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Peculiarities of the structure and properties of highly cross-linked polymer networks

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Abstract. Data on the structure and properties of highly cross-linked polymer networks in which the distance between cross-link points is several repeating units or even less than one unit, up to the networks consisting of nothing but cross-link points containing no linear fragments, are generalised. The dependences of a number of physical properties (the glass transition temperature, the modulus of elasticity, *etc*.) on the degree of cross-linking and the influence of various defects (branchings, dangled chains, *etc*.) on the properties of highly cross-linked networks are analysed. It is shown that the passage from sparse networks to highly cross-linked networks is accompanied by fundamental changes in their properties and that these properties can be described quantitatively taking into account the chemical structure of the network. The influence of the chemical structure of a cross-link point of the network on the properties is analysed; it is shown that the distances between the cross-link points in such networks can be estimated by nontraditional methods. Particular attention is paid to the cross-linked systems that are the basis for gradient-modulus materials in which the modulus of elasticity, the refractive index, and other properties vary over a wide range. The bibliography includes 93 references.

I. Introduction

The aim of this review is to analyse the influence of the structure of highly cross-linked polymer networks on their physical properties. The concept of the network structure includes the chemical structure of cross-link points and linear fragments between them, branchings, isolated loops, and other defects always present in the network. We will solve the above problem on the basis of an approach that is being developed by the author (in collaboration with Yu I Matveev) over many years and that makes it possible to take into account the influence of the energies of intermolecular interaction and chemical bonds on the properties of polymers. According to this approach, the repeating unit of a polymer or the repeating fragment of a network is represented as a set of anharmonic oscillators interconnected by different types of intermolecular interactions (*e.g*., dispersion, dipole-dipole, and hydrogen interaction) and chemical interactions. The temperature at which the set of oscillators loses its stability characterises the onset of such processes as glass transition or melting (energy changes on the level of intermolecular interaction), or the onset of intense thermal degradation (energy changes on the level of chemical bonds). Only the chemical structure of polymers needs to be known for calculating their properties. Any change in the topology of the network is related to changes in its chemical structure, which in turn affect its properties.[1–4]

A purely empirical approach developed by Van Krevelen based on group contributions to a particular property is often used for calculating properties of polymers. Compared to the approach used in this study, it has a number of limitations and certain advantage. The limitations are the following: (1) if a group makes no contribution, then the properties of a polymer containing this group cannot be calculated; (2) the applicability of the approach only to linear polymers; there is no mention of polymer networks even in the third edition of the book by D W Van Krevelen *Properties of Polymers* Third Ed. (Amsterdam: Elsevier, 1990); and (3) group contributions to properties have no physical sense. The simplicity of calculations is an advantage of Van Krevelen's approach.

In this review, we have analysed the results obtained to date of studies of the influence of the above-mentioned structural network peculiarities on the properties of polymers. In the preparation of the review, the author not only compiled the published data, but also carried out numerous additional calculations of the properties of highly cross-linked polymer networks. This was associated with an attempt to answer the most frequently asked questions of specialists concerning the influence of the degree of cross-linking, the topology of the network, the chemical structure of the cross-linking agent (*i.e*., the chemical structure of cross-link points), 'dangled' chains, branchings, loops, and other structural features on the properties.

Before considering peculiarities of the structure and properties of highly cross-linked polymer networks, it is necessary to define the concepts of a cross-link point, of a highly cross-linked network, and of a sparse network. *A cross-link point of the network is a group of atoms comprising an atom from which the chain branching occurs, neighbouring atoms chemically bonded to this*

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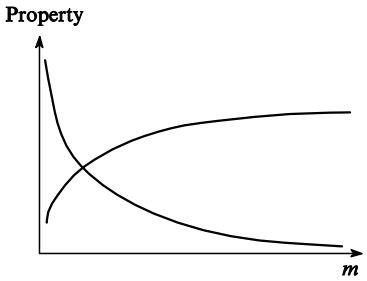


Figure 1. Examples of dependences illustrating sharp changes in properties on the number of repeating units (m) between the neighbouring cross-link points of a network.

atom, and their nearest substituents.[5, 6] A decrease in the number of repeating units between cross-link points (if it amounts to several tens) affects insignificantly the glass transition temperature, the molar volume, the refractive index, and some other characteristics. However, when the number of the repeating units between cross-link points is very small (several units), its decrease results in abrupt changes in the properties (Fig. 1). This is particularly noticeable when none of 'normal' polymer units remains between the cross-link points. Such systems are the most highly cross-linked polymer networks; cured epoxy resins, phenol-formaldehyde resins, graphite, diamond, and a number of other compounds can serve as examples.

A detailed study of the properties of highly cross-linked polymer networks was carried out for hypothetical tri- and tetrafunctional polyethylene-based networks, networks based on styrene–divinylbenzene copolymers, *etc*.[1] Abrupt changes in the properties of all polymers considered occurred when the number of repeating units in the linear fragments between cross-link points decreased down to 4–5. It is these networks that will be classified as highly cross-linked networks. Principal changes in both the structure and properties of highly cross-linked networks occur if the network virtually consists of nothing but cross-link points.

II. Density and the molar volume

The concept of 'a repeating fragment of a network' is illustrated in Fig. 2 in which tri- and tetrafunctional networks are represented schematically. The functionality of a network is characterised by the number of chains issuing out of one cross-link point. The molecular weight M_f of a repeating fragment of a trifunctional network (Fig. 2*a*) is calculated using the following formula

$$M_f = M_{c\text{-}l} + 1.5M_0 m\,, \qquad (1)$$

where $M_{c\text{-}l}$ is the molecular weight of the cross-link point, M_0 is the molecular weight of the repeating unit of linear fragments connecting the cross-link points, and m is the average number of the repeating units in the linear fragments between the cross-link points.

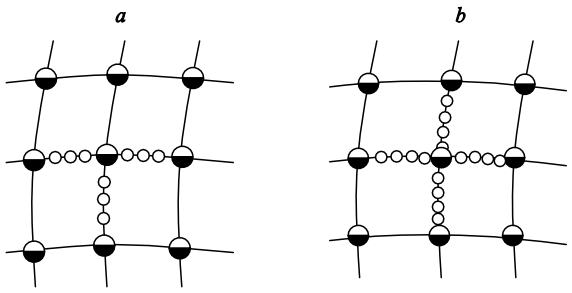


Figure 2. Trifunctional (*a*) and tetrafunctional (*b*) networks with the same chemical structure of linear fragments.

The van der Waals volume of the repeating fragment of the network can be found from the relationship

$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{c\text{-}l} + 1.5\left(\sum_i \Delta V_i\right)_0 m\,, \qquad (2)$$

where $\left(\sum_i \Delta V_i\right)_{c\text{-}l}$ and $\left(\sum_i \Delta V_i\right)_0$ are the van der Waals volumes of the cross-link point and of the repeating unit of the linear fragments between the cross-link points, respectively.

The formulae for calculating density (ρ_c) and molar volume (V_c) of a polymer network have the form

$$\rho_c = \frac{M_f k}{N_A\left(\sum_i \Delta V_i\right)_f} \quad \text{and} \quad V_c = \frac{N_A\left(\sum_i \Delta V_i\right)_f}{k}\,,$$

where N_A is the Avogadro constant and k is the average value of the molecular packing coefficient.†

The van der Waals volumes of carbon, oxygen, sulfur, nitrogen, and other atoms chemically bonded to other atoms have been reported.[3, 7] Using these data, the van der Waals volumes of repeating fragments of networks of different chemical nature (Table 1) can be calculated easily.

Studies of the bulk properties of polymer networks have shown that the average molecular packing coefficient at room temperature k_{25} is equal to ~ 0.7, which is somewhat larger than that of linear polymers (0.681).

The relationships (1) and (2) are valid for rather sparse polymer networks in which the number of repeating units in the linear fragments between the cross-link points exceeds 10. The following relationships are valid for highly cross-linked polymer networks

$$M_f = M_{c\text{-}l} + 3M_0^* + 1.5(m-2)M_0$$

and

$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{c\text{-}l} + 3\left(\sum_i \Delta V_i\right)_0^* + 1.5(m-2)\left(\sum_i \Delta V_i\right)_0\,, \qquad (3)$$

where M_0^* and $\left(\sum_i \Delta V_i\right)_0^*$ are respectively the molecular weight and the van der Waals volume of the repeating units of linear chains immediately adjacent to the cross-link point (these units are of different chemical structure as compared to the 'normal' units).

For tetrafunctional sparse networks (see Fig. 2*b*) we have

$$M_f = M_{c\text{-}l} + 2M_0 m \quad \text{and}$$

$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{c\text{-}l} + 2\left(\sum_i \Delta V_i\right)_0 m\,.$$

For highly cross-linked networks we get

$$M_f = M_{c\text{-}l} + 4M_0^* + 2(m-2)M_0$$

and

$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{c\text{-}l} + 4\left(\sum_i \Delta V_i\right)_0^* + 2(m-2)\left(\sum_i \Delta V_i\right)_0\,. \qquad (4)$$

† It will be recalled that the molecular packing coefficient is the ratio of the van der Waals molar volume of a body to the molar volume of the body.[2]

Table 1. Parameters of networks of different structure.

Network structure	$\left(\sum_i \Delta V_i\right)_{c\text{-}l}$/Å^3	$\left(\sum_i \Delta V_i\right)_l$/Å^3	$\left(\sum_i \Delta V_i\right)_f$/Å^3	$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_l$/Å^3 K$-$1	$\left(\sum_i K_i \Delta V_i\right)_{c\text{-}l}$/Å^3 K^{-1}
1	73.4	$17.1m-34.2$	$5.0+34.2m$	$160.4m-320.8$	102.9
2	39.2	0	39.2	0	54.3
3	5.0	0	5.0	0	5.7
4	62.3	$17.1m-34.2$	$11.0+25.6m$	$119.9m-239.8$	87.9
5	34.6	0	34.6	0	46.8
6	11.0	0	11.0	0	14.96
7	48.3	$152.3m+252.3$	$300.6+152.3m$	$519.3+490.6m+175.6$	66.1
8	53.3	$109.7m-17.1+29.4$	$109.7m+64.6$	$294.0m-80.2+67.6$	72.9
9	36.2	29.4	65.6	67.6	48.6
10	35.2	29.4	65.6	67.6	47.4
11	17.1	92.6	109.7	213.8	24.3
12	0	109.7	109.7	294	0
13	198.0	$41.8+108.1n$	$239.8+108.1n$	$176.0+721.5n$	252.3
15	73.4	$17.1m-34.2$	$11.1+34.2m$	$160.4m-336.2$	102.9
16	0	96.8	96.8	255.8	0
17	62.7	208.8	146.1	401.0	69.9
18a	92.2	0	92.2	0	136.9
18b	111.1	0	111.1	0	172.8
18c	92.2	$18.9n-18.9$	$73.3+18.9n$	$141.7n-283.5$	172.8
18d	0	81.5	81.5	400.7	0
19	35.0	$339.7+72.1m$	$714.4+144.2m$	$2120.6+481m$	47.6
20a	47.1	54.0	101.1	71.6	21.5
20b	0	123.05	123.05	$505.5-263.2$	0
20c	0	99.05	99.05	$331.9-123.6$	0
20d	47.15	44.1	91.25	120.7	56.5
20e	0	123.05	123.05	$505.4-94.8$	0

Notes. All the components of the parameters are listed. For the structures of networks **1**–**13** and **15**–**20**, see text. The subscripts c-l, l, and f correspond to the cross-link point of the network, the linear fragment, and the repeating fragment, respectively.

It has been found [7, 8] that for all polymers irrespective of their chemical structure the molecular packing coefficient near absolute zero k_0 is nearly the same and is equal to ~ 0.731.

At a glass transition temperature T_g, which is specific to each polymer, the molecular packing coefficient is also almost constant and is assessed as $k_g \approx 0.667$. For highly cross-linked polymer networks, $k_g \approx 0.681$ (see Ref. 4).

Since the molar volume of a polymer at the glass transition temperature is

$$V_g = V_0(1 + \alpha T_g)\,,$$

where V_0 is the molar volume at absolute zero, α is the thermal coefficient of volume expansion, and

$$V_g = \frac{N_A\left(\sum_i \Delta V_i\right)}{k_g} \quad \text{and} \quad V_0 = \frac{N_A\left(\sum_i \Delta V_i\right)}{k_0},$$

then

$$\frac{k_0}{k_g} = 1 + \alpha T_g \quad \text{and} \quad \alpha = \frac{k_0/k_g - 1}{T_g}.$$

The coefficient of volume expansion in the rubbery state α_L can be approximately calculated using the φ_f constant from the Simkha–Boyer equation; the experimental constant for cured resins is equal to 0.106, *i.e.*,

$$\varphi_f = (\alpha_L - \alpha)T_g = 0.106.$$

Hence

$$\alpha_L = \frac{0.106 + \alpha T_g}{T_g}.$$

The molecular packing coefficient at 293 K and the density at the same temperature can be calculated using the following formulae

$$k_{293} = \frac{k_0}{1 + \alpha 293} \quad \text{and} \quad \rho_{293} = \frac{k_{293} M_f}{N_A\left(\sum_i \Delta V_i\right)_f} = \frac{1}{V_{u\,293}},$$

where $k_0 = 0.731$ and V_{u293} is the specific volume of the network at 293 K.

The calculated and experimental dependences of ρ_{293} on M_f for a number of epoxy resins based on bisphenol A and dicarbox-

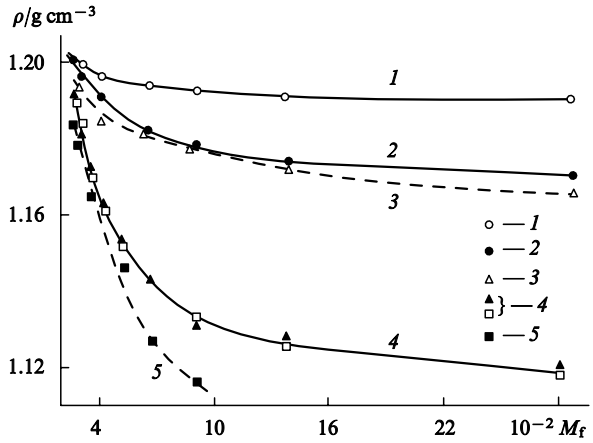


Figure 3. Dependences of the density on the molecular weight of the repeating fragment obtained by the hydrostatic weighing method (*1*, *4*), calculations (*2*, *4*), and according to thermal dilatometric data (*3*, *5*) for cured epoxy resins containing azelaic acid (*1*–*3*) and oleic acid (*4*, *5*).

