Computer Modelling of Structure and Dynamics of C-50 n-Paraffin Crystal, Hexagonal Phase of C-50 Crystal and Ethylene/Propylene Statistical Copolymers

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SUMMARY: 3D crystal of n-paraffin C-50 was created by computer molecular dynamics method. The crystal consists of 48 chain molecules containing 48 $-CH_2-$ groups and two $-CH_3$ end groups each. Constant temperature-constant pressure calculations, spatially periodic boundary conditions, integration step 0.001 ps were used. Chemical bonds were treated as absolutely rigid, bond angles bending were treated trough $U(\theta)=^1/_2K_\theta(\theta-\theta_0)^2$ function and torsion rotations trough $U_\varphi=C_\varphi/2[1+Z_\varphi(3\cos^3(\varphi)-2\cos(\varphi))]$ function. Non-bonded interactions were represented as truncated and shifted L-D 6-12 potential function. All atoms were introduced explicitly. At 200K and 36 ps of relaxation we got computer C-50 crystal with orthorhombic symmetry (o-phase) and cell parameters a=7,416Å, b=4,723Å, c=2,625Å and density ρ=1,014 g/cm^3 which are close to known from literature. Heating of the crystal up to 450K have shown thermal expansion along all crystallographic axes well coinciding with known experiment. At 400K the system posses transition to hexagonal phase (h-phase). At 450K the crystal melts, but high orientation of chain axes still exists in the system. Analysis of rotational and translation mobility of h-phase at 400K have shown that all chains undergo fast rotation around chain axes for angles about 200-360^0 during 15 ps. Quenching of the h-phase to 200K decrease the rotation amplitude up to ±12^o corresponding to vibrations. The same type vibration motions (around chain axes) exists in o-phase at 200K. Replacing of some H-atoms in chains of initial crystal by $-CH_3$ groups gave us the possibility to mimic Ethylene/Propylene copolymers. In this work we have created only random E/P copolymers with propylene (PP) units content up to 20%. At constant temperature (200K) increase of PP units in the copolymer produce a disordering

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initially perfect C-50 crystal. The process goes anisotropically: long range order becomes violated along ***b***-direction of the initial crystal at [PP]=3,5% and along ***a***-direction pronounced order still exists at [PP]=10%. Analysis of structural alterations which appear in the system upon introduction of chemical defects (-CH_3 groups) was done by calculations of local volumes (V_{loc}) of each site containing three chain carbon atoms with the closest neighbours from the surrounding chains. Increase of [PP] concentration in copolymer increases V_{loc} and broaden it up considerably. The result shows broad distribution of crystalline cell sizes in copolymers. Local volumes of cells containing -CH_3 groups might be larger or smaller than mean V_{loc} value. Some conclusions about conformation defects in chains appearing due to "copolymerisation" (appearing of PP-units in chains) are drawn.

Introduction

Many laboratories in the world, both, academic and industrial, are active now in the field of synthesis, characterisation and measurements of properties of ethylene and propylene copolymers with different α-olefins [1,2]. Variety of catalytic systems are used for preparation of the copolymers with different microstructure of chains [3,4]. Such parameters of the copolymer macromolecular structure as length of branches, comonomer concentration and distribution of comonomers along main chains are responsible for variation of many macroscopic properties of the copolymers.

We have decided to take insight into the problem with methods of computer simulation. Computer "synthesis" of olefin copolymers with different type and concentration of comonomer open good possibility to follow for details of local and global structural and dynamic features of macromolecules in the copolymers.

The general strategy of our approach was the following.

1. Creation of initial system consisting of long -(CH_2)- chains, to which we would be able on the later simulation stages to introduce co-monomers (chemical defects) of different types and concentration. As an initial system we choose the chains of n-paraffin C-50 (48 -CH_2- groups and 2 end -CH_3 groups) which were arranged in 3D crystal consisting of 48 such chains.

2. Computer "synthesis" of copolymers. Basic procedure for synthesis in our case was an introduction of chemical defects replacing one H-atom in -CH_2- groups of n-paraffin chains (substitution defects). Clearly, by using of this procedure one may introduce into -CH_2- chains chemical defects of different nature and length with steriochemical variations of the each substitution and also with different distribution of the defects along n-paraffin chains.

