Digital model of polymer molecules

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Abstract. The article is devoted to the construction and analysis of a digital model of polymer molecules. In this regard, the pseudo-random value generator (the Mersenne Vortex) from the C++ library of the C++11 standard was investigated. A method for spatial modelling of a polymer chain with free and fixed valence angles is developed and described. A software for building polymer molecules with given parameters is implemented within C++. A program for visualization of polymer structures is implemented in C#. Fractal dimensions for polymer chains with different stochastic properties were calculated. The basis for the further development of the software for simulation of radiolysis of polymers has been introduced.

1. Introduction
Currently, worldwide production and consumption of plastics and rubbers are constantly increasing. According to experts, more than 8.3 billion tons of polymers have been produced since the middle of the last century.

In Russia the industry for the production of polymers, particularly, synthetic rubbers, is developed at a fairly high level. However, the overall adherence to technology at the beginning of the second half of the 20th century affects production [1]. Thus, taking into account the global trend to increase the consumption of polymers, particularly, synthetic rubbers, one of the main priorities for the industry as a whole is the intensification of production using innovative technologies to make the final product with desired set of properties [2-3].

Also, there is an important problem of processing and/or disposal of products from polymers that become unsuitable for further use as intended. But for the implementation of such well-known processing methods as pyrolysis, methanolysis, hydrolysis and glycolysis, a high temperature is required, which entails additional energy costs.

One of the most promising methods for processing polymer waste and creating products with desired characteristics is the irradiation of polymers using ionizing radiation, the so-called radiolysis. During the radiolysis many polymer characteristics change, the most important of which is the molecular-weight distribution. Such properties of the final product as tensile strength, chemical resistance and so on depend on the molecular-weight distribution [4].

However, due to a high complexity, this technique is not widespread. To introduce it into production process, it is necessary to develop mathematical and software modelling tools that allow to build spatial models of the internal structures of various polymer materials and reliably simulate the processes occurring during radiolysis.
2. Features of the structure of polymers
In general, a polymer macromolecule consists of numerous repeating elementary units connected via rigid bonds, the so-called monomers.

One of the most important fundamental characteristics of polymer macromolecules is the molecular weight distribution, which describes the ratio of the amount of macromolecules of different molecular weights in the sample [5-7]. For example, the strength of polymers grows while the mass fraction of molecules with high molecular weight increases, but only to a certain limit [8].

Characteristics that describe the internal spatial structure of polymers both in the melt and solution, as well as in the solid state, are the angle of internal rotation (an angle of rotation of some groups of atoms in the molecule relative to others), and the valence angle (an angle formed by directions of chemical bonds from one atom to neighboring). In the case of a carbochain (carbon based) polymer of polyethylene shown schematically in Figure 1 the valence angle between two neighboring carbon-carbon bonds is $109^\circ 28'$. The carbon-carbon bonds can rotate relative to each other by the angle of internal rotations. Therefore, the polyethylene chain in solution or melt can take various conformations, in other words, it can be flexible. In the solid phase of the polymer rotation of the bonds does not arise.

If the valence angle is usually a fixed value, the angle of internal rotation depends on many factors of various kinds. In real-life systems polymer molecules are surrounded by similar molecules and there is always an intermolecular interaction between them that effects rotation. Since accounting of this interaction is very complicated, for quantitative calculations it is often limited by the intermolecular interaction of chemically unbounded atoms and groups of atoms of the same polymer molecule. Rotations of the links and their transition from an arrangement corresponding to one minimal energy conformation to an arrangement corresponding to another minimal energy conformation can occur only if there is a necessary energy reserve. To simulate different distributions of the angle of internal rotations, it is necessary to have a statistically qualitative generator of pseudorandom variables (PRNG) [9] with a uniform distribution, since from this distribution we can get others using various transforms, e.g., the normal distribution via the Box-Muller transform.

