the chain.

4. Rotating mobility of molecules. Since all the molecules in the cell in average exist in planar zigzag conformations we can determine the momentary plane of the carbon atoms for each molecule. All simulations have shown a wide spectrum of motions of these planes changing from a rather fast rotation to weak vibrations around equilibrium. The intensity of these rotations increases with the temperature.

No correlation between rotational mobility of the molecules, their average orientation and the position in the structural cell has been observed. However, at 155 K the system tends to the orthorhombic phase: some molecules located close to the boundary vibrate near the positions corresponding to the regular orthorhombic lattice of n-alkanes.

Fig.2 represents the average coefficients of rotational diffusion D_r for mobile molecules versus temperature. D_r was determined as ratio of mean square deviation of the rotation angles to time, here the time is equal to 1 ps. It is interesting, that the order of magnitude of D_r value is close to experimental data /4/.

The temperature and chemical defects influence markedly the dynamics of rotational mobility: the rotational mobility of the defective chain and of surrounding chains is less. The deceleration of the rotation is accounted for by the increase both the average inertia moment of the defective chain and the interchain friction due to the defect volume. The value of D_r for surrounding chains drops when introducing defects but is practically independent of the defect mass.

The examination of various factors characterizing the structure and the dynamics of single molecules in the model has shown that they do not depend on their position in the structural cell. This indicates that the boundary conditions are not too bad, though the potential U_b may considerably in-

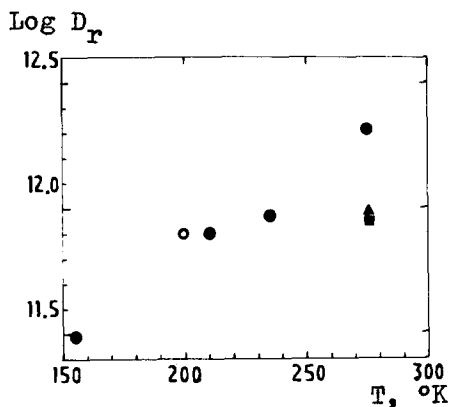


Figure 2: Logarithms of coefficients (D_r) of rotational diffusion of n -alkane chains vs temperature.

- - runs without chemical defect;
- - run without potential U_b ;
- ▲ - run with the methyl-defect;
- - run with Cl defect.

fluence molecular dynamics above 200 K.

Qualitative analysis of the rotational mobility of molecules proved it more complex than was previously assumed /12-14/. For example, no sudden rotations of single molecules or groups of adjacent molecules through large angles (90° or 180°) were observed. We have neither found explicit relation between longitudinal diffusion of molecules and their rotational mobility. It is clear that this problem needs further investigation.

It should be noted that such a strong influence of the chemical defect upon the rotational mobility may be taken into consideration when analysing mobility of chemically labeled systems.

The study of the dynamics of solid polymeric systems of higher defect concentrations is in progress.

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