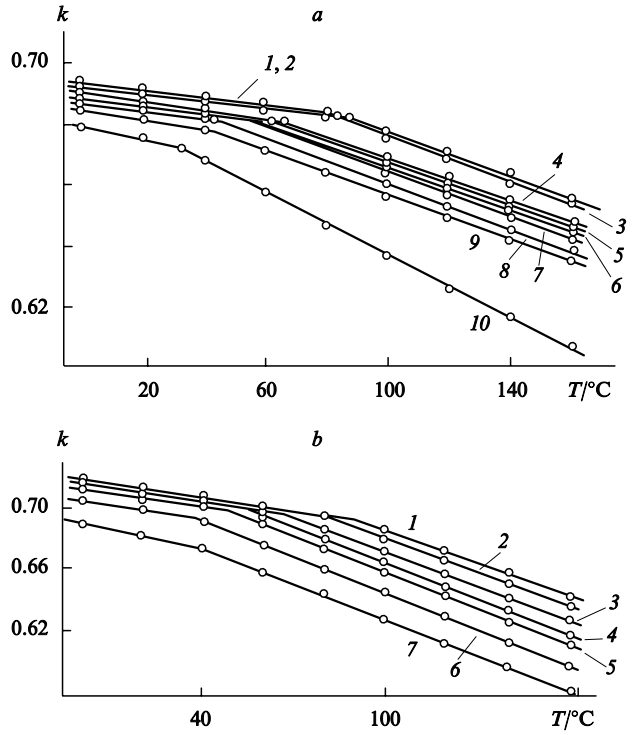


Figure 4. Temperature dependences of the molecular packing coefficient for epoxy resins containing azelaic acid (*a*) and oleic acid (*b*) cured with methyltetrahydrophthalic anhydride.
The content of azelaic acid, mole fraction: (*1*) 0.1; (*2*) 0.2; (*3*) 0.3; (*4*) 0.4; (*5*) 0.5; (*6*) 0.6; (*7*) 0.7; (*8*) 0.8; (*9*) 0.9; and (*10*) 1.0;
the content of oleic acid, mole fraction: (*1*) 0.1; (*2*) 0.2; (*3*) 0.3; (*4*) 0.4; (*5*) 0.5; (*6*) 0.6; (*7*) 0.7; (*8*) 0.8; and (*9*) 0.9.

ylic azelaic acid (or monocarboxylic oleic acid) added to the compositions to lengthen the linear fragments or to introduce 'dangled' chains are shown in Fig. 3.

Temperature dependences of the molecular packing coefficient k for these networks are of interest (Fig. 4). These dependences were calculated using the specific volume measured at different temperatures

$$k(T) = \frac{N_A\left(\sum_i \Delta V_i\right)_f}{V_u(T)M_f}.$$

The empty volume ΔV_{ev}, which is the difference between the volume of the body at a given temperature and its van der Waals volume, is calculated as follows:

$$\Delta V_{ev}(T) = V(T) - N_A\left(\sum_i \Delta V_i\right)_f,$$

where $V(T)$ is the molar volume at temperature T.

At the glass transition temperature T_g, we have

$$\Delta V_{ev}(T_g) = V(T_g) - N_A\left(\sum_i \Delta V_i\right)_f,$$

and the fraction of the empty volume is

$$\frac{V_{ev}(T_g)}{V(T_g)} = 1 - k_g,$$

where k_g is the molecular packing coefficient at the glass transition temperature T_g. For highly cross-linked polymer networks, this parameter is constant in the first approximation and is equal to 0.322.

III. Analysis of the structure of highly cross-linked polymer networks

Analysis of the structure of highly cross-linked polymer networks is hampered by the fact that the initial oligomers (*e.g.*, epoxy oligomers) are, as a rule, polydisperse and contain various impurities. In addition, chemical processes occurring in the course of curing are complicated by side reactions. Therefore preference should be given to direct spectroscopic investigation techniques; however, indirect methods also can be useful.

The structure of polymer networks is analysed by both chemical and physical methods. Among purely chemical methods, mention may be made of a method based on a polymer chain fragmentation by unambiguous reactions.[9] The network structure can be judged from the composition of the products formed. Another method consists in introducing stable nitroxyl radicals into the polymer matrix and estimating their molecular mobility from EPR spectra.[10] IR spectroscopy is also used for analysing the structure of highly cross-linked networks.

The last method was used to study curing of bisphenol A diglycidyl ether with *m*-phenylenediamine.[11] The degree of curing with respect to epoxy groups was estimated from the decrease in the absorption band at 914 cm^{-1}. If the epoxy groups are in excess compared to the amino groups, they react mainly with hydroxyl groups at deep stages of curing. The network structure is also established by NMR spectroscopy and elemental analysis. These methods were used, *e.g.*, by Yu and Bell[12] who studied the reaction of bisphenol A diglycidyl ether with diphenyl carbonate in the presence of various catalysts. The epoxy resin reacts with polycarbonate to form polymer networks with a maximum glass transition temperature $T_g \simeq 120$ °C. In studies of reactions of epoxy resins with aromatic polyesters,[13–15] it has been found that the epoxy groups react with the ester groups to form networks possessing increased heat resistance.

NMR spectroscopy is used not only for analysing the chemical structure, but also for assessing the topology of the network structure. Using nuclear magnetic cross-relaxation data, a study was carried out of a number of epoxyamine polymers obtained with different ratios of the epoxy and the amino groups (diepoxide was partially replaced by monoepoxide so that the stoichiometric ratio was retained).[16] The two-component spectrum of the cross-relaxation times and the values and the nature of temperature and concentration changes in the populations of selected groups of protons are due to the topology of the network structure.

Pulse NMR was used to study the relaxation properties of a number of model epoxy polymers based on resorcinol diglycidyl ether with different concentrations of cross-links, degrees of branching, and the nature of the cross-link point. On glass transition, the molecular motion in polymer networks occurs by at least two types of segments, *viz.*, by cross-link points with adjacent chain fragments and by linear fragments.

New results were obtained in pulse NMR studies of epoxy oligomers and networks based on them.[17–20] This method was used to study the relaxation properties of epoxy oligomers.[17] The kinetic inhomogeneity of these substances is associated either with phase separation or with a broad fractional composition. A comparison of the results obtained by pulse NMR with those of viscosimetric and dielectric studies has shown that the free volume of the system mainly affects the nature of the temperature dependence of relaxation parameters. NMR cross-relaxation, differential microcalorimetry, and IR spectroscopic studies of the process of structure formation of a polymer based on bisphenol A diglycidyl ether and 1,3-bis(aminomethyl)adaman-tane have shown[18] that native specimens possess an ensemble of slowly relaxing protons with a glass transition temperature 20 K higher than that of a fully cured polymer. The temperature of freeing the mobility of the structural elements of native and fully cured polymers decreases as the temperature of isothermal curing increases. A model of large-scale motion in highly cross-linked polymer networks was pro-

posed,[20] which allowed one to rationalise the experimental results obtained in a pulse NMR study of epoxy networks.

Physical methods for the analysis of the structure of highly cross-linked networks are most widely used.[21–23] They include swelling, mechanical measurements, osmometry, cryoscopy, measurements of ultrasound velocity, dielectric measurements, *etc*. Methods of determining hardness and penetration have been used widely to judge the degree of curing of thermosetting resins; the apparatus for such measurements was described by Ciecierski and Kohman.[24] Dynamic mechanical analysis is most widely used.[25, 26] The degree of conversion is judged from changes in the modulus of elasticity and in the loss factor tan δ.

A method for assessing the linear network fragment M_c based on measuring the depression of the solvent freezing temperature in the swollen network has been described.[27] The degree of curing can also be estimated from changes in the refractive index;[28] however, this method is only suitable at the initial curing stage. Another method consists in measuring linear expansion of a specimen and comparing this parameter with that of a standard specimen.[29] These studies are closely related to investigations of the kinetics of network curing.[30–37] However, mechanical measurements (the equilibrium rubbery modulus) and sorption methods (the equilibrium degree of swelling or measurements of mechanical properties of swollen networks) remain most widely used methods for assessing the M_c value in polymer networks. Another method for assessing the structure of highly cross-linked polymer networks based on comparison of the calculated and experimental values of the glass transition temperature is also possible. As to the equilibrium rubbery modulus, the classical theory of rubber elasticity is, as a rule, inapplicable to highly cross-linked systems and another approach described in detail below is required in this case.

IV. Calculations of glass transition temperatures of polymer networks

Like many other properties of cross-linked systems, the glass transition temperature depends on the number (m) of repeating units between cross-link points (see Fig. 1). The glass transition temperature of a sparse network depends slightly on m; however, a sharp increase in the glass transition temperature occurs to reach very high values as the number of repeating units of linear chains between adjacent cross-link points decreases substantially. The results of experiments and calculations show that the onset of sharp increase in the glass transition temperature is observed as the number of units in the linear fragments connecting cross-link points becomes less than 4 or 5. As was mentioned above, it is just the value m that suggests the passage from sparse networks to highly cross-linked networks.

Let us consider two limiting cases.

1. The network is too sparse, and $m \to \infty$. In this case, the network properties are virtually the same as those of a linear polymer of the same chemical structure. The glass transition temperature can be calculated using the following equation [7,8]

$$T_g = \frac{\left(\sum_i \Delta V_i\right)_0}{\sum_i a_i \Delta V_i + \sum_j b_j}, \tag{5}$$

where a_i and b_j are parameters characterising the energy of a weak dispersion interaction averaged for each atom and the energy of strong intermolecular interaction (different kinds of the dipole-dipole interaction and hydrogen bonds), respectively.

2. The network is extremely highly cross-linked and consists of nothing but cross-link points. In this case, softening of the network upon heating can occur only because of its thermal degradation due to the cleavage of chemical bonds in the cross-link points. The softening temperature (more rigorously, the temperature of the onset of intense thermal degradation) of this network can be calculated using the following equation [38]

$$T_d = \frac{\left(\sum_i \Delta V_i\right)_{c\text{-}l}}{\sum_i K_i \Delta V_i}, \tag{5a}$$

where K_i is a parameter dependent on the energy of chemical bonds

$$K_i = \frac{63}{2} \frac{R}{(ad_0E)_i},$$

R is the universal gas constant, and a, d_0, and E are parameters of the Morse potential

$$\phi(d) = E\{(\exp[-a(d-d_0)]-1)^2-1\},$$

where d is the distance between the chemically bonded atoms, d_0 is the equilibrium distance, and E is the bond dissociation energy.

Detailed calculations of glass transition temperatures of linear polymers and softening temperatures of highly cross-linked polymer networks can be found in the literature.[3, 7, 8]

For the most part, actual networks correspond to an intermediate case since they contain rather long but finite-length linear fragments between cross-link points. Generalisation of Eqns (5) and (5a) taking into account the effects of both linear fragments and cross-link points of the network on the glass transition temperature resulted in the following relationship:[5, 6]

$$T_g = \frac{\left(\sum_i \Delta V_i\right)_f}{\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_l + \left(\sum_i K_i \Delta V_i\right)_{c\text{-}l}}, \tag{6}$$

where the denominator is the sum of the sets of the increments of the linear chains constituting the repeating fragment (the 'l' subscript) and of the cross-link point (the 'c-l' subscript).

This equation can be applied both to extremely sparse and to most highly cross-linked networks as well as to the networks of intermediate structure. In fact, if the network consists virtually of nothing but linear fragments, the effect of cross-link points can be neglected and Eqn (6) becomes Eqn (5). On the contrary, if the network consists of nothing but cross-link points, then Eqn (6) becomes Eqn (5a). For intermediate cases both terms in the denominator of Eqn (6) are taken into account.

Let us consider two important methodological problems. The first problem is associated with the assessment of the van der Waals volume of the repeating fragment of the network. For networks with tri- and tetrafunctional cross-link points considered above (see Fig. 2), the van der Waals volumes of repeating fragments are calculated using Eqns (3) and (4), respectively.

Yet another type of network is shown in Fig. 5. In such a network, linear chains and cross-linking bridges are of different chemical nature. The formula for calculating the van der Waals volume of the repeating network fragment has the form

$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{l,1}(m_1 - 2) + 2\left(\sum_i \Delta V_i\right)^*_{l,1} + \left(\sum_i \Delta V_i\right)_{l,2} \frac{m_2 - 2}{2} + \left(\sum_i \Delta V_i\right)^*_{l,2} + \left(\sum_i \Delta V_i\right)_{c\text{-}l},$$

where $\left(\sum_i \Delta V_i\right)_{l,1}$ is the van der Waals volume of the repeating unit of linear fragments of chains that are being cross-linked, m_1 is

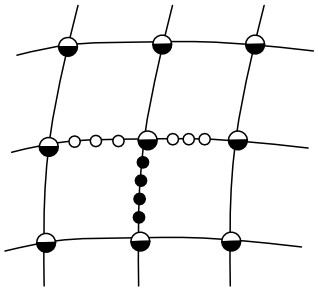


Figure 5. A network built of linear chains of the same chemical nature and cross-linking bridges of other chemical nature (a trifunctional cross-link point is shown).

the average number of such units between the cross-link points; $\left(\sum_i \Delta V_i\right)^*_{1,1}$ is the van der Waals volume of the unit immediately adjacent to the cross-link point (this unit differs in its chemical structure from 'normal' units); $\left(\sum_i \Delta V_i\right)_{1,2}$ is the van der Waals volume of the repeating unit of linear fragment of cross-linking bridges, m_2 is the number of such units; and $\left(\sum_i \Delta V_i\right)^*_{1,2}$ is the van der Waals volume of the unit immediately adjacent to the cross-link point.

Let us dwell once again on the concept of 'a cross-link point of the network'. To formulate this concept, Eqn (6) was 'calibrated' using experimental glass transition temperatures of numerous well-characterised cross-linked systems.[5] It turned out that the best agreement between the calculated and experimental results is achieved with the definition of the cross-link point given in the Introduction.

