Principle of computer synthesis of network polymers possessing a specified interval of glass temperatures

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Abstract: For the first time, the model and the principle of constructing a corresponding computer program for the electronic synthesis of polymer networks with a given glass transition temperature range have been proposed. A repeating network fragment is synthesized from the smallest basic fragments that are connected to each other using a steering matrix of interactions. As an example, 10 cross-linked points, 16 basic fragments for constructing inter cross-linked chains and 5 repeating fragments of polymer networks are presented, the glass transition temperatures of which are within the specified range from 450 to 480K.

1. Introduction
The problem of predicting the glass transition temperature Tg of cross-linked polymers based on their chemical structure was considered in detail in monographs [1-7]. In monographs [8-9], such an approach is absent, and they only make corrections to the methods for calculating linear polymers, which make it possible to estimate the Tg values of cross-linked polymers.

In the works [1-7], a model and a computer program have been developed that allow the computer synthesis of linear polymers. The synthesis is carried out on the basis of the smallest basic fragments that cannot be "cut" along the axis of the macromolecule. As an example, Table 1 shows a number of such fragments.

Table 1. The chemical structure of the basic fragment, the length of bonds with neighboring chemically bonded atoms; labels characterizing the possibility of chemical bonding with one or another atom; van der Waals volume of the basic fragment

| Fragment number | The chemical structure of the fragment | Bond lengths with neighboring atoms, Å | Markers | Van der Waals volume, Å³ |
|-----------------|--------------------------------------|---------------------------------------|---------|-------------------------|
| 1.              | [CH₂]                                | 1.48; 1.48; 1.54                     | l       | 17.1                    |

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| Fragment number | The chemical structure of the fragment | Bond lengths with neighboring atoms, Å | Markers | Van der Waals volume, Å³ |
|-----------------|-------------------------------------|----------------------------------------|---------|-------------------------|
| 2.              | ![Image](image1.png)                | 1.48; 1.54; 1.48; 1.54                 | 2 2     | 92.6                    |
| 3.              | ![Image](image2.png)                | 1.48; 1.54; 1.48; 1.54                 | 1 1     | 27.1                    |
| 4.              | ![Image](image3.png)                | 1.48; 1.54; 1.48; 1.54                 | 2 2     | 18.6                    |
| 5.              | ![Image](image4.png)                | 1.48; 1.48; 1.48; 1.48                 | 3 3     | 75.6                    |
| 6.              | ![Image](image5.png)                | 1.54; 1.50; 1.54; 1.54                 | 2 4     | 54.9                    |
| 7.              | ![Image](image6.png)                | 1.37; 1.37; 1.37; 1.37                 | 5 5     | 115.5                   |
| 8.              | ![Image](image7.png)                | 1.50; 1.54; 1.54; 1.54                 | 9 8     | 2.7                     |
| 9.              | ![Image](image8.png)                | 1.54; 1.37; 1.54; 1.37                 | 1 6     | 18.6                    |
| 10.             | ![Image](image9.png)                | 1.54; 1.37; 1.54; 1.37                 | 2 6     | 20.1                    |
| 11.             | ![Image](image10.png)               | 1.37; 1.48; 1.48; 1.54                 | 11 14   | 28.4                    |
| 12.             | ![Image](image11.png)               | 1.76; 1.76; 1.76; 1.76                 | 7 7     | 78.0                    |
| 13.             | ![Image](image12.png)               | 1.76; 1.76; 1.76; 1.76                 | 12 12   | 16.5                    |
The chemical structure of the fragment

| Fragment number | The chemical structure of the fragment | Bond lengths with neighboring atoms, Å | Markers left | Markers right | Van der Waals volume, Å³ |
|-----------------|--------------------------------------|----------------------------------------|-------------|--------------|-------------------------|
| 14.             | ![Image](image1.png)                  | 1.37 1.37                              | 11          | 11           | 144.6                   |
| 15.             | ![Image](image2.png)                  | 1.64 1.64                              | 13          | 13           | 71.6                    |
| 16.             | ![Image](image3.png)                  | 1.64 1.64                              | 10          | 10           | 0.5                     |

Markers determine the possibility of chemical attachment of atoms to the structure of the basic fragment. Among the atoms are carbon C, hydrogen H, oxygen O, nitrogen N, sulfur S, etc. The left marker means that this atom is attached to the left side of the basic fragment, and the right marker means that this atom is attached to the right side of the basic fragment. In this case, the attached atoms can be different; for example, oxygen is attached to the left and carbon is attached to the right.

In the proposed work devoted to the computer synthesis of cross-linked polymers, linear chains are the structural elements of a repeating fragment of the network connecting the cross-linked points. In works [1-4], 96 basic fragments were used, some of which are presented in Table 1. The possibility of attaching one or another atom to the basic fragment in the process of computer synthesis is determined by the so-called connectivity matrix, presented below (Table 2):

**Table 2.** Matrix of markers, which controls the computer synthesis of polymers.

| Marker | 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 | 1  | 0  | 0  | 0  | 0  |
| 7      | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0  | 1  | 0  | 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  | 1  | 0  | 0  |
| 11     | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0  | 0  | 0  | 0  | 0  |
| 12     | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0  | 0  | 0  | 0  | 0  |
| 13     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0  | 0  | 0  | 0  | 0  |
| 14     | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0  | 0  | 0  | 0  | 1  |

If \( (I, K) = 0 \), then the fragment marked \( I \) cannot connect to the fragment marked \( K \); if \( (I, K) = 1 \), then the fragment marked \( I \) can connect to the fragment marked \( K \).
Let us proceed directly to the consideration of the principles of computer synthesis of network polymers.