![Figure 1. Fragment of a polyethylene molecule with the valence angle of 109°28' between carbon atoms.](image)

3. Generator of pseudo-random variables
As a PRNG, the Mersenne Vortex was selected (this generator is included in the C++ library of the C++11 standard). This PRNG was developed in 1997 by Japanese scientists Makoto Matsumoto and Takuji Nishimura. The Mersenne Vortex is based on the properties of Mersenne primes and provides fast generation of high-quality (by the randomness criterion) pseudorandom numbers. The Mersenne Vortex is free of many shortcomings inherent in other PRNGs, such as a short period, predictability, and easily identifiable statistical patterns. We used the algorithm implemented in the standard C++ library (std::mt19937). To check the quality of the PRNG, a text file was generated with a sample of random real numbers from 0 to 1, with a size of 1,000,000 values. A histogram of a sample of ten columns is shown in Figure 2.
Figure 2. Random sample histogram generated by the Mersenne Vortex.

Check the sample for uniform distribution using the $\chi^2$ test

$$\chi^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i}$$

(1)

where $O_i$ is the observed frequency of the interval, and $E_i$ is the theoretical frequency. We take the number of intervals equal to 10, then the degree of freedom of the $\chi^2$ test is 9, and $E = 100000$ for all all intervals. During the calculations, the value of criterion 5.59772 was obtained, which is less than the critical value of 16.9 for degree of freedom 9 with a significance level of 5%. Thus, the null hypothesis of a uniform distribution is not rejected.

Also the Kolmogorov-Smirnov $\lambda$ test was applied according to the expression

$$\lambda = \frac{\max |F(x_i) - F^*(x_i)|}{\sqrt{N}}$$

(2)

where $F$ is an empirical distribution function, $F^*$ is the theoretical one, $x_i, 1 \leq i \leq N$ is the sample element in the variational series, and $N$ is the sample size. During the calculations, the value of criterion $\lambda = 0.0081247$ was obtained, which is less than the critical value for the significance level of 5%, which confirms the given null hypothesis of uniform distribution.

To check the set of obtained pseudorandom numbers according to the Shapiro-Wilk test $W$, the Box-Muller transform was applied to the obtained sample of random numbers, which allows one to obtain values distributed according to the normal law from uniformly distributed values. Then, first 50 values were taken out from the sample, since this criterion is intended for small sample sizes, then the criterion itself was directly calculated using the expression

$$W = \frac{\sum_{i=1}^{k} \sigma_{p+i+1}(x_{n+i+1} - x_i)^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

(3)

where $a$ are tabular coefficients of the criterion, $x_i, 1 \leq i \leq N$ are the sample elements, $\bar{x}$ is the expectation of the sample. During numerical simulations the value of criterion $W = 0.95797$ was
obtained which is higher than the critical value for the significance level of 5%. Therefore, there is no reason to reject the null hypothesis about the normal distribution of the transformed sample. Thus, the PRNG Mersenne Vortex is a qualitative source of random numbers satisfying the uniform distribution law.

4. Free-jointed polymer chains

In the simplest statistical theories, a polymer molecule is modelling as a free-joint chain, individual links of which are subjected to chaotic thermal motion.

When modelling a polymer molecule in three-dimensional Euclidean space, each monomer is characterized by three spatial coordinates, while the process of constructing a chain can be represented as a sequential process of calculating all the coordinates of the monomers. Coordinates of the first monomer are set by a specific point in space or in an arbitrary way, to calculate the coordinates of the second monomer (in the case of a free-joint chain for all subsequent ones), the Euler angles describing a sequential combination of passive rotations around the axes of a rotating coordinate system can be used. The rotational matrix in terms of Euler angles can be presented as follows

\[
R = \begin{pmatrix}
\cos(\alpha)\cos(\gamma) - \cos(\beta)\sin(\alpha)\sin(\gamma) & -\cos(\gamma)\sin(\alpha) - \cos(\alpha)\cos(\beta)\sin(\gamma) & \sin(\beta)\sin(\gamma) \\
\cos(\beta)\cos(\gamma)\sin(\alpha) + \cos(\alpha)\sin(\gamma) & \cos(\alpha)\cos(\beta)\cos(\gamma) - \sin(\alpha)\sin(\gamma) & -\cos(\gamma)\sin(\beta) \\
\sin(\alpha)\sin(\beta) & \cos(\alpha)\sin(\beta) & \cos(\beta)
\end{pmatrix}
\]

