

Computer Synthesis of Network Polymers

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Abstract—A model and the principle of constructing a corresponding computer program are proposed for the electronic synthesis of polymer networks with a specified range of glass transition temperatures have been proposed for the first time. A repeating fragment of the network is synthesized from the smallest basic fragments, which are connected to each other using a control matrix of interactions. As an example, there are presented 27 chemical structures of the cross-linked points, 26 basic fragments for constructing polymer chains connecting the cross-linked points, and five repeating fragments of polymer networks with glass transition temperatures falling within the range 450–480 K.

Keywords: polymer networks, glass transition temperature, van der Waals volume, computer synthesis, cross-linked points

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The problem of predicting the glass transition temperature T_g and other physical properties of network polymers from their chemical structure has been considered in detail in monographs [1–4]. In monographs [5, 6], such an approach is absent, and only corrections are made to the methods for calculating linear polymers, which make it possible to evaluate the T_g values of network polymers.

Earlier [1–4], a model and a computer program have been developed that allow the computer synthesis of linear polymers. The synthesis is performed from the smallest basic fragments that cannot be “cut” along the axis of the macromolecule. As an example, Table 1 shows a number of these fragments.

Labels define the possibility of chemical bonding of atoms to the basic fragment structure. Among the atoms are carbon, hydrogen, oxygen, nitrogen, sulfur, etc. The left label means that this atom is attached to the left side of the basic fragment, and the right label means that this atom is attached to the right side of the basic fragment. The attached atoms can be different; for example, oxygen is attached to the left and carbon is attached to the right.

In the present work devoted to the computer synthesis of network polymers, linear chains are structural elements of a repeating fragment of a network connecting cross-linked points. For highly cross-linked polymers, the variety of repeating fragments of the network during its computer synthesis is achieved by specifying a relatively large number of basic fragments. In [1–4], 96 basic fragments have been used, some of which are presented in Table 1. Experiments performed earlier for linear polymers show that an increase in the number of basic fragments by one (for example, from 3 to 4, from 4 to 5, from 5 to 6, etc.) increases the number of synthesized structures by an order of magnitude.

The possibility of addition of an atom to the basic fragment in the course of computer synthesis is determined by the so-called connectivity matrix presented in Table 2.

If there is 0 at the intersection of the horizontal and vertical lines, it means that the structures cannot be chemically bonded; if there is 1 at such an intersection, it means that the structures can be chemically bonded.

In addition to the above, the influence of the homogeneous and inhomogeneous distribution of the number of repeating units in linear chains connecting the cross-linked points has been analyzed [2, 4]. We have also analyzed the influence of inhomogeneities in the network structure (dangling chains and rings) on the T_g value.

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Table 1. Chemical structure of the basic fragment, bond lengths for neighboring chemically bound atoms, labels characterizing the possibility of chemical bonding with an atom, and the van der Waals volume of the basic fragment

Fragment no.	Chemical structure of the fragment	Bond lengths with neighboring atoms, Å		Labels		Van der Waals volume V_i , Å ³
		left	right	left	right	
1		1.48; 1.54	1.48; 1.54	1	1	17.1
2		1.48; 1.54	1.48; 1.54	2	2	34.2
3		1.48; 1.54	1.48; 1.54	2	2	92.6
4		1.48; 1.54	1.48; 1.54	2	2	107.5
5		1.48; 1.54	1.48; 1.54	1	1	27.1
6		1.48; 1.54	1.48; 1.54	2	2	18.6
7		1.48	1.48	3	3	75.6
8		1.54	1.50	1	4	20.2
9		1.54	1.50	2	4	54.9
10		1.37	1.37	5	5	115.5
11		1.5	1.50	9	8	2.7
12		1.5	1.50	9	9	2.1
13		1.54	1.50	2	8	25.1
14		1.54	1.37	1	6	18.6
15		1.54	1.37	2	6	20.1
16		1.37	1.48; 1.54	11	14	28.4
17		1.76	1.76	7	7	78.0

Table 1. (Contd.)

Fragment no.	Chemical structure of the fragment	Bond lengths with neighboring atoms, Å		Labels		Van der Waals volume V_i , Å ³
		left	right	left	right	
18		1.76	1.76	12	12	16.5
19		1.76	1.76	12	12	26.1
20		1.37	1.37	11	11	144.6
21		1.37	1.37	11	11	190.2
22		1.37	1.37	5	11	113.4
23		1.64	1.64	13	13	71.6
24		1.64	1.64	10	10	0.5
25		1.37	1.37	11	9	39.7
26		1.37	1.37	11	11	38.8

Let us proceed directly to the consideration of the principles of computer synthesis of networked polymers.

RESULTS AND DISCUSSION

Previously [2, 4], a model and a calculation scheme have described for a quantitative assessment of the glass transition temperature T_g , for which the van der Waals volume of a repeating network fragment, atomic constants for linear chains connecting the cross-linked points, and atomic constants for cross-linked points have been taken into account in the calculations.