2. Network polymers

Earlier, in [2, 4, 11], the model and calculation scheme were described for a quantitative assessment of the glass transition temperature $T_g$ of cross-linked polymers. The $T_g$ value is calculated using the equation (1)

$$T_g = \frac{\left(\sum_i \Delta V_i\right)_{r.f.}}{\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{l_j} + \left(\sum_i K_i \Delta V_i\right)_{c.p.}}$$

where $\left(\sum_i \Delta V_i\right)_{r.f.}$ is the van der Waals volume of a repeating fragment of polymer network,

$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{l_j}$ are the atomic constants for linear chains connecting cross-linked points;

$\left(\sum_i K_i \Delta V_i\right)_{c.p.}$ are the atomic constants for linear chains connecting cross-linked points.

From the point of view of chemical structure, a network node consists of an atom, from which chain branching begins, and neighboring atoms chemically bonded to it. The latter contain chemical substituents, which are also included in the cross-linked point.

Table 3 lists a number of atoms and atomic structures from which chain branching occurs. In total, in this work, there are 78 such structures that form cross-linked points of polymer networks.

**Table 3.** The chemical structure of the network node, the length of bonds with neighboring, chemically bonded atoms; markers characterizing the possibility of chemical bonding with one or another atom; van der Waals volume of a cross-linked point.

| Fragment | Bond length, Å, (markers) | Van der Waals volume, Å³ | $aK_iDV_i$, £1⁻¹Å³ |
|----------|--------------------------|--------------------------|-------------------|
|          | left | right | from below | from above | C----CH----C | 1.54  | 1.54  | 1.54          | -   | 11.0  | 15.00  |
|          |      |       |            |            | C----H----N | 1.54  | 1.40  | 1.40          | -   | 14.1  | 18.53  |
|          |      |       |            |            | C----N----C | 1.40  | 1.40  | 1.40          | -   | 1.5   | 3.78.  |
| Fragment | Bond length, Å, (markers) | Van der Waals volume, Å³ | $a K^{-1} \cdot \text{Å}^3$ |
|----------|--------------------------|--------------------------|-------------------------------|
|          | left  right  from below  from above |                          |                              |
| C---CH---C | 1.54 (2) 1.54 (2) 1.50 (4) - | 14.2                      | 15.00                        |
| C---C     | 1.54 (2) 1.54 (2) 1.54 (2) 1.54 (2) | 5.0                      | 5.75                         |
| C---Si---C | 1.88 (2) 1.88 (2) 1.64 (13) 1.64 (13) | 27.6                      | 24.84                        |
| O---Si---O | 1.64 (13) 1.64 (13) 2.32 (10) - | 49.6                      | 58.9                         |
| C---C     | 1.48 (3) 1.48 (3) 1.37 (5) - | 72.5                      | 90.32                        |
| Fragment | Bond length, Å, (markers) | Van der Waals volume, Å³ |
|----------|---------------------------|------------------------|
|          | left  | right | from below | from above | $\alpha^K_i\cdot DV_i$ |
| C-----S  | 1.48  | 1.76  | 1.48       | -          | 70.5   | 88.02 |
|          | (3)   | (7)   | (3)        |            |        |
| O-----O  | 1.37  | 1.37  | 1.37       | -          | 65.7   | 98.52 |
|          | (5)   | (5)   | (5)        |            |        |

As an example, let us choose the range of glass transition temperatures of cross-linked polymers from 450 K to 480 K. The program synthesizes many repeating fragments of polymer networks, of which, for example, select only 5 structures (Table 4):

| № | Chemical structure of a repeating fragment | Glass transition temperature $T_g$, K |
|---|------------------------------------------|-------------------------------------|
| 1. | ![Chemical structure](attachment:1.png)   | 474                                 |
| 2. | ![Chemical structure](attachment:2.png)   | 479                                 |
| №  | Chemical structure of a repeating fragment | Glass transition temperature $T_g$, K |
|----|------------------------------------------|-------------------------------------|
| 3. | ![Chemical structure 3](image1)           | 457                                 |
| 4. | ![Chemical structure 4](image2)           | 473                                 |
| 5. | ![Chemical structure 5](image3)           | 465                                 |

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 was developed by us earlier [1-4], but also of network polymers has been shown. Further work in this direction is related to taking into account the networks 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 possess different chemical structures. It depends on where the chain links are located, not to mention structural defects (the formation of cycles, the presence of branching chains, at one end of which they do not join 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:

![Radiation-cross-linked polymer chains of polyethylene](image4)
This network is 4-functional, i.e. 4 chains come out of its cross-linked point. For such a network, the glass transition temperature is calculated by the ratio

\[ T_g = \frac{2(m-2)\left(\sum_i \Delta V_i \right) + 4\left(\sum_i \Delta V_i \right)^* + \left(\sum_i \Delta V_i \right)_{cr.p.}}{2(m-2)\left(\sum_i a_i \Delta V_i + \sum_j b_j \right) + 4\left(\sum_i a_i \Delta V_i + \sum_j b_j \right)^* + \left(\sum_i K_i \Delta V_i \right)_{cr.p.}} \]  

(2)

where \( \left(\sum_i a_i \Delta V_i + \sum_j b_j \right) \) is a set of atomic constants and increments for a repeating unit of linear inter-cross-linked chains; \( \left(\sum_i a_i \Delta V_i + \sum_j b_j \right)^* \) is the same for the extreme links directly connected to the cross-linked points; \( \left(\sum_i K_i \Delta V_i \right)_{cr.p.} \) is the set of atomic constants for cross-linked points.

Using the proposed approach and the corresponding equations, it is possible to construct polymer networks of the most diverse topology with a constant chemical structure.

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