where \( \alpha, \beta, \gamma \) are rotation angles around the coordinate axes, which are determined by the PRNG according to a certain distribution law. In this case, the calculation of the monomer coordinates is performed as follows: a vector with norm equal to the length of the intermolecular link is constructed (for simplicity it can be chosen along one of the coordinate axes), then \( R \) is multiplied by the column vector \( \{x, y, z\} \), where \( x, y, z \) are coordinates of the vector. To get the final result, the obtained coordinates are adding to the corresponding coordinates of the previous monomer.

A model of the polymer molecule with a free-joint chain, constructed using Euler angles according to the uniform distribution law and visualized using software implemented in the Microsoft Visual Studio 2019 environment, is shown in Figure 3.

![Figure 3. A model of free-joint molecular chain with number of links \( n = 500 \).](image)

5. Polymer chains with a fixed valence angle

In the case of a chain with fixed valence angles, the rotational matrix around an arbitrary axis has the form:
where $\vec{v} = (x,y,z)$ is the unit vector defining the axis of rotation and $\theta$ is the angle of rotation. In this case, the process of searching the coordinates of each $n_{i+1}$ monomer with known $n_i$ and $n_{i-1}$, will occur in several stages. Introduce vector
\[
\vec{v}_i = \vec{n}_{i+1} - \vec{n}_i
\]

To avoid the accumulation of errors during the operation of a computer software, this vector is normalized when calculating the coordinates of each subsequent monomer. Additionally, we introduce a point $n'$ with coordinates identical to the vector $\vec{v}_i$, then the coordinates $n_{i+1}$ of the monomer can be obtained by two rotations of the point relative to the vector in space: first, turning point $n'$ around the normal to vector $\vec{n}_i$ by angle $180^\circ - \alpha$, where $\alpha$ is the given valence angle, then, turning again, but around vector $\vec{n}'$ by angle $\beta$ corresponding to the angle of internal rotation. If necessary, the intermolecular link length is reduced to the required one by means of appropriate auxiliary transformations. Vector $\vec{n}'$ which is normal to vector $\vec{v}$ can be found by fixing two of three spatial coordinates of vector $\vec{v}$, for example $x$ and $y$, and the $z$-coordinate can be calculated by:
\[
z = -\left(v_x \cdot x + v_y \cdot y\right) / v_z
\]

A model of the polymer chain with the fixed valence angle $\alpha = 75^\circ$, which is inherent in some rubbers, and the angle of internal rotation which is uniformly distributed, is shown in Figure 4.

Figure 4. A model of the polymer molecule with the fixed valence angle $\alpha = 75^\circ$ and the number of links $n = 500$.

6. Fractal dimension of polymer chains with different stochastic properties
Fractal objects are those objects that have properties of self-similarity (scale invariance). Some fragments of a system whose structures are repeated at different scales can be self-similar.

To characterize fractal structures, the term "fractal dimension" is commonly used [10]. This characteristic is the only measurable for structures of this kind.
There are a number of methods and approaches to the determination (and interpretation) of fractal dimensions, among which the Minkowski dimension plays a special role (due to the relative simplicity of determination and prevalence). The procedure for calculating the dimension is carried out in several stages. First, the object is covered with a grid of cells of known size, then the number of cells that contain the considered object is counted. Further, the size of cells decreases, and, accordingly, the number of cells containing the object increases. The procedure is repeating many times. In general, the expression for the Minkowski dimension can be presented as follows:

\[ D = \frac{\log N(\varepsilon)}{\log \frac{1}{\varepsilon}} \]

(8)

**Figure 5.** The Minkowski dimension for a polymer chain with the uniform distribution law for the angle of internal rotation.