From the point of view of chemical structure, a cross-linked point consists of an atom from which chain branching begins and neighboring atoms chemically bonded to it. The latter contain chemical sub-

Table 2. Label matrix controlling the computer synthesis of polymers

Labels	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	1	1	1	0	0	0	0	0	0	0	0	0	0	0
2	1	0	1	0	0	0	0	0	0	0	0	0	0	0
3	1	1	1	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	1	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	1	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	1	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0	1	0	0
8	0	0	0	1	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	1	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	1	0
11	0	0	0	0	0	1	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	1	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	1	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0	1

Table 3. Chemical structure of cross-linked points, bond lengths involving neighboring chemically bond atoms, labels characterizing the possibility of chemical bonding with an atom, and the van der Waals volume of the cross-linked point

Fragment	Bond length, Å (labels)				Van der Waals volume V_i , Å ³	$\sum K_i \Delta V_i^*$, Å ³ K ⁻¹
	left	right	bottom	top		
$\begin{array}{c} \text{C} \cdots \text{CH} \cdots \text{C} \\ \\ \text{C} \end{array}$	1.54 (2)	1.54 (2)	1.54 (2)	—	11.0	15.00
$\begin{array}{c} \text{H} \\ \\ \text{C} \cdots \text{C} \cdots \text{N} \\ \\ \text{N} \end{array}$	1.54 (14)	1.40 (6)	1.40 (6)	—	14.1	18.53
$\begin{array}{c} \text{H} \\ \\ \text{N} \cdots \text{C} \cdots \text{N} \\ \\ \text{N} \end{array}$	1.40 (14)	1.40 (6)	1.40 (6)	—	17.6	20.25
$\begin{array}{c} \text{C} \cdots \text{N} \cdots \text{C} \\ \\ \text{C} \end{array}$	1.40 (11)	1.40 (11)	1.40 (11)	—	1.5	3.78
$\begin{array}{c} \text{C} \cdots \text{CH} \cdots \text{C} \\ \\ \text{O} \end{array}$	1.54 (2)	1.54 (2)	1.50 (4)	—	14.2	15.00
$\begin{array}{c} \text{C} \cdots \text{CH} \cdots \text{C} \\ \\ \text{N} \\ \\ \text{C} \end{array}$	1.54 (2)	1.54 (2)	1.40 (11)	—	12.6	15.00
$\begin{array}{c} \text{C} \\ \\ \text{C} \cdots \text{C} \cdots \text{C} \\ \\ \text{C} \end{array}$	1.54 (2)	1.54 (2)	1.54 (2)	1.54 (2)	5.0	5.75
$\begin{array}{c} \text{O} \\ \\ \text{C} \cdots \text{C} \cdots \text{C} \\ \\ \text{O} \end{array}$	1.88 (2)	1.88 (2)	1.64 (13)	1.64 (13)	27.6	24.84
$\begin{array}{c} \text{C} \cdots \text{Si} \cdots \text{C} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$	1.64 (13)	1.64 (13)	1.88 (2)	—	49.6	58.9
$\begin{array}{c} \text{O} \cdots \text{Si} \cdots \text{O} \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array}$	1.64 (13)	1.64 (13)	2.32 (10)	—	49.6	58.9
$\begin{array}{c} \text{O} \cdots \text{Si} \cdots \text{O} \\ \\ \text{Si} \end{array}$						

Table 3. (Contd.)

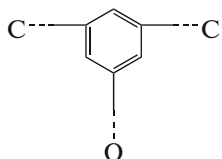
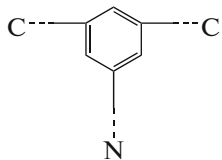
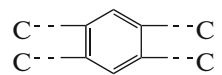
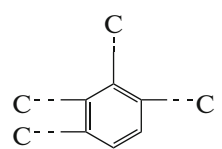
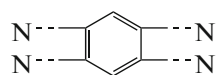
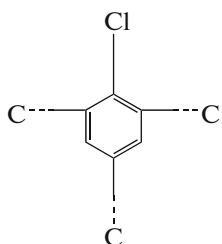
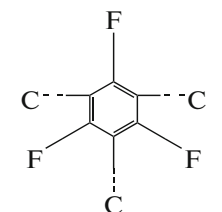
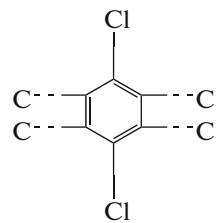
Fragment	Bond length, Å (labels)				Van der Waals volume V_i , Å ³	$\sum K_i \Delta V_i^*$, Å ³ K ⁻¹
	left	right	bottom	top		
	1.48 (3)	1.48 (3)	1.37 (5)	—	72.5	90.32
	1.48 (3)	1.48 (3)	1.37 (6)	—	71.1	88.71
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	63.1	77.08
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	63.1	77.08
	1.37 (6)	1.37 (6)	1.37 (6)	1.37 (6)	70.2	85.36
	1.48 (3)	1.48 (3)	1.48 (3)	—	83.3	126.7
	1.48 (3)	1.48 (3)	1.48 (3)	—	84.3	102.5
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	90.7	159.7

Table 3. (Contd.)