The molecular weight of averaged linear fragment can be estimated based on the chemical structure of the network and the experimental glass transition temperature. To this end, one must substitute the experimental T_g value into Eqn (6) and solve it with respect to m. Let us perform such an analysis in a general form for different types of networks.

First, we consider the network shown in Fig. 2*b*; four chains issue out of each cross-link point of this network and all the linear fragments have the repeating units of the same chemical structure. Using relationship (3) and Eqn (6), we can write for the repeating network fragment

$$T_g = \left[2(m-2)\left(\sum_i \Delta V_i\right)_1 + 4\left(\sum_i \Delta V_i\right)^*_1 + \left(\sum_i \Delta V_i\right)_{c\text{-}1}\right] \Bigg/ \Bigg/ \left[2(m-2)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_1 + 4\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)^*_1 + \left(\sum_i K_i\Delta V_i\right)_{c\text{-}1}\right], \quad (7)$$

where the first term in the denominator is the set of increments for the repeating unit of linear chains, the second term is the set of the increments for the outer units immediately adjacent to the cross-link points, and the third term is the set of increments for the cross-link point of the network.

The molecular weight M_c of linear chains between the cross-link points can be determined using the following formula

$$M_c = (m-2)M_0 + 2M_0^* + \frac{1}{2}M_{c\text{-}1}, \quad (8)$$

where M_0 is the molecular weight of a 'normal' unit, M_0^* is the molecular weight of the unit immediately adjacent to the cross-link point, and $M_{c\text{-}1}$ is the molecular weight of the cross-link point.

Let us introduce the following designations:

$$\left(\sum_i \Delta V_i\right)_1 = A, \quad 2\left(\sum_i \Delta V_i\right)_1 + \frac{1}{2}\left(\sum_i \Delta V_i\right)_{c\text{-}1} = B,$$

$$\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_1 = C,$$

$$2\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)^*_1 + \frac{1}{2}\left(\sum_i K_i\Delta V_i\right) = D.$$

Then, after some transformations relationships (7) and (8) respectively take the form

$$m-2 = \frac{B - T_gD}{T_gC - A}, \quad M_c = \frac{B - T_gD}{T_gC - A}M_0 + 2M_0^* + \frac{1}{2}M_{c\text{-}1}.$$

Let us analyse a network with trifunctional cross-link points and chain fragments of the same chemical structure issuing out from the cross-link point (see Fig. 2*a*). We can write for the repeating fragment of such a network

$$T_g = \left[(m-2)\frac{3}{2}\left(\sum_i \Delta V_i\right)_1 + 3\left(\sum_i \Delta V_i\right)^*_1 + \left(\sum_i \Delta V_i\right)_{c\text{-}1}\right] \Bigg/ \Bigg/ \left[(m-2)\frac{3}{2}\left(\sum_i a_i\Delta V_i + \sum_j b_j\right) + 3\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)^*_1 + \left(\sum_i K_i\Delta V_i\right)_{c\text{-}1}\right]. \quad (9)$$

Taking into account the designations introduced we have

$$m-2 = \frac{2}{3}\frac{B_1 - T_gD_1}{T_gC - A},$$

where

$$B_1 = 3\left(\sum_i \Delta V_i\right)^*_1 + \left(\sum_i \Delta V_i\right)_{c\text{-}1},$$

$$D_1 = 3\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)^*_1 + \left(\sum_i K_i\Delta V_i\right)_{c\text{-}1}.$$

Hence

$$M_c = (m-2)M_0 + 2M_0^* + \frac{2}{3}M_{c\text{-}1} = \frac{2}{3}\frac{B_1 - T_gD_1}{T_gC - A}M_0 + 2M_0^* + \frac{2}{3}M_{c\text{-}1}.$$

For the network shown in Fig. 5, the dependence of T_g on the composition has the form

$$T_g = \left\{(m-2)\left(\sum_i \Delta V_i\right)_{1,1} + 2\left(\sum_i \Delta V_i\right)^*_{1,1} + \frac{2}{3}\left(\sum_i \Delta V_i\right)_{c\text{-}1} + \frac{m_2-2}{2}\left(\sum_i \Delta V_i\right)_{1,2} + \left(\sum_i \Delta V_i\right)^*_{1,2} + \frac{1}{3}\left(\sum_i \Delta V_i\right)_{c\text{-}1}\right\} \Bigg/ \Bigg/ \left\{(m_1-2)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{1,1} + 2\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)^*_{1,1} + \left(\sum_i K_i\Delta V_i\right)_{c\text{-}1} + \frac{m_2-2}{2}\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{1,2} + \left(\sum_i a_i\Delta V_i + \sum_j b_j\right)^*_{1,2}\right\}, \quad (10)$$

where m_1 and m_2 are the numbers of 'normal' units in the linear chains and in the cross-linking bridges between adjacent cross-link points, respectively, and the asterisked parameters correspond to the units immediately adjacent to the cross-link points. The m_1/m_2 ratio is equal to the mole ratio of the components 1 and 2

$$\frac{m_1}{m_2} = \frac{q_1}{q_2},$$

where q_1 and q_2 are the numbers of moles of the components 1 and 2, respectively. Substituting this relationship into formula (10), we get

$$m_1 - 2 = \Bigg[B_2 - 2A_1 - A_2 - T_g(D_2 - 2C_1 - C_2) - \\ - 2T_g\left(C_1 - \frac{q_1}{2q_2}C_2\right) + 2\left(A_1 - \frac{q_1}{2q_2}A_2\right)\Bigg] \Bigg/ \\ \Bigg/ \left[T_g\left(C_1 + \frac{q_1}{2q_2}C_2\right) - \left(A_1 + \frac{q_1}{2q_2}A_2\right)\right],$$

where

$$B_2 = 2\left(\sum_i \Delta V_i\right)_{1,1} + \frac{2}{3}\left(\sum_i \Delta V_i\right)_{c\text{-}1} + \left(\sum_i \Delta V_i\right)_{1,2} + \\ + \frac{1}{3}\left(\sum_i \Delta V_i\right)_{c\text{-}1};$$

$$A_1 = \left(\sum_i \Delta V_i\right)_{1,1}; \quad A_2 = \left(\sum_i \Delta V_i\right)_{1,2},$$

$$D_2 = 2\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)^*_{1,1} + \left(\sum_i K_i \Delta V_i\right)_{c\text{-}1} + \\ + \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)^*_{1,2};$$

$$C_1 = \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{1,1}; \quad C_2 = \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{1,2}.$$

Let us introduce the following designations:

$$B^* = B_2 - 2A_1 - A_2 + 2\left(A_1 + \frac{q_1}{q_2}A_2\right),$$

$$D^* = D_2 - C_2 + \frac{q_1}{q_2}C_2,\ C^* = C_1 + \frac{q_1}{q_2}C_2;\ A^* = C_1 + \frac{q_1}{q_2}A_2.$$

Taking into account these designations, we obtain

$$m_1 - 2 = \frac{B^* - T_g D^*}{T_g C^* - A^*}. \qquad (11)$$

For a network consisting of the fragments of different nature, it is expedient to calculate two values of the molecular weight of the linear chains between cross-link points, *viz*., $M_{c,1}$, which is the molecular weight of the linear chain fragment between cross-link points for the chains that are being cross-linked, and $M_{c,2}$, which is the molecular weight of the linear chain fragment between cross-link points for the cross-linking bridges

$$M_{c,1} = (m_1 - 2)M_1 + 2M_1^* + M_{c\text{-}l,1}, \qquad (12)$$

$$M_{c,2} = (m_2 - 2)M_2 + 2M_2^* + M_{c\text{-}l,2} = \qquad (13)$$

$$= \left(\frac{q_1}{q_2}m_1 - 2\right) + 2M_2^* + M_{c\text{-}l,2},$$

where $M_{c\text{-}l,1}$ is the molecular weight of a part of the cross-link point shared by the chains that are being cross-linked (see Fig. 5, filled segments of the circles) and $M_{c\text{-}l,2}$ is the molecular weight of a part of the cross-link point shared by cross-linking bridges (see Fig. 5, open segments of the circles). The sum $M_{c\text{-}l,1} + M_{c\text{-}l,2}$ is equal to the molecular weight of the entire cross-link point $M_{c\text{-}l}$.

Taking into account formula (11), expressions (12) and (13) take the form

$$M_{c,1} = \frac{B^* - T_g D^*}{T_0 C^* - A^*}M_1 + 2M_1^* + M_{c-l,1},$$

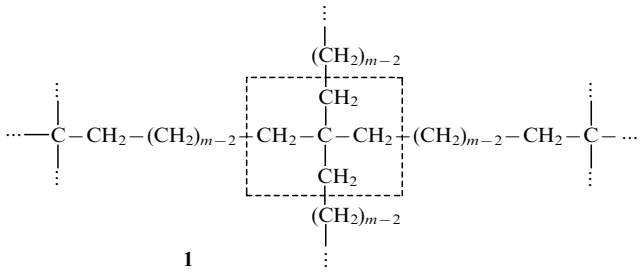
$$M_{c,2} = \frac{q_1}{q_2}M_2\left(\frac{B^* - T_g D^*}{T_0 C^* - A^*} + 1\right) + 2(M_2^* - M_2) + M_{c\text{-}l,2}.$$

The average molecular weight M_a of the chain between cross-link points of the network can be calculated using the following formula

$$M_a = \alpha M_{c,1} + (1-\alpha)M_{c,2},$$

where $\alpha = q_1/(q_1 + q_2)$.

Networks with tetrafunctional cross-link points. Let us consider calculations of T_g and M_c for three types of networks in more detail. We will analyse a hypothetical polyethylene-based network (structure **1**) as the simplest example of a network with a tetrafunctional cross-link point and linear chains of the same chemical structure issuing out of the cross-link point.



1

For such a network, the van der Waals volume of the repeating fragment can be determined using the following relationship

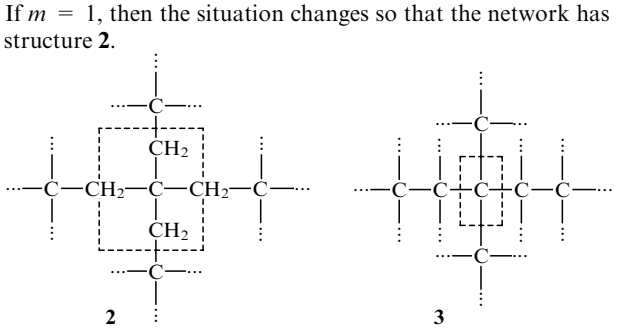
$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{c\text{-}1} + 2\left(\sum_i \Delta V_i\right)_0 (m-2),$$

where the first term is the van der Waals volume of the cross-link point (enclosed by dashes), and the second term is the van der Waals volume of the CH_2 group. The values of all the parameters of the network are given in Table 1. By substituting them into Eqn (7), it is possible to calculate the glass transition temperature

$$T_g = \frac{34.2m + 5}{160.4m - 217.86} \times 10^3. \qquad (14)$$

Relationship (14) is valid if $m \geqslant 2$. The dependence of T_g on m calculated using this formula is shown in Fig. 6*a*.

If $m = 1$, then the situation changes so that the network has the structure **2**.



2 **3**

Such a network consists of nothing but cross-link points, each CH_2 group being shared by two adjacent cross-link points. For the calculated values of the above mentioned parameters of the network, see Table 1.

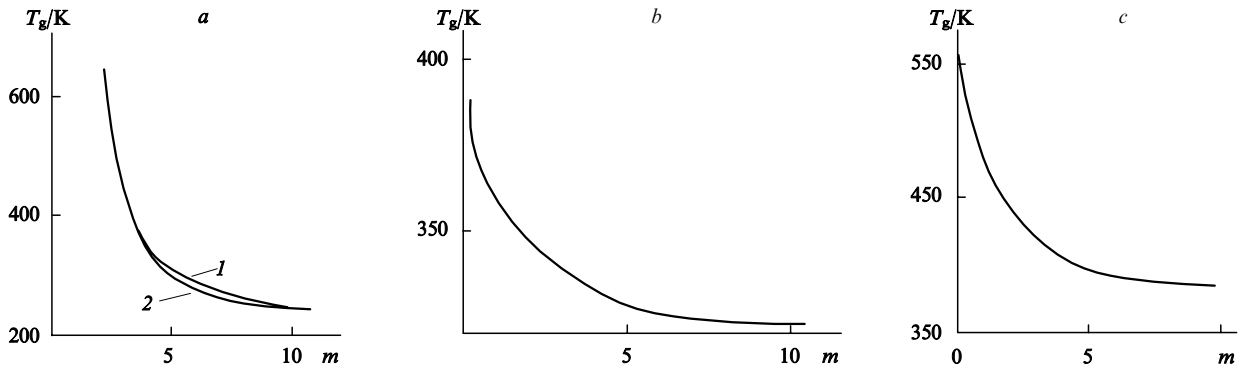


Figure 6. Dependences of T_g on m for a model polyethylene-based network with a trifunctional (*1*) and tetrafunctional (*2*) cross-link points (*a*), for cured epoxy resin (*b*), and for a network based on polystyrene and divinylbenzene (*c*).

This network contains no linear fragments; hence $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right) = 0$ and softening of such a network occurs only because of thermal degradation (*i.e.*, decomposition through cleavage of chemical bonds). Substitution of all the parameters into Eqn (7) gives

$$T_g = T_d = \frac{39.2}{54.3} \times 10^3 = 721\ \text{K}\ .$$

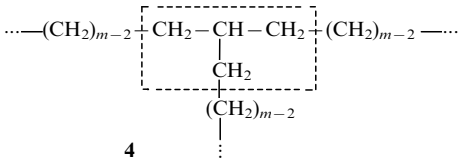
The network with $m = 0$ has structure **3** (the ideal diamond structure). The parameters of such a network are also listed in Table 1.

After substituting the numerical values into Eqn (7) we obtain

$$T_g = T_d = \frac{5.0}{5.7} \times 10^3 = 870\ \text{K}\ .$$

Thus, the calculated temperature of the onset of thermal degradation of diamond is equal to ~873 K; it is known that the complete combustion of diamond occurs on heating to 1273 K.