**Figure 6.** The Minkowski dimension for a polymer chain with the normal distribution law for the angle of internal rotation.
We calculate the Minkowski fractal dimension for a polymer chain of $10^5$ monomers with fixed valence angle $\alpha = 75^\circ$ in cases of uniform, normal and exponential distribution of the angle of internal rotation at 100 iterations of the algorithm, while limiting the minimum cell size $\varepsilon$ greater than the length of link between monomers. Following the above described method the value of dimension is equal to the angular coefficient of the regression line built on the plane in a series of $\log N(\varepsilon)$ and $\log(1/\varepsilon)$.

The following expression is used to calculate the vector of regression coefficients $\vec{\theta}$:

$$\vec{\theta} = (X^T X)^{-1} X^T \vec{y}$$

where $X$ is the matrix of independent variables, and $\vec{y}$ is the vector of dependent variables.

For the normal distribution law the following parameters were established: standard deviation $\sigma^2 = 1$, expectation $\mu = 0$. The exponential distribution is characterized by parameter $\lambda = 1.0$. Plots and the corresponding values of fractal dimension for uniform, normal and exponential distribution are shown in Figures 5, 6 and 7, respectively.

7. Modeling of radiation destruction

Based on these algorithms and developed software, we suppose to create a software package which will make it possible to simulate the radiolysis process for various polymers with a wide variety of configurations and conformations, as well as to relate theoretical and experimental data. In our further researches, we are planning to realize intermolecular interactions of polymer chains taking into account possible probabilistic characteristics. These features can be considered as a basis for a novel methodology which will make it possible not only to create polymer materials with desired properties, but also to utilize/recycle final products, which can have, among other things, a significant environmental effect.

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9. References

[1] Aksenov V I, Zolotarev V L, Malygin A V and Rakhmatullin A I 2015 Industrial production and use elastomers 1 10-17.
[2] Rajoka M S R, Zhao L, Mehwish H M, Wu Y and Mahmood S 2019 Chitosan and its
derivatives: Synthesis, biotechnological applications, and future challenges. *Appl. Microbiol.
Biotechnol.* **103** 1557-1571 DOI: 10.1007/s00253-018-9550-z.

[3] Yadav M, Goswami P, Paritosh K, Kumar M, Pareek N and Vivekanand V 2019 Seafood waste:
A source for preparation of commercially employable chitin/chitosan materials *Bioresour.
Bioprocess.* **6** 8 DOI: 10.1186/s40643-019-0243-y.

[4] Tikhomirov S G, Karmanova O V, Bityukov V K, Podvalny S L and Khvostov A A 2018 Study
and modeling of polymer degradation in bulk *Theoretical Foundations of Chemical Engineering*
**52**(1) 78-86.

[5] Tikhomirov S G, Polevoy P S, Semenov M E and Karmanov A V 2019 Modeling of the
destruction process of butyl rubber *Radiation physics and chemistry* **158** 205-208.

[6] Gusev Yu K, Tikhomirov S G, Khvostov A A and Khaustov I A 2012 *Proceedings of VSUET* **2**
85-87.

[7] Journot C, Nicolle L, Lavanchy Ya and Gerber-Lemaire S 2020 Selection of water-soluble
chitosan by microwave-assisted degradation and ph-controlled precipitation *Polymers* **12**(6)
1-14.

[8] Tikhomirov S G, Khaustov I A, Bitukov V K, Karmanova O V, Popov A P, Semenov M E and
Khvostov A A 2018 *Theoretical Foundations of Chemical Engineering* **52**(4) 568-573.

[9] Podvalny S L, Belyanin A M, Tikhomirov S G and Khvostov A A 2016 Simulating dynamic
modes of polymer synthesis, based on the method of moments for multimodal distributions
*Bulletin of the Russian Academy of Sciences: Physics* **80**(9) 1150-1151.

[10] Kuznetsov S P 2001 *Dynamical chaos* (Moscow: Fizmatlit).