Fragment	Bond length, Å (labels)				Van der Waals volume V_i , Å ³	$\sum K_i \Delta V_i^*$, Å ³ K ⁻¹
	left	right	bottom	top		
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	73.1	87.86
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	108.6	134.15
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	108.6	134.15
	1.37 (6)	1.37 (6)	1.37 (6)	1.37 (6)	115.8	142.43
	1.37 (6)	1.37 (6)	1.37 (6)	1.37 (6)	115.8	142.43
	1.48 (3)	1.48 (3)	1.48 (3)	1.48 (3)	164.0	299.3
	1.48 (3)	1.76 (7)	1.48 (3)	—	70.5	88.02
	1.40 (11)	1.40 (11)	1.40 (11)	—	70.35	122.17
	1.37 (5)	1.37 (5)	1.37 (5)	—	65.7	98.52

* K_i is the atomic constant of the i th atom related to the equilibrium distance between chemically bonded atoms and the chemical bond dissociation energy; ΔV_i^* is the van der Waals volume of the i th atom.

Table 4. Repeating fragments of polymer networks and their glass transition temperature

No.	Chemical structure of the repeating fragment	Glass transition temperature T_g , K
1		474
2		479
3		457
4		473
5		465

stituents, which are also included in the cross-linked point.

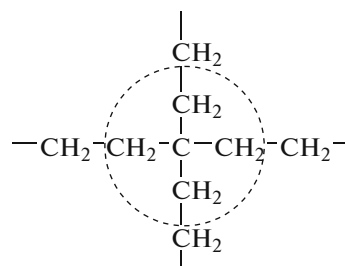
Table 3 shows, for example, a number of atoms and atomic structures from which chain branching occurs.

In total, in [2–4], there are 78 such structures that form cross-linked points of polymer networks.

As an example, let us choose the range of glass transition temperatures of network polymers from 450 to 480 K. The program synthesizes many repeating fragments of polymer networks, of which, for example, we select only five structures (Table 4).

All T_g values fall within the specified glass transition temperature range.

Thus, the fundamental possibility of carrying out electronic synthesis of not only linear polymers, which has been developed by us earlier [1–4], but also of network polymers. Further work in this direction is related to taking into account the network topology. Indeed, with the same chemical structure of the basic fragments and their amount, as well as with the same cross-linked points, polymer networks can have different chemical structures. It depends on where the chain crosslinks are located, not to mention structural defects (the formation of cycles, the presence of branched chains one end of which is not linked to the network structure, etc.). Let's give an example of this influence. For radiation cross-linked polymer chains of polyethylene, the following structure is possible:



This network is four-functional; i.e., four chains come out of its cross-linked point. For such a network, the glass transition temperature is calculated by the relationship

$$T_g = \frac{2(m-2) \left(\sum_i \Delta V_i \right)_l + 4 \left(\sum_i \Delta V_i \right)_l^* + \left(\sum_i \Delta V_i \right)_{\text{cr.p.}}}{2(m-2) \left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_l + 4 \left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_l^* + \left(\sum_i K_i \Delta V_i \right)_{\text{cr.p.}}}, \quad (1)$$

where m is the number of repeating units in linear chains connecting the cross-linked points; a_i are atomic constants related to the energy of the intermolecular bond of the i th atom with neighboring atoms; b_j are the increments related to the energies of dipole-dipole interactions and hydrogen bonds; $\left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_l$ is the

set of atomic constants and increments for the repeating unit of the chains connecting cross-linked points; $\left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_l^*$ is the same for the end units directly bonded to the cross-linked points; $\left(\sum_i K_i \Delta V_i \right)_{\text{cr.p.}}$ is the set of atomic constants for cross-linked points.

CONCLUSIONS

The proposed approach allows the computer synthesis of network polymers. Using this approach and the corresponding equations, it is possible to construct polymer networks of the most diverse topology with constant chemical structure.

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REFERENCES

1. Askadskii, A.A., *Physical Properties of Polymers. Prediction and Control*, Amsterdam: Gordon and Breach, 1996.
2. Askadskii, A.A., *Computational Materials Science of Polymers*, Cambridge: Cambridge Int. Sci. Publ., 2003.
3. Askadskii, A.A., *Analysis of the Structure and Properties of High-Cross-linked Polymer Networks*, Paris: Harwood Acad. Publ., 1992.
4. Askadskii A.A. and Kondrashchenko, V.I., *Komp'yuternoe materialovedenie polimerov* (Computer Materials Science of Polymers), vol. 1: *Atomno-molekulyarnyi uroven'* (Atomic and Molecular Level), Moscow: Nauchnyi Mir, 1999.
5. Van Krevelen, D.W., *Properties of Polymers*, 3d ed., Amsterdam: Elsevier, 1990.
6. Bicerano, J., *Prediction of Polymer Properties*, New York: Marcel Dekker, 2002.

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