In this paper we will consider only one type of chemical defects namely -CH_3 groups which have substituted H-atoms of paraffin chains statistically which mimics random E/P copolymers. By using the same procedure we have introduced in the C-50 chains groups of

other type, such as: butene, hexene and octene. However, structure and dynamics of these copolymers we will consider in other our publications.

3. Analysis of structure and dynamics of chains in the bulk of computer synthesised copolymers. During this step we were able to follow structural alterations of initial crystal upon introduction of defects of any kind, with different concentration of defects or upon introduction blocks of them. Local and global dynamics of chains with defects was also the question of this calculation stage.

4. And last stage of the approach will be the "measurements" of macroscopic properties of the computer copolymers. We are planning in near future to compute such properties as: T_m, T_g, C_p, E (Young modulus) and it's anisotropy, density. This paper is the first one in the announced approach and we will mainly concentrate our attention on:

-Preparation of initial crystal of CH_3-$(-CH_2-)_{48}$-CH_3 containing 48 chains of this type, careful check of its structure and compare the computed structural results with experimental data from literature;

-Analysis of the hexagonal phase of C-50 appearing at heating of initially orthorhombic C-50 phase;

-Statistical introduction of -CH_3 groups in C-50 chains as substitution defects up to 20% of PP units and analysis of structural and dynamic features of the copolymers.

The Model and Method of MD Simulation

We have used molecular dynamic (MD) simulations with general approach described in [5,6]. All atoms of n-paraffins were introduced explicitly. But -CH_3 groups as the substitution defects were introduced as united atoms (pseudo-atoms) of mass 15 amu. The bond lengths were fixed, bond angles bending were represented as $U(\theta)=^1/_2K_\theta(\theta-\theta_0)^2$, and torsional rotations as $U_\varphi=C_\varphi/2[1+Z_\varphi(3\cos^3(\varphi)-2\cos(\varphi))]$. Interaction of the atoms separated by more than two neighbours or belonging to different molecules was governed by the potential with a finite radius of interaction R_{ij}: $U_{LJ}=U_{LJ}(r_{ij})-U_{LJ}(R_{ij})$, $r_{ij}<R_{ij}$, $U_{LJ}=0$, $r_{ij}\geq R_{ij}$, where $U_{LJ}(r_{ij})=4\varepsilon[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^6]$, r_{ij} is a distance between i^{th} and j^{th} atoms, $R_{ij}=2\cdot2^{1/6}\sigma_{ij}$, $\varepsilon_{ij}=(\varepsilon_i\cdot\varepsilon_j)^{1/2}$, $\sigma_{ij}=0.5\cdot(\sigma_i+\sigma_j)$. Values of the potential parameters are listed in Table 1. For the comparison purposes we have also investigated, to a limited extent, 3D crystals of C-100 n-paraffin. In all cases we found good correspondence of structural results for C-50 and C-100, but slower global dynamics in the later case. The equations of motion under geometric constraints were integrated numerically by using the approach developed previously by N.K. Balabaev et al.

[5,6]. The method of Berendsen et al. [7] has been applied for the relaxation processes and simulation of systems at constant temperature and pressure (NPT system). Integration step was 0.001 ps. Introduction of $-CH_3$ was done through random replacing of -H atoms by $-CH_3$ group. Two limitations were taken into account: no one carbon atom of main chain can be connected with two $-CH_3$ groups and replacing -H atoms belonging to three consequent -C- atoms of main chain is denied.

Table 1. Constants used for potential functions.

	Bond lengths	
C-H:	l=1.10 Å	
C-C:	l=1.54 Å	
$C-CH_3$:	l=1.54 Å	
	Bond angle bending	
C-C-C:	θ_0=112.0	K_θ=19.34 Kcal/mol
H-C-H:	θ_0=109.5	K_θ=31.22 Kcal/mol
H-C-C:	θ_0=108.8	K_θ=20.57 Kcal/mol
	Torsional rotations	
C-C-C-C	C_φ=3.01 Kcal/mol,	Z_φ=1.0
C-C-C-H	C_φ=3.01 Kcal/mol,	Z_φ=1.0
	Non-bonded interactions	
ε_{C-C}=0.040 Kcal/mol,	σ_{C-C}=0.365 nm	
ε_{H-H}=0.029 Kcal/mol,	σ_{H-H}=0.236 nm	
$\varepsilon_{CH3-CH3}$=0.060 Kcal/mol,	$\sigma_{CH3-CH3}$=0.380 nm	

The starting set of atomic coordinates was prepared by location of perfect trans-chains at positions of the perfect orthorhombic PE crystal [8]. Initial system contained 48 n-paraffin chains of $C_{50}H_{102}$ in computational box with spatially periodic boundary conditions. Than, at 200K system relaxed. When saturation of energy, cell parameters and density of the system was reached we stopped the calculations and analysed structure.