Networks with trifunctional cross-link points. Let us consider the behaviour of a network with a trifunctional cross-link point (marked by dashes).



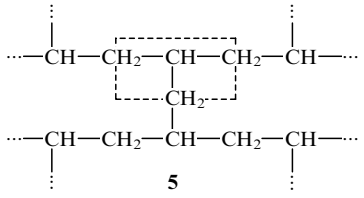
4

Substitution of all parameters of the network (see Table 1) into Eqn (9) gives

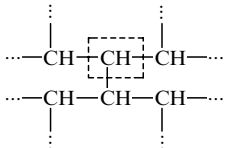
$$T_g = \frac{11 + 25.65m}{119.9m - 151.9} \times 10^3\ . \qquad (15)$$

The dependence of T_g on m is shown in Fig. 6,*a*. It can be seen that T_g decreases sharply as m increases, *i.e.*, with increase in the size of linear fragments between cross-link points.

Formula (15) is valid if $m \geqslant 2$. If $m = 1$, we have the structure **5**.



5



6

Network **5** consists of nothing but cross-link points, which are the repeating network fragments (indicated by dashed lines in the scheme).

Substituting the parameters of this network (see Table 1) into Eqn (9), we get

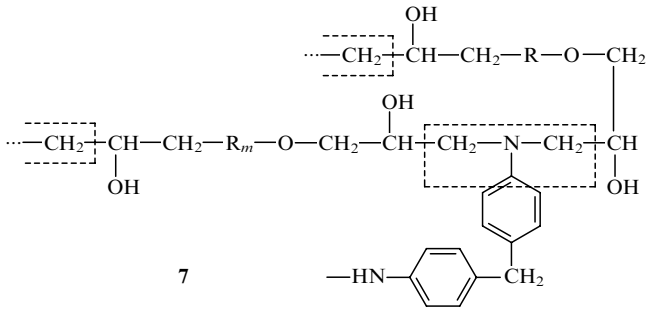
$$T_g = T_d = \frac{34.65}{46.88} \times 10^3 = 740\ \text{K}\ .$$

If $m = 0$, we have the structure **6**, in which each carbon atom is a branching point.

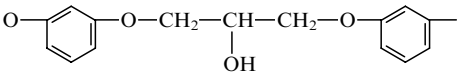
Substitution of the network parameters (see Table 1) into Eqn (9) gives

$$T_g = T_d = \frac{11.0}{14.96} \times 10^3 = 735\ \text{K}\ .$$

Let us consider a network in which linear chains and cross-linking bridges are of different chemical structure. We will analyse an actual epoxy resin-based network **7** [5] as an example.



7

where R = 

The stoichiometric composition of the network was 2 moles of an epoxy oligomer per 1 mole of a curing agent (diamine). The cross-link point of the network is indicated by dashed lines.

Substituting the values of the network parameters (see Table 1) into Eqn (10), we get

$$T_g = \frac{300.6 + 152.3m}{519.3 + 490.6m + 175.6 + 66.1} \times 10^3\ . \qquad (16)$$

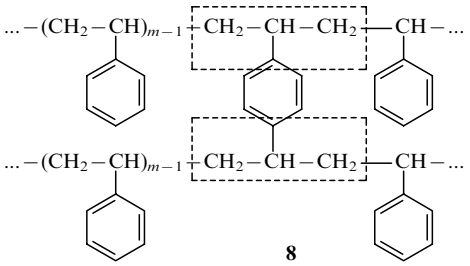
If $m = 0$, we have the structure of cured epoxy resin based on diglycidyl ether of the corresponding bisphenol. For such a resin the calculated $T_g = 395$ K, while the experimental $T_g = 396$ K.

The dependence of T_g on m calculated using formula (16) is shown in Fig. 6*b*. The glass transition temperature increases as the

linear network fragment between cross-link points decreases, which is particularly noticeable if $m \to 0$.

1. The effect of the cross-link distribution in the network on the glass transition temperature

Let us analyse the effect of the cross-link distribution along the chains on the glass transition temperature of the network taking a well-studied network **8** based on polystyrene cross-linked with divinylbenzene as an example. This is a trifunctional network, *i.e.*, three chains issue out of each cross-link point (marked by dashed lines).



8

Substituting the values of the network parameters (see Table 1) into Eqn (10), we get

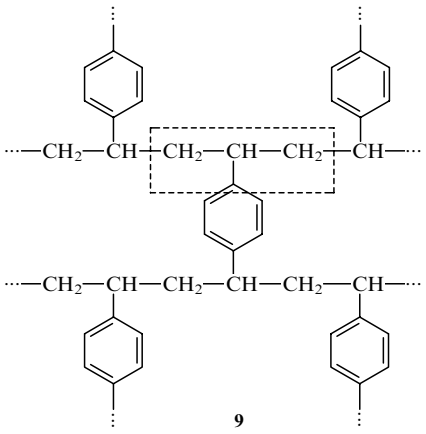
$$T_g = \frac{53.3 + 109.7m - 17.1 + 29.4}{72.9 + 294.0m - 80.2 + 67.6} \times 10^3 = \quad (17)$$

$$= \frac{64.6 + 109.7m}{60.3 + 294.0m} \times 10^3 .$$

Formula (17) is valid if $m \geqslant 1$.‡ The dependence of T_g on m calculated using formula (17) is presented in Fig. 6 *c*.

It can be seen that the glass transition temperature increases sharply as the number of polystyrene units between adjacent cross-link points decreases, particularly when the number of these units $(m - 1) \to 0$.

If $m = 0$, then the degree of cross-linking of the network is equal to 100%. In structure **9**, the cross-link point of such a network is outlined by dashes.



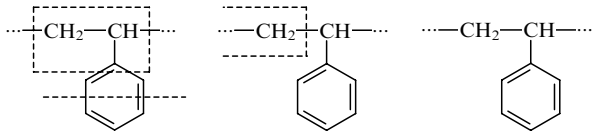
9

Substituting the values of the network parameters (see Table 1) into Eqn (10), we obtain

$$T_g = \frac{36.2 + 29.4}{48.6 + 67.6} \times 10^3 = 656\,\text{K} .$$

Let us consider the effect of the cross-link distribution along linear chains on the glass transition temperature using the concept of the degree of cross-linking α.

‡ It should be noted that if m $\to \infty$, we obtain the calculated T_g of linear polystyrene (373 K).



10 **11** **12**

Let us calculate the values of all parameters of Eqn (10) for a fragment of network **10** (see Table 1).

Account must be taken of the fact that the CH_2 group in the polystyrene repeating unit immediately adjacent to the cross-link point of the network (marked by dashes) is a constituent of the cross-link point. The parameters for this unit are listed in Table 1. The parameters for the 'normal' polystyrene unit (**12**) are also given in Table 1. Having calculated all parameters of Eqn (10), let us consider three cases.

a. Uniform cross-link distribution

In the case of uniform cross-link distribution Eqn (10) takes the form

$$T_g = \left[\alpha\left(\sum_i \Delta V_i\right)_1 + (1-\alpha)\left(\sum_i \Delta V_i\right)_{12}\right] \Bigg/ \quad (18)$$

$$\Bigg/ \left[\alpha\left(\sum_i a_i \Delta V_i + \sum_j b_j + \sum_i K_i \Delta V_i\right)_1 + \right.$$

$$+ \alpha\left(\sum_i a_i \Delta V_i + \sum_j b_j + \sum_i K_i \Delta V_i\right)_2^* +$$

$$\left. + (1-2\alpha)\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{12}\right] ,$$

where α is the degree of cross-linking, which characterises the portion of phenyl groups involved in cross-links and is equal to $1/m$. Substituting the values of all the network parameters into Eqn (18), we get

$$T_g = \frac{\alpha 65.6 + (1-\alpha)109.7}{\alpha 116.2 + \alpha 238.1 + (1-2\alpha)294.0} \times 10^3 . \quad (19)$$

Formula (19) is valid only if $0 < \alpha \leqslant 0.5$. If $\alpha \geqslant 0.5$, the network is free of polystyrene units and formula (19) takes the form

$$T_g = \frac{\alpha 65.6 + (1-\alpha)109.7}{\alpha 116.2 + (1-\alpha)238.1} \times 10^3 . \quad (20)$$

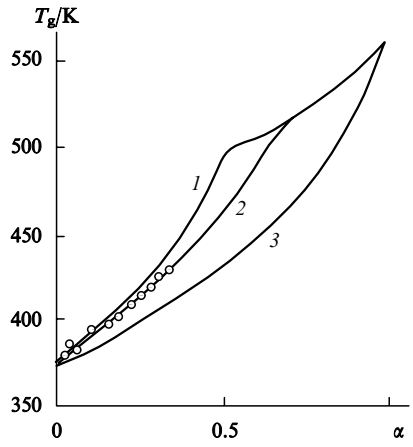


Figure 7. Dependence of T_g on the degree of cross-linking α for the network based on polystyrene and divinylbenzene. The distribution of cross-link points: (*1*) uniform; (*2*) random; and (*3*) the most non-uniform. The points represent the experimental values.

If $\alpha = 0$, we get the calculated glass transition temperature of linear polystyrene.

The dependence of T_g on the degree of cross-linking α calculated using Eqns (19) and (20) is shown in Fig. 7 (curve *1*). Two portions, in which fast and slow increase in T_g are observed can be distinguished in the curve of this dependence. From the analysis performed above, it follows that this is due to a specific effect of cross-link points of the network on T_g.

b. Random cross-link distribution

The function of distribution in distances for a random field of points distributed along a straight line takes the form

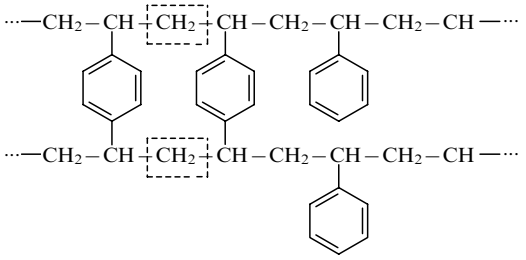
$$\bar{f}(l) = 1 - e^{-l/l_a},$$

where l is the distance between neighbouring points (in our case it is the distance between cross-link points), and l_a is the average distance.

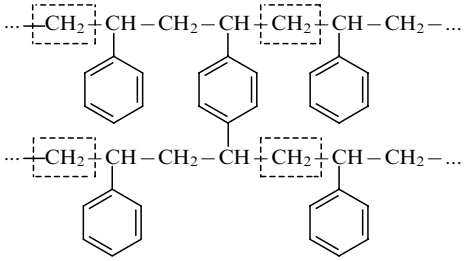
Going to the degree of polymerisation m, we get

$$\bar{f}(m) = 1 - e^{-m/m_a}.$$

In the case of neighbouring cross-link points, the number of the CH_2 groups belonging both to styrene units and to cross-link points (marked by dashed lines)



will be less than in the case when cross-link points are separated by linear fragments.



As a result, the $\alpha\left(\sum_i a_i\Delta V_i + \sum_j b_j + \sum_i K_i\Delta V_i\right)^*_2$ value decreases by an amount proportional to the number of adjacent cross-links. Simultaneously, the $(1-\alpha)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{12}$ value increases by the same amount.

Since our interest is focused on neighbouring cross-link points, at $m = 1$ the function $\bar{f}(m)$ has the form $\bar{f}(m) = 1 - e^{-1/m}$, and taking into account that $m_1 = 1/\alpha$, we obtain

$$\bar{f}(1) = 1 - e^{-\alpha}.$$

Then we should substitute $\alpha - \alpha(1 - e^{-\alpha}) = \alpha/e^{\alpha}$ for α in the second term and $1 - 2\alpha + \alpha(1 - e^{-\alpha}) = 1 - \alpha - \alpha/e^{\alpha}$ for $(1-2\alpha)$ in the third term in the denominator of relationship (19).

On substitution, we obtain

$$T_g = \left[\alpha\left(\sum_i \Delta V_i\right)_1 + (1-\alpha)\left(\sum_i \Delta V_i\right)_{12}\right] \Bigg/ \tag{21}$$

$$\Bigg/ \alpha\left(\sum_i a_i\Delta V_i + \sum_j b_j + \sum_i K_i\Delta V_i\right)_1 +$$

$$+ \frac{\alpha}{e^{\alpha}}\left(\sum_i a_i\Delta V_i + \sum_j b_j + \sum_i K_i\Delta V_i\right)^*_2 +$$

$$+ \left(1 - \alpha - \frac{\alpha}{e^{\alpha}}\right)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{12}.$$

Substituting the parameters of networks **8**, **10**–**12** (see Table 1) into Eqn (21), we get

$$T_g = \frac{\alpha 65.6 + (1-\alpha)109.7}{\alpha 116.2 + (\alpha/e^{\alpha})238.1 + (1 - \alpha - \alpha/e^{\alpha})294.0} \times 10^3. \tag{22}$$

Formula (22) is valid if $(\alpha + \alpha/e^{\alpha}) \leqslant 1$, which corresponds to $\alpha \leqslant 0.66$.

If $(\alpha + \alpha/e^{\alpha}) \geqslant 1$, there are no uncross-linked polystyrene units and formula (22) goes over into relationship (20). The dependence of T_g on α obtained using Eqns (22) and (20) is shown in Fig. 7 (curve *2*).

c. The most non-uniform cross-link distribution

The most non-uniform distribution corresponds to the case where a large number of cross-link points are adjacent and form long sequences connected by linear fragments of polystyrene chains (Fig. 8). For such a distribution of cross-link points, the number

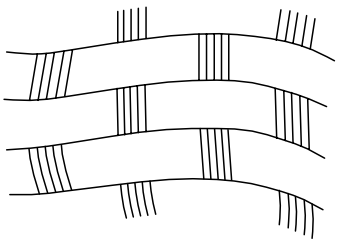


Figure 8. The most non-uniform distribution of cross-link points.

of polystyrene units immediately adjacent to the point can be neglected and we can write

$$T_g = \left[\alpha\left(\sum_i \Delta V_i\right)_1 + (1-\alpha)\left(\sum_i \Delta V_i\right)_{12}\right] \Bigg/ \tag{23}$$

$$\Bigg/ \alpha\left(\sum_i a_i\Delta V_i + \sum_j b_j + \sum_i K_i\Delta V_i\right)_1 +$$

$$+ (1-\alpha)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{12}.$$

Substituting all values of the network parameters (see Table 1) into formula (23), we obtain

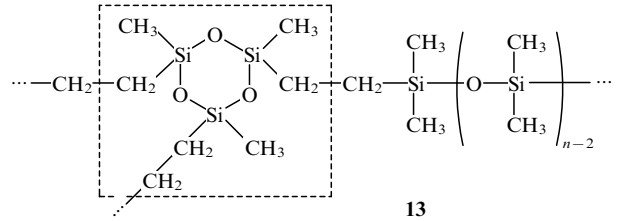
$$T_g = \frac{\alpha 65.6 + (1-\alpha)109.7}{\alpha 116.2 + (1-\alpha)294.0} \times 10^3. \tag{24}$$

The dependence of T_g on α calculated using relationship (24) is shown in Fig. 7 (curve *3*). The experimental data obtained by Shefer and Gottlieb [39] are also shown in this figure. Curve *2* fits well the experimental points; this indicates a random distribution of cross-link points in the actual network.

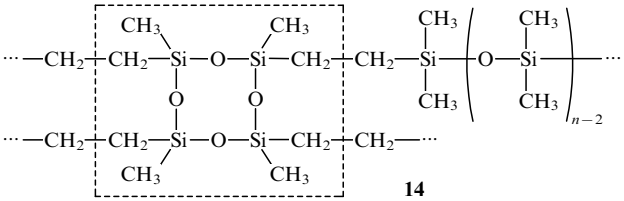
2. The influence of the structure of the cross-link point on the glass transition temperature of the network

Let us consider the problem of the influence of the chemical structure of the network on its glass transition temperature taking networks with linear fragments between cross-link points of the same chemical structure and cross-link points of different chemical

structure as an example. Polydimethylsiloxane networks with the following chemical structure [40]



13



14

are suitable for such an analysis.

The synthesis of highly cross-linked polymer networks with small n values is based on the use of individual compounds with a precisely set value of n; therefore, if the degree of conversion is close to 100%, then the M_c value of such networks is given with sufficient accuracy.

The values of all increments entering into Eqn (6) are given in Table 1. Substituting them in Eqn (6), we get the following dependence of the glass transition temperature T_g of the network on the degree of polymerisation

$$T_g = \frac{239.8 + 108.1n}{428.3 + 721.5n} \times 10^3 . \qquad (25)$$

This dependence fits well the experimental points corresponding to glass transition temperatures; the plot is shown in Fig. 9. It can easily be shown for the networks with tetrafunctional cross-link points (**14**) that the calculated $T_g(n)$ dependence is described by the same formula (25), since each value in the numerator and in the denominator of this formula is multiplied by the same number (4/3). The experimental $T_g(n)$ dependence for network **13** is the same as that for network **14**.

Let us consider the influence of the structure of the cross-link point of polydimethylsiloxane networks on their glass transition temperature.

To calculate T_g values of the networks containing cross-link points of different structure, it is expedient to determine first the $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{lf}$ and $\left(\sum_i \Delta V_i\right)_{lf}$ values for one linear network fragment between two neighbouring cross-link points. The calculations lead to the following values of these parameters:

$$\left(\sum_i \Delta V_i\right)_{lf} = 72.1n - 0.5 \text{ Å}^3,$$

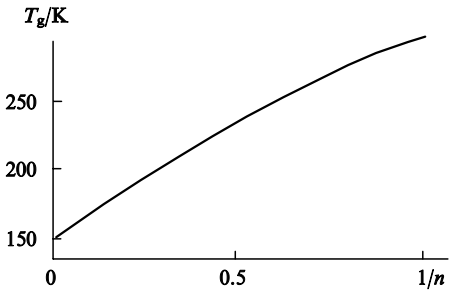
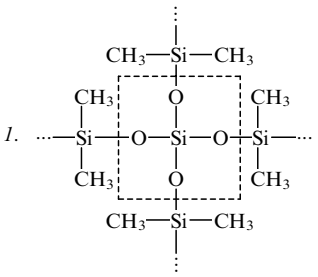


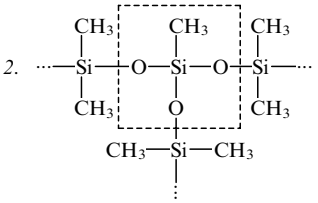
Figure 9. Dependence of T_g on n for the structures **13** and **14**.

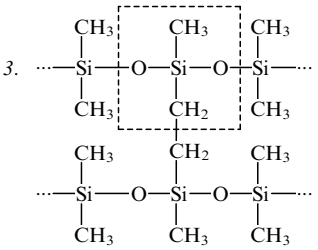
$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{lf} = (481n - 11.5) \times 10^{-3} \text{ Å}^3 \text{ K}^{-1} .$$

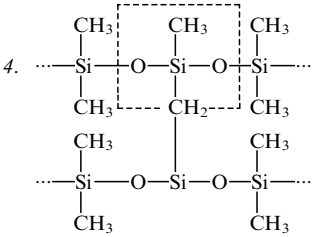
The $\left(\sum_i \Delta V_i\right)_{lf}$ and $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{lf}$ values found are the same for all the networks under consideration.

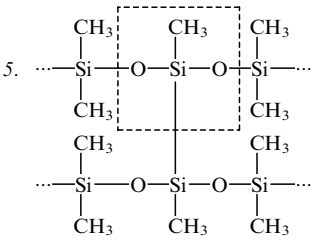
Using Eqn (21), the relationships were obtained that make it possible to calculate the T_g value depending on the number of repeating units n in the linear fragments connecting cross-link points of polydimethylsiloxane networks.

1. 
$$T_g = \frac{144.2n + 33.7}{962n + 11.3} \times 10^3$$

2. 
$$T_g = \frac{108.15n + 52.9}{721.5n + 46.5} \times 10^3$$

3. 
$$T_g = \frac{72.1n + 66.1}{481n + 72.6} \times 10^3$$

4. 
$$T_g = \frac{72.1n + 58.1}{481n + 61.2} \times 10^3$$

5. 
$$T_g = \frac{72.1n + 49.3}{481n + 48.8} \times 10^3$$

The $T_g(n)$ dependences for polydimethylsiloxane networks calculated using these relationships are shown in Fig. 10. It can be seen that the structure of the cross-link point affects considerably the T_g value only if n varies from 1 to 4 ($\alpha = 1 - 0.25$). The effect of cross-link points rapidly decreases as the distance between them increases, and glass transition temperatures of all networks approach that of polydimethylsiloxane (150 K) already at $n = 10$.

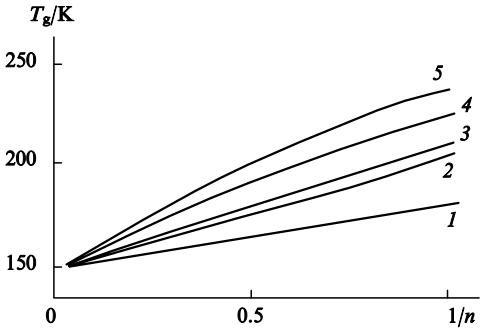
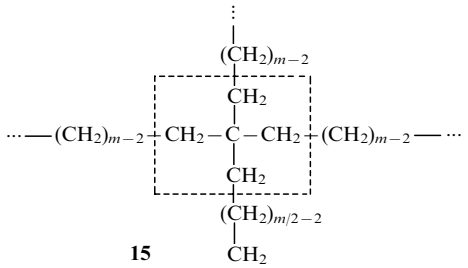


Figure 10. Dependences of T_g of polydimethylsiloxane networks on n for different types of cross-link points. For the designations of fragments (*1–5*), see text.

3. The influence of dangled chains and other defects of the network on the glass transition temperature of polymer networks

Among a wide variety of types of dangled chains we will dwell only on two types. The first type is a modification of network **1** with a portion of cross-linking bridges 'cut' in two.



15

In this case the cross-link point of the network is retained; however, it becomes trifunctional (as can be seen in the scheme, the chemical structure of the cross-link point is also retained).

The repeating fragment of this structure consists of the repeating fragment of a trifunctional network and a dangled chain. Then, we can write for the van der Waals volume

$$\left(\sum_i \Delta V_i\right)_f = \left(\sum_i \Delta V_i\right)_{c\text{-}1} + 1.5\left(\sum_i \Delta V_i\right)_0 (m-2) + \left(\sum_i \Delta V_i\right)_{dc},$$

where the first, the second, and the third terms are the van der Waals volumes of the cross-link point of the network (outlined by dashes in the scheme), of the CH_2 group, and of the dangled chain, respectively. In this case

$$\left(\sum_i \Delta V_i\right)_{dc} = \left(\sum_i \Delta V_i\right)_0 \left(\frac{m}{2}-2\right) + \left(\sum_i \Delta V_i\right)_{CH_3},$$

where the last term is the van der Waals volume of the end CH_3 group.

It should be noted that, in principle, it is impossible for a network free of dangled chains and for a network containing them to be of the same chemical structure. In other words, the appearance of dangled chains always leads to changes in the chemical structure of the network, which affects the glass transition temperature and other properties.

Substituting the values of the parameters of structure **15** (see Table 1) in Eqn (6), we obtain

$$T_g = \frac{\alpha(11.1+34.2m)+(1-\alpha)(5.0+34.2)}{\alpha(160.4m-336.2+102.9)+(1-\alpha)(160.4m-217.86)} \times 10^3$$

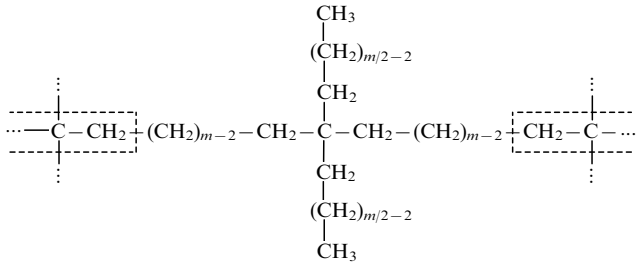
or

$$T_g = \frac{5.0+34.2m+6.1\alpha}{160.4m-15.44\alpha-217.86} \times 10^3 . \qquad (26)$$

Relationship (26) is valid if $\alpha \leqslant 0.5$ since if $m \geqslant 2$, then two cross-link points, out of which dangled chains issue, appear as a result of 'breaking' each linear chain.

The $T_g(\alpha)$ dependence calculated using formula (26) is shown in Fig. 11*a*. It can be seen that T_g increases slightly as α increases and that the slope of this dependence decreases as the number of units (m) between cross-link points increases. At first glance, it may seem that the appearance of network defects such as dangled chains must result in a decrease in the glass transition temperature rather than in its increase. However, it should be kept in mind that in this case the appearance of dangled chains does not reduce the number of cross-link points; even their chemical structure is retained. In addition, the appearance of each branching requires introducing a b_j increment, which favours the increase in T_g.

If upon 'breaking' of the chains the cross-link point ceases to fulfil its initial function (*i.e.*, it is no longer a cross-link point of the network), it is natural that the glass transition temperature will decrease. An example of such a network is shown below.



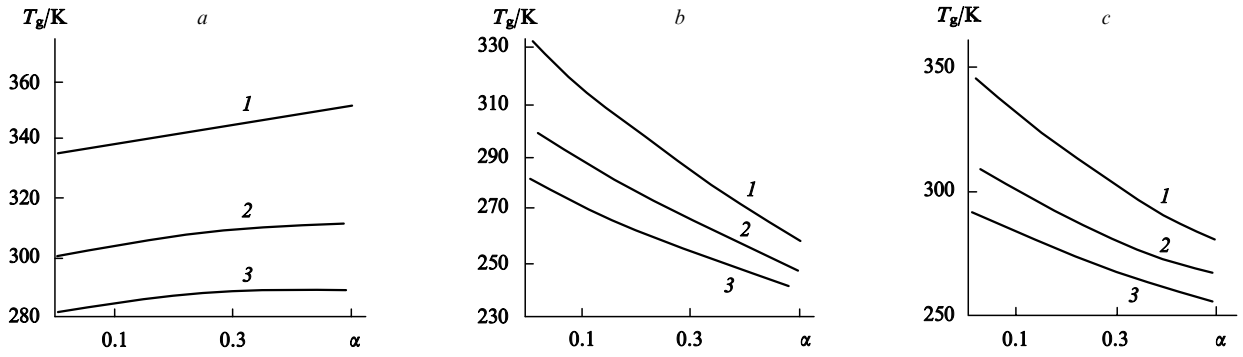


Figure 11. The dependences of T_g on α (for different m) for a tetrafunctional polyethylene network with dangled chains with a constant (*a*) and variable (*b*) number of cross-link points and for a trifunctional polyethylene network with dangled chains (*c*).
m: (*1*) 4; (*2*) 5; (*3*) 6.

Linear chains are formed upon 'breaking' of linear fragments of the network; therefore, calculations for the former cross-link point should be carried out using a_i and b_j increments instead of K_i increments, *i.e.*,

$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{\text{c-l}} = 320.9 \times 10^{-3}\ \text{Å}^3\ \text{K}^{-1}\ .$$

Taking account of this fact and using Eqn (6), we get

$$T_g = \frac{\alpha(17.2 + 34.2m) + (1-\alpha)(5.0 + 34.2m)}{\alpha(80.2m + 160.4m) + (1-\alpha)(160.4m - 217.86)} \times 10^3$$

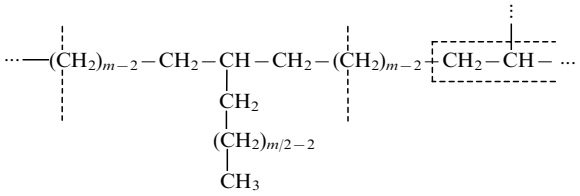
or

$$T_g = \frac{5.0 + 12.2\alpha + 34.2m}{160.4m + 298.1\alpha - 217.86} \times 10^3\ , \qquad (27)$$

where α is the proportion of former cross-link points out of which two 'broken' chains issue.