Results

C-50 Crystal

At Fig.1 initial crystal which have appeared after 36 ps relaxation of starting system at 200K is shown. The crystal shows orthorhombic symmetry (o-phase, Fig.1c) with crystallographic cell parameters (for crystal without chain ends) a=7,416Å, b=4,723Å, c=2,625Å and density ρ=1,014g/cm^3 which well corresponds to experimental data [8,9]. Some fine details of the structure are well reproduced in the simulation. In the projections *(ac)* and *(bc)* chains of n-paraffin are a little inclined. This effect appears due to the tendency of chain ends (-CH_3

groups) reach high packing density with the same chain ends of next cell (spatially periodic boundary conditions).

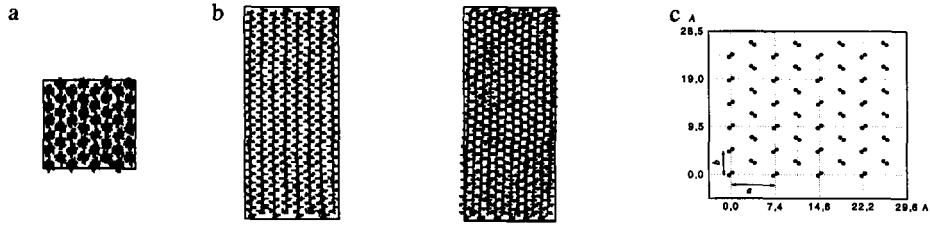


Fig.1: (a,b). Time average projections of C-50 crystal on crystallographic planes ***(ab)***, ***(ac)***, ***(bc)***. The structure had appeared in computer after 36 ps relaxation of starting structure at 200K. (c). Time and space average projection of the crystal on ***(ab)*** plane at 200K. Orthorhombic symmetry is clearly seen.

Obtained computer crystal has appeared to be very perfect from conformational point of view. Only one chemical bond through all chains exists in the *gauche* (g^+=300±10°, g^-=60±10°) conformation (from total number of such bonds in the system is 2256). Change of fraction of *g*-conformations in the crystal at heating is shown at Fig.2.

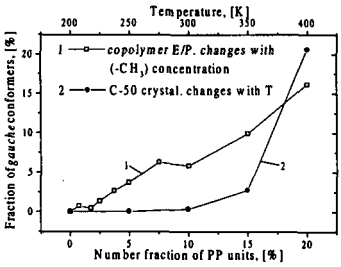


Fig.2: Content of *gauche*(±) conformers in C-50 crystal as a function of: concentration of $-CH_3$ (PP units) groups in the system at 200K (1), temperature (2).

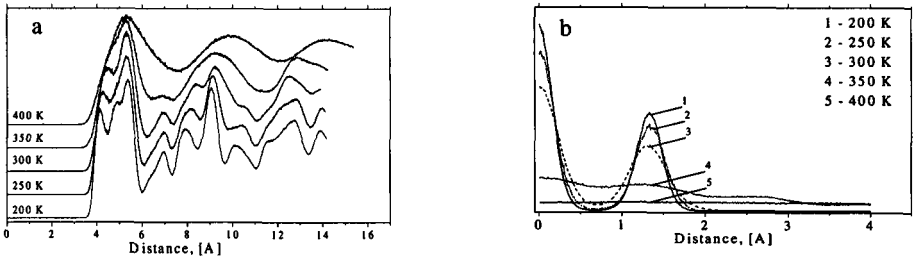


Fig.3: (a). Calculated 3D Radial Distribution Function (RDF) as a function of temperature for all atoms in the system. (b). Distribution function of register shift of adjacent chains along crystallographic ***c***-axes direction.

The long range order of the C-50 computer crystal is clearly reflected in calculated of intermolecular 3D Radial Distribution Functions (RDF) represented at Fig.3. Many well resolved peaks clearly seen at the RDF at low T (Fig.3a). Above 350K RDF curves loose their fine details, which reflects disordering of the system. At 450K system melts. At Fig.4a the loss of positional order for chain axes at ***(ab)*** plane is evident.