Relationship (27) is valid if $\alpha \leqslant 0.25$. The $T_g(\alpha)$ dependence calculated using formula (27) is shown in Fig. 11*b*. It can be seen that the glass transition temperature rapidly decreases with the increase in the proportion of cross-link points out of which two 'broken' chains issue. This is explained by the fact that the branching point ceases to play the role of the cross-link point and the linear fragment between neighbouring cross-link points becomes twice as long.

Let us consider a trifunctional network with dangled chains. The scheme of such a hypothetical polyethylene-based network is shown below.



In this case upon 'breaking' the cross-linked chains the point from which the dangled chain issues ceases to play its role and becomes a constituent of a linear fragment with branching.

Using Eqn (6), we obtain

$$T_g = \frac{\alpha(25.652m + 17.1) + (1-\alpha)(25.65m + 11)}{\alpha(24.8 + 120.3m) + (1-\alpha)(120.3m - 152.76)} \times 10^3$$

or

$$T_g = \frac{6.1\alpha + 25.65m + 11.0}{177.56\alpha + 120.3m - 152.76} \times 10^3\ ,$$

where α is the proportion of structures with dangled chains.

The $T_g(\alpha)$ dependences for the network with dangled chains are shown in Fig. 11*c*. The glass transition temperature of the network rapidly decreases with an increase in the proportion of dangled chains (especially for small m).

We have already considered hypothetical polyethylene-based networks in which the fragments between cross-link points and dangled chains are of the same chemical structure. Let us consider now a system in which the chemical structure of dangled chains differs from that of chains forming the network. Such a system based on an epoxy resin has been synthesised and studied.[4] The ED-20 epoxy resin was cured with methyltetrahydrophthalic anhydride. To obtain a network with dangled chains, methyltetrahydrophthalic anhydride was partially replaced by oleic acid. The results of calculations and experimental studies of such networks have been reported in detail.[4,6]

In addition to dangled chains, a network can also contain such defects as isolated loops. Different types of defects are illustrated by Fig. 12. Only those branching sites out of which the chains

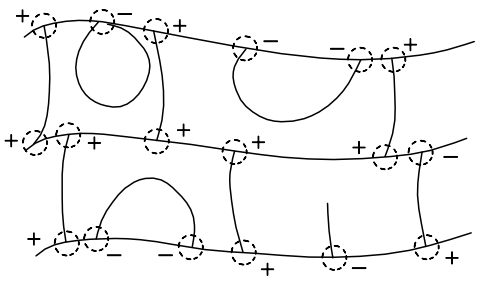
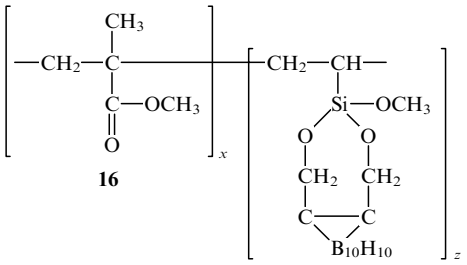


Figure 12. Schematic view of various network defects.

forming cross-links (*i.e.*, chains connecting neighbouring chains) issue are cross-link points. Such structures are marked by the 'plus' sign. The branching sites, out of which the chains issue representing either offshoots or isolated loops (formed through end attachment to the initial point or to some other point of the same chain) rather than cross-links, are not cross-link points (marked by the 'minus' sign).

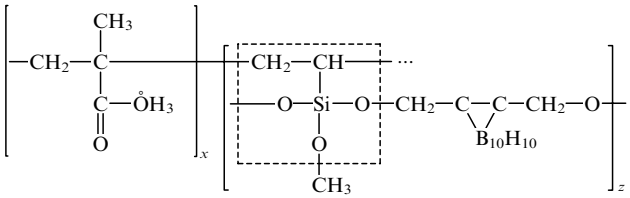
Such defects must be taken into account when calculating the glass transition temperature using relationship (6). If the branching site is a cross-link point (in the sense mentioned above), K_i increments should be used. If the branching site does not play the role of a cross-link point, then a_i and b_j increments for the same atoms should be substituted in relationship (6).

It is possible to estimate the proportion of defects in an actual network by comparing the calculated and experimental T_g values. Let us perform such an analysis taking a network based on methyl methacrylate – 1-methoxy-1-vinyl-1-sila-2,7-dioxa-4,5-(1,2-carborano)cycloheptane copolymer as an example. The chemical structure of this copolymer has the form [41]



16 **17**

When the copolymer is exposed to heat, ring opening occurs in the fragment **17** to form a network of the following chemical structure:



The cross-link point is marked by dashes.

The values of $\left(\sum_i \Delta V_i\right)$, $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)$ and $\left(\sum_i K_i \Delta V_i\right)$ for the fragments **16** and **17** of this network are given in Table 1.

Let us consider the dependence of the glass transition temperature on the chemical structure of the network in general form with taking account of the fact that the network has structural defects and branching (see Fig. 12). Then, relationship (6) can be written in the form

$$T_g = \left(\sum_i \Delta V_i\right) \Big/ \left[\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1 + y\left(\sum_i K_i \Delta V_i\right)_{c\text{-}1} + (1-y)\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)\right], \quad (28)$$

where y is the proportion of branching sites that function as cross-link points. Comparing the calculated and experimental glass transition temperature, one can find the y value from the transformed expression (28):

$$y = \left[T_g^{-1}\left(\sum_i \Delta V_i\right) - \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1 - \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{c\text{-}1}\right] \Big/ \left[\left(\sum_i K_i \Delta V_i\right)_{c\text{-}1} - \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1\right],$$

where T_g is the experimental glass transition temperature.

When copolymers are used for the network formation, as in our case, the situation becomes more complicated. Let us assume that one of the copolymer components does not form a network. Then, in an ideal case (the degree of cross-linking is equal to 100%) we have

$$T_g = \left[(1-n)\left(\sum_i \Delta V_i\right)_{\mathbf{16}} + n\left(\sum_i \Delta V_i\right)_{\mathbf{17}}\right] \Big/ \left\{(1-n)\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{\mathbf{16}} + n\left[\left(\sum_i a_i \Delta V_i + \sum_j b_j\right) + \left(\sum_i K_i \Delta V_i\right)\right]_{\mathbf{17}}\right\}$$

(n is the proportion of the units of structure **17**).

If some of the branching sites do not act as cross-link points, then

$$T_g = \left[(1-n)\left(\sum_i \Delta V_i\right)_{\mathbf{16}} + n\left(\sum_i \Delta V_i\right)_{\mathbf{17}}\right] \Big/ \left\{(1-n)\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{\mathbf{16}} + n\left[\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1 + y\left(\sum_i K_i \Delta V_i\right)_{c\text{-}1} + (1-y)\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)\right]_{\mathbf{17}}\right\}. \quad (29)$$

Let us use relationship (29) to calculate the proportions of active and inactive cross-link points [y and (1 — y), respectively]. According to our calculations,

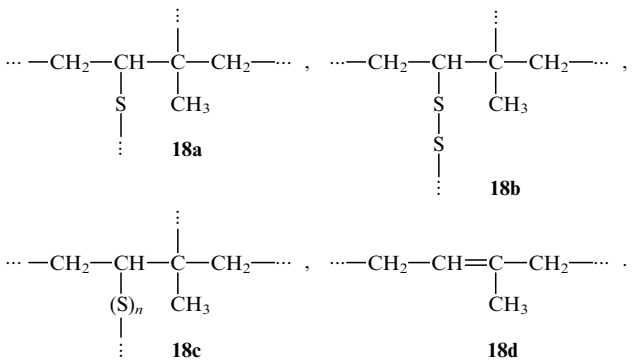
$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{c\text{-}1,\mathbf{16}} = 490.4 \times 10^{-3}\ \text{Å}^3\ \text{K}^{-1}.$$

Substituting the $\left(\sum_i \Delta V_i\right)_{\mathbf{16}}$, $\left(\sum_i \Delta V_i\right)_{\mathbf{17}}$, $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1$, $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{\mathbf{17}}$, $\left(\sum_i K_i \Delta V_i\right)_{c\text{-}1}$, and $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{c\text{-}1,\mathbf{17}}$ values (see Table 1) in formula (29), we get

$$T_g = \frac{96.8 + 112.1n}{255.8 - 420.5ny + 635.6n} \times 10^3. \quad (30)$$

The experimental and calculated dependences of T_g on the content of the component **17** for different proportions of active cross-link points y are shown in Fig. 13. The calculations were performed using formula (30). It can be seen that, *e.g.*, if a proportion of the component **17** is 20%, the proportions of active and inactive cross-link points are equal to 58% and 42%, respectively; if a content of this component is 10%, the proportion of active cross-link points is equal to ~55%, *etc.* Thus, these networks (Ref. 41), despite being highly cross-linked, possess considerable defectiveness. If a content of the structure **17** in the copolymer is 20%, the proportion of the sol fraction is equal to 18.5%. Therefore, some portion of inactive cross-link points (42% – 18.5% = 23.5%) is incorporated into the network and form branchings or isolated loops.

Let us take yet another example of assessing the network structure on the basis of comparing the calculated and experimental glass transition temperatures.[42] Let us consider ebonites, since different types of networks can be formed in them and also because a considerable body of contradictory experimental data on their structure and mechanical properties has been accumulated. Let us calculate the T_g value of a polyisoprene-based ebonite assuming that the amount of sulfur used in the reaction corresponds to one sulfur atom per one polyisoprene repeating unit. Let us consider several variants of the formation of a network that may comprise four types of structures.



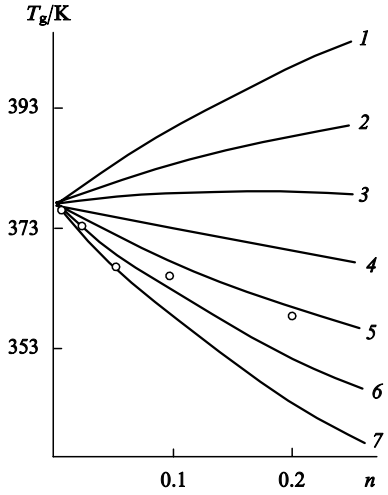


Figure 13. Dependences of T_g on the proportion of 1-methoxy-1-vinyl-1-sila-2,7-dioxa-4,5-(1,2-carborane)cycloheptane (n) in the **16**–**17** copolymer. The proportion of active cross-link points: (*1*) 1; (*2*) 0.9; (*3*) 0.8; (*4*) 0.7; (*5*) 0.6; (*6*) 0.5; and (*7*) 0.4. The points represent experimental values.

The structures **18a**–**c** contain respectively mono-, di-, and polysulfide bridges, and structure **18d** is the initial polyisoprene repeating unit. In the structure **18a**, all the atoms constitute the cross-link point of the network; hence, $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right) = 0$ for this structure. The values of all parameters of structures **18a**–**d** are listed in Table 1.

The glass transition temperature of the structure **18a** calculated using Eqn (6) coincides with the temperature of the onset of intense thermal degradation T_d (since all the atoms constitute the cross-link point of the network)

$$T_g = T_d = 673\,\text{K}\,.$$

Hence, if all sulfur is consumed for curing of the polyisoprene so that only monosulfide bonds are formed, then T_g should coincide with the temperature of the onset of intense thermal degradation, which is equal to 673 K. In practice, the glass transition temperature of ebonites lies in the interval 333–493 K (see Ref. 43); therefore it is likely that di- and possibly polysulfide bridges are formed in addition to the monosulfide bonds. Let us calculate the T_g value of a cross-linked system with different types of bridges between the polyisoprene chains.

Let us find a relation connecting the T_g value of ebonite with the mole fractions of bridges containing mono-, di-, and polysulfide groups. Let $\beta_1, \beta_2, \ldots, \beta_n$ be the mole fractions of cross-link points (bridges) containing mono-, di-, and n-sulfide groups, respectively. With a given stoichiometric ratio of sulfur and polyisoprene, the appearance of one disulfide bond leads to one uncross-linked polyisoprene unit; the appearance of a trisulfide bond leads to two uncross-linked polyisoprene units, *etc*. Hence, the proportion of uncross-linked polyisoprene units will be equal to

$$\beta_u = \beta_2 + 2\beta_3 + \ldots + (n-1)\beta_n = \sum_{i=2}^{i=n}\beta_i(i-1)\,.$$

Then, having regard to the foregoing and this relation, we obtain

$$T_g = \left[\beta_1\left(\sum_i \Delta V_i\right)_1 + \beta_2\left(\sum_i \Delta V_i\right)_2 + \ldots + \beta_n\left(\sum_i \Delta V_i\right)_3 + \left(\sum_i \Delta V_i\right)_4 \sum_{i=2}^{i=n}\beta_i(i-1)\right] \Bigg/ \left\{\beta_1\left(\sum_i K_i\Delta V_i\right)_1 + \beta_2\left(\sum_i K_i\Delta V_i\right)_2 + \ldots + \beta_n\left[\left(\sum_i K_i\Delta V_i\right)_3 + \left(\sum_i a_i\Delta V_i\right)_3\right] + \left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_4 \sum_{i=2}^{i=n}\beta_i(i-1)\right\}\,. \quad (31)$$

Here account is taken of the fact that

$$\sum_{i=2}^{i=n}\beta_i(i-1) = 1-\beta_1-\beta_2-\ldots-\beta_n = 1-\sum_{i=1}^{i=n}\beta_i\,.$$

Let us consider several particular cases. If the network is formed only by mono- and disulfide cross-linking bridges, then

$$T_g = \left[\beta_1\left(\sum_i \Delta V_i\right)_1 + \beta_2\left(\sum_i \Delta V_i\right)_2 + (1-\beta_1-\beta_2)\left(\sum_i \Delta V_i\right)_4\right] \Bigg/ \left[\beta_1\left(\sum_i K_i\Delta V_i\right)_1 + \beta_2\left(\sum_i K_i\Delta V_i\right)_2 + (1-\beta_1-\beta_2)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_4\right].$$

Taking account of the fact that $\beta_2 = 1-\beta_1-\beta_2$, finally we obtain

$$T_g = \left[(1-2\beta_2)\left(\sum_i \Delta V_i\right)_1 + \beta_2\left(\sum_i \Delta V_i\right)_2 + \beta_2\left(\sum_i \Delta V_i\right)_4\right] \Bigg/ \left[(1-2\beta_2)\left(\sum_i K_i\Delta V_i\right)_1 + \beta_2\left(\sum_i K_i\Delta V_i\right)_2 + \beta_2\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_4\right]. \quad (32)$$

Relationship (32) relates the T_g value of the ebonite network to the mole fraction of disulfide cross-linking bridges β_2. Substituting the numerical values of all the increments in this relationship, we obtain

$$T_g = \frac{92.2 + 8.2\beta_2}{136.9 + 299.7\beta_2}\times 10^3\,.$$

The dependence of T_g on β_2 is shown in Fig. 14. As the proportion of disulfide bonds increases, the glass transition temperature gradually decreases and becomes equal to $\sim$330 K at $\beta_2 = 0.5$ (in the case of disulfide bridges only).