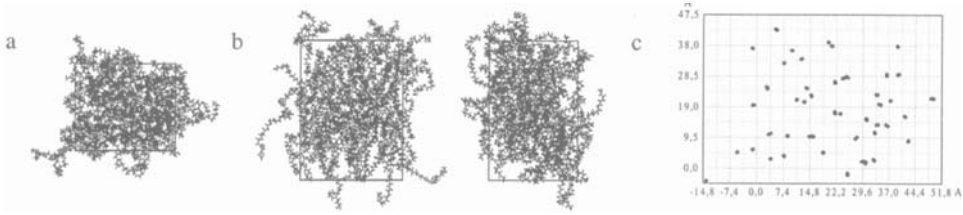


Fig.4: (a,b). Time average projections of C-50 crystal on crystallographic planes ***(ab)***, ***(ac)***, ***(bc)***. The structure had appeared in computer after 120 ps relaxation of initial structure at 450K. (c). Time and space average projection of the crystal on ***(ab)*** plane at 450K.

Intermolecular register of chains along ***c***-direction disappears completely at 400K (Fig.3b). However, chains still keep high level of orientation (Fig.4b). From the changes of cell parameters with T we have calculated thermal expansion coefficients. Results are shown at Fig.5 together with experimental data [9].

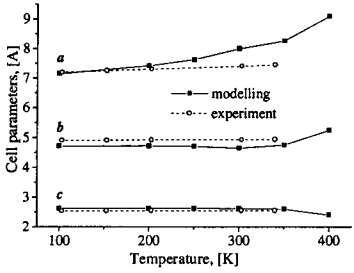


Fig.5: Calculated temperature changes of crystal lattice parameters (solid line), experimental data (doted line [9])

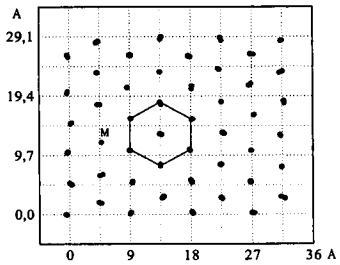
Calculation of 1D RDF for crystallographic directions ***a*** and ***b*** gave the anisotropy of thermal expansion. In the ***b*** crystallographic direction disorder appears at above 350K. In the direction ***a*** it happens at higher T.

All results related to structure and thermal expansion for computer C-50 crystal reasonably well correspond to existing literature data. It is possible, of course, to improve calculated structural data by refining used potentials. However, it is not the goal of our calculations. By using standard set of potentials (Table 1) we were able to get sufficiently good C-50 3D crystal with quite reasonable structural parameters and high enough density. In our view such crystal might be good starting point for computer "synthesis" of copolymers of ethylene with different α-olefins.

Hexagonal Phase of C-50

At T=400K the orthorhombic C-50 crystal posses transition to the new phase with hexagonal symmetry (***a***=9,100Å, ***b***=5,241Å) and density ρ_{400}(h)=0,816g/cm^3 (h-phase). The structure is shown at Fig.6. Chain axes keeps perfect positional order. X-ray diagrams calculated from 3D RDF show the changes corresponding to such transition in PE [10]. The calculated X-ray

diffraction pattern shows the transition from orthorhombic lattice with two most intensity 110 and 200 reflections to hexagonal one.



Hexagonal phases of PE and n-paraffin's became very popular recently [11]. One reason for such popularity is the suggestion that the metastable h-phase may play important role in PE crystallisation [12,13].

Fig.6: Time and space average projection of the C-50 crystal on ***(ab)*** plane at 400K.

Experiments [14] have shown that h-phase of n-paraffin's under normal conditions exists only for n-paraffins not longer than n=43 and does not exists for C-50. However, relation of laboratory experiments to results of computer simulations one has to keep in mind much smaller size of computing cell in comparison with real laboratory size n-paraffin crystals. Recently it was shown [15] that size factor may seriously change the relative phase stability of coexisting phases and h-phase of PE might be more stable at some conditions as compared to o-phase. We believe such situation is realised in our computer experiments. H-phase of -(-CH_2-)- chains should be the "highly mobile phase" [11,12].

We have checked rotational and translation mobility of h-phase of our C-50 crystal at 400 and 200K (quenched sample). Rotational mobility was measured for each -C-atoms in all chains of h-phase. As the mobility measure the positions of bisector vector end during 15 ps was chosen. Way of such vector definition is shown at Fig.7. Result for one h-phase chain (this chain is marked by symbol M at Fig.6) is shown at Fig.7. Each little point is the trace of the bisector vector endor every 0,06ps.

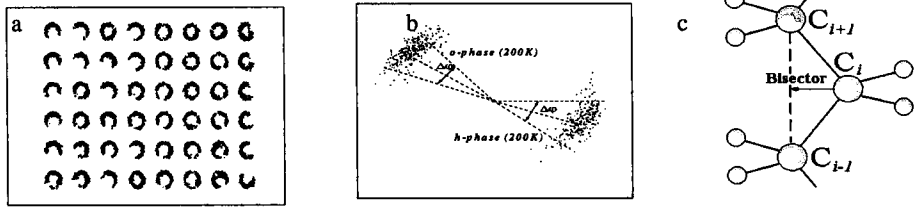
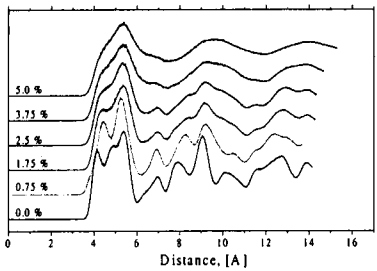


Fig.7: (a) Rotational mobility of one chain (chain M at Fig.6). We have defined the positions of the end of bisector vector (c) during 15 ps at 400K.

From the Fig.7 one can see that during 15 ps each chain C-atom (not chain end C-atoms) show pronounced rotation mobility, wipe out angles from 180 - 220^0 up to 330 - 360^0. The density of little black points reflects the population density of angular positions of the bisector

ends. It is evident that some rotational angles are less populated than others. The same picture is valid practically for all chains in h-phase of C-50. At 200K rotation mobility of the chains in h-phase becomes much lower. It is seen from picture at Fig.7b. At 200K rotational mobility for both h- and o-phases (fast quench of h-phase) looks like vibrations of each -C-C-C- plane with angle ± 12^0 around chain axes. Chains in h-phase at 400K posses also translation mobility along ***c***-axes. Centers of mass of all chains deviate from their initial positions up to 4-7Å during 15 ps. However, translation mobility of chains disappears in the quenched h-phase. These results show that during quenching from 400K to 200K h-phase of C-50 overcame glass transition temperature region. We found that rotational mobility of chains in h-phase happens in correlated manner.

Ethylene/propylene copolymers



Random introduction of -CH_3 groups as substitution chemical defects to C-50 chains leads to serious structural changes of initial o-phase crystal.

Fig.8: Calculated 3D Radial Distribution Function (RDF) for E/P statistical copolymers at 200K for different concentrations of PP units in the system

3D RDFs. show expected isothermal disordering of the system (Fig.8) with increase of the defects content and projection of computational cell on different plans of the initial orthorhombic crystal demonstrate details of such disordering (Fig.9).

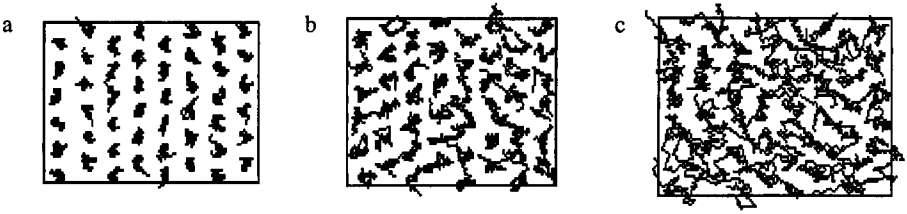


Fig.9: Time average projections of the C-50 system on crystallographic planes of initial crystal with introduced PP units at 200K. Concentration of -CH_3: (a) 2,5%, (b) 10%, (c) 20%

At Fig.10 calculated density changes in E/P copolymers of different compositions. Starting from 5% of PP units calculated density (again without chain end fragments) well corresponds to known experimental data [16]. Evidently, experimental points at lower PP units

concentrations are erroneous, because density of PE crystals should be higher than measured one [16]. Probably initial experimental samples had contained some branches in PE chains due to some mistakes in catalytic chain propagation process.