It has been reported that only bridges with a small number of sulfur atoms are formed (the average number is taken to be 2.6).[43] Taking account of this fact, let us evaluate the effect of the proportion of bridges with different length (up to three sulfur atoms) on T_g.

We shall designate the number of cross-linked units as

$$m_c = m_1 + m_2 + m_3\,,$$

where m_1, m_2, and m_3 are the numbers of units connected by mono-, di-, and trisulfide bridges, respectively. The total number of units (both cross-linked and free) is equal to

$$m_{\text{å}} + m_2 + 2m_3 = m_1 + m_2 + m_3 + m_2 + 2m_3 = m_1 + 2m_2 + 3m_3\,.$$

Then

$$\beta_1 = \frac{m_1}{m_1+2m_2+3m_3}\,,\quad \beta_2 = \frac{m_2}{m_1+2m_2+3m_3}\,,$$

$$\beta_3 = \frac{m_3}{m_1+2m_2+3m_3}\,,\quad \beta_4 = \frac{m_2+2m_3}{m_1+2m_2+3m_3}\,.$$

Dividing the numerators and the denominators of these expressions by m_3 and substituting the relations obtained in Eqn (31), we get

$$T_g = 10^3\left[92.2\frac{m_1}{m_3} + 111.1\frac{m_2}{m_3} + 130.0 + 81.5\left(\frac{m_2}{m_3}+2\right)\right] \Bigg/ \left[136.9\frac{m_1}{m_3} + 172.8\frac{m_2}{m_3} + 239.5 + 413.25\left(\frac{m_2}{m_3}+2\right)\right].$$

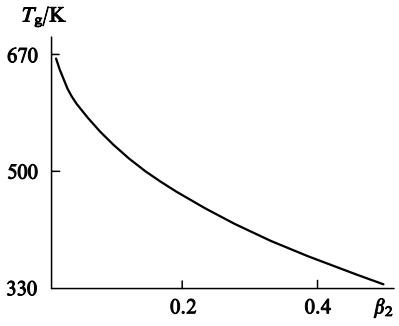


Figure 14. The calculated dependence of T_g of ebonites containing only mono- and disulfide cross-linking bridges on the proportion of the disulfide bonds.

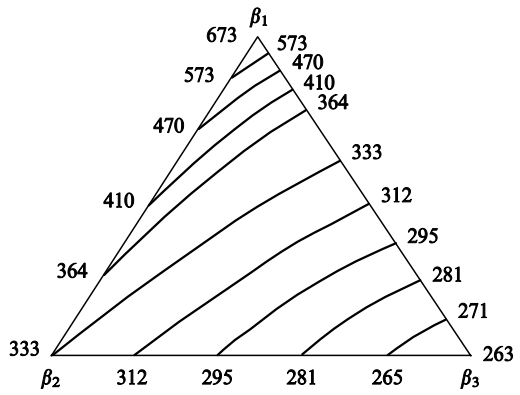


Figure 15. The triangle diagram characterising the effect of the composition of the ebonite network on T_g.
The numbers at isolines are the T_g (K) values.

Let us consider a triangle similar to the Gibbs triangle; the proportions of bridges with different bonds are plotted on the sides of the triangle, while the isolines represent the lines of equal glass transitions temperatures (Fig. 15). It can be seen that the T_g values of ebonites can vary over a very wide range if mono-, di-, and trisulfide bridges are present. The maximum softening temperature corresponding to the presence of monosulfide bridges only and coinciding in this case with the temperature of intense degradation is equal to 673 K; the minimum T_g (263 K) is characteristic of a network containing only trisulfide bridges.

It is also possible to conceive the cases where the sulfide bridges can have variable lengths and there is certain distribution in bridge lengths in the actual system. Such a situation has been considered in the literature;[42] the glass transition temperatures of ebonites were calculated taking into account the function of length distribution of sulfide bridges. It has been concluded that the bridges cannot contain large number of sulfur atoms and that the claims of other authors that the bridges are formed mainly by disulfide chains are correct.

It thus follows that the glass transition temperature of a polymer increases upon cross-linking in all cases. This is particularly noticeable when the number of repeating units in linear fragments between cross-link points is small. However, a slight increase in T_g upon cross-linking is also observed in the case of a large number of repeating units in linear fragments. The reasons for such a behaviour of T_g have been considered.[6,44,45] According to Shefer and Gottlieb,[39] one of the reasons is the decrease in the concentration of end groups leading to a complete loss of chain mobility. Other reasons are associated with transformation of low-molecular-weight molecules resulting in the formation of offshoots and cross-links, with non-Gaussian chain statistics, and with cyclisation.[46–53]

According to a theory proposed by Hale, Macosko, and Bair,[45] the glass transition temperature of a polymer network is determined using the following equation

$$T_g = \frac{T_{g,u}}{(1 - K_2 X_e)/(1 - Y X_e^2)},$$

where K_2 is the DiMarzio constant dependent on the chemical structure of the polymer network, X_e is the density of active cross-link points, and Y is the parameter accounting for the non-Gaussian 'behaviour'. The $T_{g,u}$ value is determined from the following equation

$$\frac{1}{T_{g,u}} = \frac{1}{T_{g,\infty}} + \frac{K_1}{M_n},$$

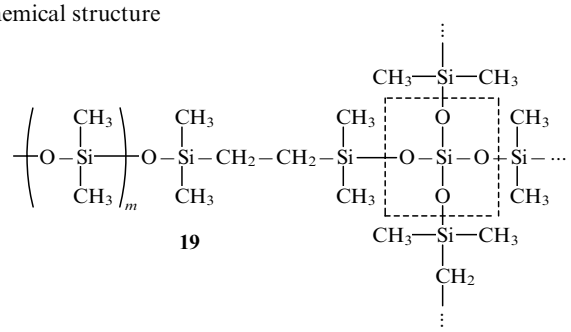
where $T_{g,\infty}$ is the glass transition temperature of a polymer with an infinite molecular weight, and M_n is the number-average molecular weight.

According to a theory proposed by Stutz, Illers, and Mertes, the T_g value is described by the following equation[44]

$$T_g = T_{g,u}\left(1 + \frac{K_2 X_c}{1 - X_c}\right),$$

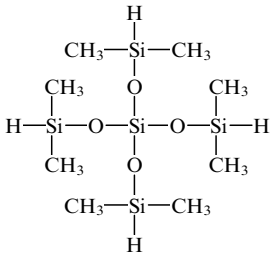
where X_c is the density of cross-links defined as the mole fraction of all cross-links in the system divided by the network functionality.

Changes in the glass transition temperature of end-linked networks in the case of some violation of the stoichiometric ratio have been studied.[43] The polymer network had the following chemical structure



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The experimental results of measuring the relative changes in T_g upon complete conversion of end groups in the reaction with a cross-linking agent are shown in Fig. 16. The following compound was chosen as cross-linking agent:



The authors of the study cited have concluded that their data correspond to the Hale–Macosko–Bair theory according to which changes in T_g become noticeable after the gel point; this is due to the contribution of elastically effective cross-link points

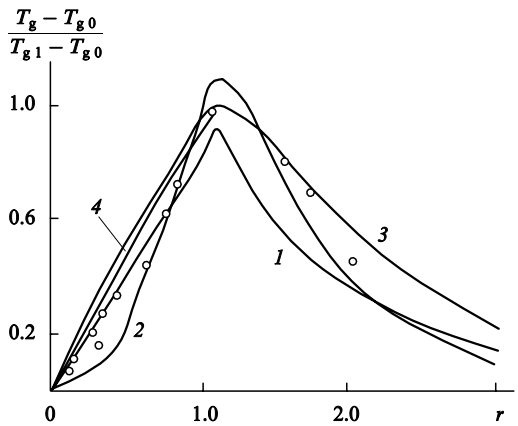


Figure 16. Relative changes in the glass transition temperatures of polymer networks estimated by different methods (r is the stoichiometric ratio).
(*1*) the Stutz–Illers–Mertes method; (*2*) the Hale–Macosko–Bair method; (*3*) the Hale–Macosko–Bair method modified by Shefer and Gottlieb; and (*4*) the Askadskii–Matveev method.

absent in the pre-gel period. It can be said that this result corresponds to the conclusion of the Gibbs–DiMarzio theory, *viz*., not any branching points but the elastically effective cross-link points make major contribution to the T_g value.

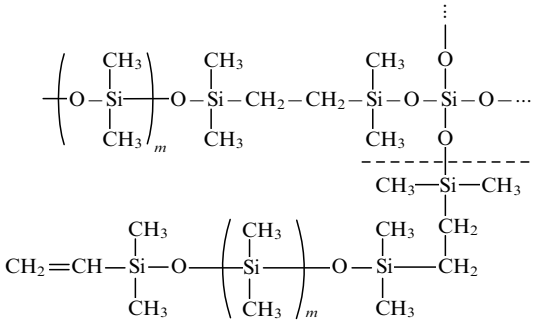
The Hale–Macosko–Bair theory modified by Shefer and Gottlieb makes it possible to approximate the dependence of the glass transition temperature T_g on the stoichiometric ratio r.

Let us consider the possibilities of application of this approach to the analysis of the changes in T_g upon cross-linking. The experimental dependence of the $(T_g - T_{g0})/(T_{g1} - T_{g0})$ ratio on the stoichiometric ratio r (here T_g is the glass transition temperature of the polymer network, T_{g0} is the glass transition temperature of the initial linear polymer, and T_{g1} is the glass transition temperature of the network at $r = 1$) can be described by Eqn (6). In this case, the initial linear polymer was polydimethylsiloxane with vinyl end groups and a number-average molecular weight M_n of 3500.

Let us consider a case with $r = 1$, where a tetrafunctional cross-link point is formed. The calculated parameters of the network with these points are given in Table 1. Substituting these values in Eqn (6), we obtain the dependence of the glass transition temperature T_g on the number (m) of polydimethylsiloxane repeating units between the cross-link points

$$T_g = \frac{714.4 + 144.2m}{4289 + 962m} \times 10^3 . \tag{33}$$

If $r < 1$ (a deficit of cross-linking agent), then 'dangled' chains are formed as a result of the reaction between one functional group of linear polydimethylsiloxane and the cross-linking agent. The structure of such a system is shown below:



The following parameters were found for a dangled chain marked by a dashed line:

$$\left(\sum_i \Delta V_i\right)_{dc} = 274 + 72.1m ,$$

$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{dc} = (1634 + 481m) \times 10^{-3} \text{ Å}^3 \text{ K}^{-1} .$$

According to the principle of calculation of the glass transition temperature (see above), if a chain issuing out of the branching point does not reach another branching point and remains dangled (*i.e*., no cross-link between two chains is formed), then such a branching point cannot be considered as a cross-link point. In this case a_i and b_j increments should be used in Eqn (6) instead of K_i increments for the atoms constituting the branching point and we obtain

$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{c\text{-}1} = 319.8 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1} .$$

In the presence of dangled chains Eqn (6) can be written in general form as follows:

$$T_g = \left\{ \left[\left(\sum_i \Delta V_i\right)_{c\text{-}1} + 2\left(\sum_i \Delta V_i\right)_1 r + \right.\right. \tag{34}$$

$$+ 2\left(\sum_i \Delta V_i\right)_{dc} (1 - r) \Bigg] \Bigg/ \Bigg[\left(\sum_i K_i \Delta V_i\right)_{c\text{-}1} r +$$

$$+ \left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{c\text{-}1} (1 - r) + 2\left(\sum_i a_i \Delta V_i + \sum_j b_j\right) r +$$

$$\left.\left. + 2\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{dc} (1 - r) \right] \right\}; \quad r \leqslant 1.$$

It is natural that if $r = 1$, then Eqn (34) becomes relationship (33). Substituting the values of all the parameters found preliminarily in Eqn (34) gives

$$T_g = \frac{583.0 + 131.4r + 144.2m}{3588 + 701r + 96.2m} \times 10^3 . \tag{35}$$

It should be noted that end-group cross-linking of polydimethylsiloxane chains with a rather high molecular weight (M_n) of 3500 leads to a very small increase in the glass transition temperature.

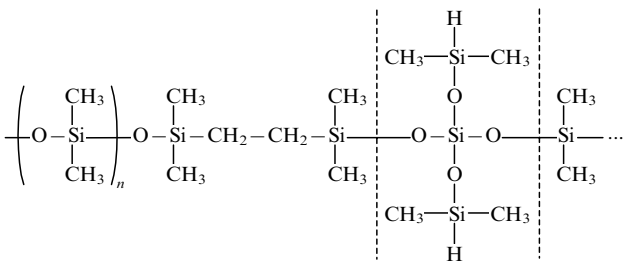
Let us express the $(T_g - T_{g0})/(T_{g1} - T_{g0})$ ratio using relationships (33) and (35). According to Eqn (35), $T_{g0} = 150.88$ K at $r = 1$; taking account of this fact, we obtain for $r \leqslant 1$

$$\frac{T_g - T_{g0}}{T_{g1} - T_{g0}} = \frac{(41.6 + 25.63r - 0.95m)(4289 + 962m)}{(3588 + 701r + 962m)(67.3 - 0.95m)} . \tag{36}$$

The results of calculations using relationship (36) are shown in Fig. 16. The experimental data as well as three theoretical dependences found by the Stutz–Illers–Mertes method, by the Hale–Macosko–Bair method, and by the Hale–Macosko–Bair method modified by Shefer and Gottlieb are also plotted in this figure. As can be seen, experimental and calculated dependences are in fairly good agreement; however, it is noteworthy that Eqn (36) contains no fitting parameters and that all the parameters of this equation are determined based on the chemical structure of the network without using experimental parameters.