Calculations of 1D RDF along ***a***- and ***b***-directions of initial crystal gave some additional information about the isothermal disordering process. The disordering goes in anisotropic manner. Long range order becomes evidently violated in the ***b***-direction at concentration PP units about 3,5%, but at ***a***-direction good long range order still exist at 10% of PP units in the copolymer.

There are several models [17] suggesting alterations in chain conformations with appearance of $-CH_3$ groups in PE chains. Computer simulations give the possibility to count easily the accumulation of *g*-conformers in the system with concentration of PP comonomer units.

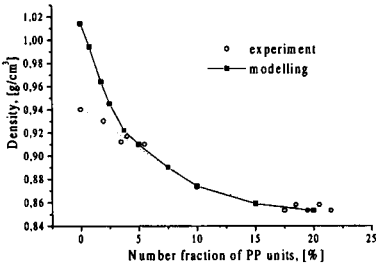


Fig.10 Calculated and experimental density of the system as a function of PP units concentration.

The data are sown at Fig.2 (curve 2). It is clearly seen that the fraction of *g*-conformers starts to grow at about 5% of PP units and increase nearly linearly with concentration of PP units in copolymers. It is evident also that accumulation of *g*-conformers in the system goes in considerably different manner as compared to orthorhombic crystal heating. Introduction of about 18% of PP units to C-50 chains produces the same fraction of *g*-conformers as heating of the orthorhombic C-50 up to 350 - 400K.

One question concerning the incorporation of $-CH_3$ groups into PE crystal lattice had received considerable attention in literature [18]. We have tried to check the situation from our computer data. For this purpose we have constructed the local cells (Fig.11b) and measured the volume changes (V_{loc}) for all such cells in the system (i.e. for all C-atoms) for different composition copolymers. At Fig.11a V_{loc} distributions for several copolymers are shown. Some definite conclusions might be drawn. Introduction of PP units in C-50 crystal increases V_{loc} and broadens up V_{loc} distribution. At small concentrations of PP all local cells containing $-CH_3$ groups are the largest. Long range order in C-50 crystal still exists and $-CH_3$ groups only expand the existing lattice. However, at higher concentration of PP-units $-CH_3$ groups are located in the cells with large and small V_{loc} And V_{loc} distribution becomes so broad (which means that the variation of cell sizes is quite broad also, comparable with mean

size of cell) that long range order can not exist further in the system. It is interesting to check mobility of chain fragments locating in larger and smaller cells (larger and smaller V_{loc}). We are planning to analyse the problem in the following publications.

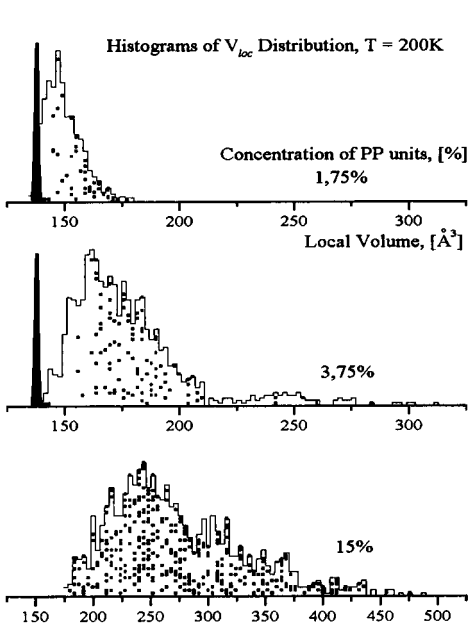


Fig.11: (a) Histograms of V_{loc} distribution for random copolymers E/P for different concentrations of PP units. (b) Definition of V_{loc}.

Conclusion

Results given in this paper show that computer simulation is suitable instrument giving excellent possibility to study the structure and dynamics of chains of PE and PP based copolymers. Especially important is the possibility to follow details of local structure and dynamics of branches and chains in close vicinity of branches and far from them. Incorporation of branches of different length permits to follow local structural alterations of crystal lattice due to appearance of given branch in structure and to analyse local dynamics of chains in such structural sites of the system. Such date is impossible to get by experiments. In near future we are planning to publish detailed results for dynamics of E/P copolymers and change of macroscopic properties of the copolymers. Our next step compute simulation of ethylene copolymers with longer branches, such as: butene, hexene and octene.

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