Let us consider a situation when the cross-linking agent is present in excess ($r > 1$). Here, (1) trifunctional cross-link points rather than tetrafunctional cross-link points, (2) long chains between cross-link points, and (3) a network with cross-link points whose functionality varies from 0 to 4 can be formed. Clearly, a portion of the cross-linking agent does not react with end groups and this substance acts as plasticiser.

Let us consider only one case where long chains between cross-link points are formed. Such a situation is possible for $r = 2$. The system has the following chemical structure



The following parameters for the fragment between the dashed lines were found for the portion of the cross-linking agent constituting the chain and forming this structure:

$$\left(\sum_i \Delta V_i\right)_{c\text{-}1} = 184.1 \text{ Å}^3;$$

$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right) = 1353.2 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1} .$$

For polydimethylsiloxane (PDMS) chains with the $-(CH_2)_2-Si-(CH_3)_2$ fragments we have

$$\left(\sum_i \Delta V_i\right)_{PDMS} = 339.7 + 72.1m \text{ Å}^3;$$

$$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{PDMS} = (2120.6 + 481m) \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}.$$

If $r = 2$, then the glass transition temperature is determined from the following relationship

$$T_g = \frac{523.8 + 72.1m}{3473.8 + 481m} \times 10^3 . \quad (37)$$

If $m = 44$, which corresponds to a M_n of 3500, then the $(T_g - T_{g0})/(T_{g1} - T_{g0})$ ratio becomes negative. However, as can be seen in Fig. 16, the experimental value of this ratio is equal to 0.5 at $r = 2$; this means that the formation of entirely linear chains is impossible. In addition to linear chains, the system must also contain cross-links. Their proportion can be determined from relationships (35) for $r = 1$ and (37), and for this network ($m = 44$) we obtain

$$T_g = \frac{7059.2\alpha + 3696.2(1-\alpha)}{46617\alpha + 24637.8(1-\alpha)} \times 10^3. \quad (38)$$

Using the experimental value (0.5) of the $(T_g - T_{g0})/(T_{g1} - T_{g0})$ ratio and Eqn (38), we can find that $\alpha = 0.7$. Hence, this system contains a mixture of linear and cross-linked fragments. Thus, the approach described also makes it possible to solve the inverse problem, *viz*., to determine the degree of cross-linking α from experimental data on changes in the glass transition temperature.

Thus, any changes in the network topology lead to changing the chemical structure of the entire system, which is of crucial importance in the case of highly cross-linked networks and considerably affects their properties. This approach takes into account all changes in the network structure, which makes possible to describe the properties with a good accuracy. The calculations do not require the use of the so-called fitting parameters, which are unknown beforehand and should be found from the experimental dependences. Alternative approaches for the description of the glass transition temperature of polymer networks have been analysed using a number of particular examples. Though they can be used to describe, *e.g*., the dependence of the glass transition temperature on the degree of cross-linking with a good accuracy, they require introducing fitting parameters, *i.e*., are devoid of predictive power.

V. The equilibrium rubbery modulus of polymer networks

1. Computational methods for estimating the equilibrium modulus

To estimate the equilibrium rubbery modulus E_∞ and the molecular weight of the network fragment M_c in the case of cross-linked elastomers with fairly sparse cross-links, the known equation of the classical theory of rubber elasticity is used

$$E_\infty = 3\rho \frac{RT}{M_c}, \quad (39)$$

where ρ is the density of the cross-linked elastomer, R is the universal gas constant, and T is the absolute temperature.

The application of Eqn (39) to highly cross-linked networks with linear fragments containing a very small number of repeating units (down to one or even less) leads to considerable discrepancies between the experimental and calculated E_∞ values.

Equation (39) can be used to describe the properties of highly cross-linked networks if the so-called front factor ϕ is introduced

$$E_\infty = \phi 3\rho \frac{RT}{M_c}.$$

However, the introduction of the front factor does not alter the situation for the better, since comparing the calculated and experimental E_∞ values allows one only to evaluate this front factor. Therefore, an attempt was made to obtain a generalised equation for estimating E and M_c that would be valid in the case of both sparse and highly cross-linked networks.[54]

Let us perform a detailed analysis of the influence of a large number of cross-link points on the equilibrium rubbery modulus. It should be noted preliminarily that the van der Waals volume of cross-link points for sparse networks is incommensurably less than that of linear network fragments; therefore, it can be neglected when estimating the compressibility of a cross-linked system. This is impossible in the case of highly cross-linked networks, since the total van der Waals volumes of cross-link points and of linear fragments are nearly the same (the former may even be larger than the latter).

Considering the cross-linked elastomer as a system consisting of two subsystems (elastic and rotational-isomeric), let us analyse first the latter subsystem. It has been shown [7] that the force constant of a rotational-isomeric subsystem can be determined if the difference in the energies of rotational isomers is known, which depends on the size of 'molecular defects' l_i^d in the polymer in the following way:

$$\Delta E_i = 4D_i a^2 (l_i^d)^2 , \quad (40)$$

where D_i is the averaged energy of intermolecular interaction characteristic of the given type of atom, and a is the constant of the Morse potential

$$\varphi(R) = D[(e^{-a(R-r_0)} - 1)^2 - 1] ,$$

where D is the depth of the potential well, and r_0 is the equilibrium interatomic distance in the harmonic approximation.

To determine the size of the molecular defect l_i^d, let us consider the 'cylinder of interaction' between two hydrogen atoms bonded to carbon atoms (Fig. 17).[55] The volume of the cylinder is the sum of the volumes of interacting atoms ΔV_i and the defect volume itself. The volumes of the 'cylinders of interaction' for the crystalline (V_c^{cr}) and amorphous (V_c^a) polymers are respectively

$$V_c^{cr} = 2\Delta V_i + \delta_i^{cr} \Delta V_i , \quad V_c^a = 2\Delta V_i + \delta_i^a \Delta V_i ,$$

where ΔV_i is the van der Waals volume of the ith atom, and the quantities δ_i^{cr} and δ_i^a enter into the relationships for the molecular packing coefficients for the crystalline and amorphous polymers.

$$k_c = \frac{\sum_i \Delta V_i}{\sum_i \Delta V_i + \sum_i \delta_i^{cr} \Delta V_i}, \quad k_a = \frac{\sum_i \Delta V_i}{\sum_i \Delta V_i + \sum_i \delta_i^a \Delta V_i}.$$

The δ_i^{cr} and δ_i^a values for each atom can be found in the literature.[54]

The defect size is

$$l_i^d = \frac{V_c^a - V_c^{cr}}{2S_c} = \frac{\delta_i^a - \delta_i^{cr}}{2} \frac{\Delta V_i}{S_c},$$

where ΔV_i is the part of the van der Waals volume of the ith atom which is overlapped by the van der Waals volume of the atom chemically bonded to it; a factor of 2 appears in the denominator because the amplitude of the jump of the ith atom is equal to half the defect size, and S_c is the base area of the 'cylinder of interaction'.

To estimate l_i^d, let us consider the limiting case where the base radius of the 'cylinder of interaction' is equal to the van der Waals radius of the ith atom. In this case we have

$$l_i^d = \frac{1}{3} R_i (\delta_i^a - \delta_i^{cr}) .$$

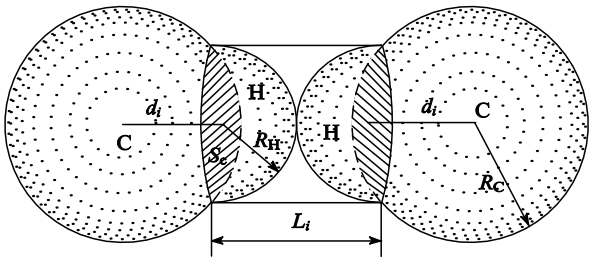


Figure 17. The 'cylinder of interaction' of two hydrogen atoms; d_i is the length of the chemical bond between the H and C atoms, and L_i and S_i are respectively the height and the base area of the 'cylinder of interaction'.

For hydrocarbon polymers, $R_i = R_H$ (R_H is the van der Waals radius of the hydrogen atom equal to 1.17 Å) and the defect size l_i^d is a constant equal to 0.053 R_H. Substituting the l_i^d value obtained in expression (40), we can determine the contribution of the hydrogen atom to the energy difference of rotational isomers: $\Delta E_H = 4.56$ kJ mol^{-1}. The value obtained corresponds in order of magnitude to spectroscopic data on the energy difference of rotational isomers.

For further analysis, we rewrite relationship (40) in the form

$$\Delta E_i = 4D_i a^2 R_i^2 \left(\frac{l_i^d}{R_i}\right)^2, \qquad (41)$$

where R_i is the van der Waals radius of the ith atom, and l_i^d is the size of the defect formed by the given atom.

The aR_i value was estimated as ~ 6 (Ref. 7).

To evaluate the contribution of the rotational-isomeric subsystem to the temperature dependence of the modulus of elasticity of the polymer in the transition zone and in the rubber-like region, it is necessary to find l_i^d values for different atoms and types of the intermolecular interaction.

The calculations of melting points of polymers (T_m) showed [7] that the energy of the intermolecular interaction D_i for a given type of atom depends on whether it is a constituent of the atomic group that forms a hydrogen bond or is involved in the dipole-dipole interaction. Therefore, the influence of specific interaction will manifest itself mainly through the energy of intermolecular interaction D_i of the given type of atom when ΔE_i is calculated using formula (41), while δ_i^a and δ_i^{cr} increments are not affected by the hydrogen bonds and dipole–dipole interactions.

If a repeating unit consists of a set of different types of atoms, it is necessary to introduce the concept of the effective energy difference ΔE_{ef} of rotational isomers, which can be found as follows. To estimate the modulus of elasticity of amorphous polymers, let us use the following relationship [7]

$$E = \left(\sum_i \Delta V_i\right) \Big/ \sum_i \frac{\Delta V_i S_i}{æ_i l_i}, \qquad (42)$$

where ΔV_i is the van der Waals volume of the ith atom of the repeating unit; S_i is the van der Waals surface of the ith atom; through this surface the intermolecular interaction occurs (see Fig. 17); $æ_i$ is the force constant of the ith atom; and l_i is the characteristic bond length.

For the rubbery state, the $æ_i$ coefficient in the denominator of expression (42) should be replaced by the force constant of the rotational-isomeric subsystem $æ_{ri}$ (see Ref. 7),

$$æ_{ri} = \frac{RT}{q_i (l_i^d)^2}, \qquad (43)$$

where $q_i = \exp(\Delta E_i/RT)$, and ΔE_i is the energy difference of rotational isomers. Taking into account relationship (43), the denominator of Eqn (42) takes the form $\sum_i \Delta V_i (l_i^d)^2 S_i q_i / RT l_i^d$.

Let us introduce the effective parameter q_{ef} in such a way that it be determined from the condition

$$\sum_i \frac{(l_i^d)^2 S_i q_i}{l_i} \Delta V_i = \frac{(l_{ef}^d)^2 q_{ef} S_{ef} \sum_i \Delta V_i}{l_{ef}}. \qquad (44)$$

Taking into account relationship (40), we obtain the following formula for l_{ef}

$$(l_{ef}^d)^2 = \frac{\Delta E_{ef}}{4 D_{ef} a^2},$$

where $D_{ef} = \alpha RT_m$, $S_{ef} = \langle S \rangle$, and $l_{ef}^d = \langle l \rangle$. The condition (44) can be written as follows:

$$\sum_i \frac{(l_i^d)^2 S_i q_i}{l_i} \Delta V_i \Big|_{T=T_m} = \frac{\Delta E_{ef} q_{ef} \langle S \rangle}{4 \alpha R T_m a^2 \langle l \rangle} \sum_i \Delta V_i. \qquad (45)$$

The left side of expression (45) and the quantities $\langle S \rangle$ and $\langle l \rangle$ in the right side are known. Therefore, the problem is reduced to the search for the solution of an equation of the type $b = xe^x$, where $x = \Delta E_{ef}/RT_m$, and b includes all the known terms of Eqn (45). This will make it possible to determine how different types of atoms affect ΔE_{ef}. If a hydrogen atom (and the corresponding ΔE_H value) is taken as the initial (the most typical) atom constituting polymers, then the appearance of other types of atoms with ΔE_i in the structure of the repeating unit will change ΔE_{ef}, the change being dependent on the statistical weight of these types of atoms in the repeating unit. The ΔE_{ef} value will either increase or decrease: $\Delta E_{ef} > \Delta E_H$ if $\Delta E_i > \Delta E_H$, and $\Delta E_{ef} < \Delta E_H$ if $\Delta E_i < \Delta E_H$.

Let us examine now the influence of the degree of cross-linking on the modulus of elasticity of a cross-linked polymer in the rubbery state. Considering a network polymer as a mixture of linear fragments and cross-link points, we write

$$\frac{1}{E_c} = \frac{\gamma}{E_l} + \frac{1-\gamma}{E_{c\text{-}l}} \quad \text{or} \quad E_c = \frac{E_l}{\gamma + (1-\gamma) E_l / E_{c\text{-}l}}, \qquad (46)$$

where E_l and $E_{c\text{-}l}$ are the moduli of elasticity for linear fragments and cross-link points, respectively, and γ is the concentration (fraction) of linear fragments.

Formula (46) was obtained by summing the compressibilities of linear fragments of the polymer chain and cross-link points, hence

$$\gamma = \left(\sum_i \Delta V_i\right)_l \Big/ \left(\sum_i \Delta V_i\right)_f.$$

The $\left(\sum_i \Delta V_i\right)_l \Big/ \left(\sum_i \Delta V_i\right)_f$ ratio can be written in the form

$$\frac{\left(\sum_i \Delta V_i\right)_l}{\left(\sum_i \Delta V_i\right)_f} = \frac{n \left(\sum_i \Delta V_i\right)_l^0}{n \left(\sum_i \Delta V_i\right)_l^0 + \left(\sum_i \Delta V_i\right)_{c\text{-}l}},$$

where n is the number of repeating units per cross-link point, and $\left(\sum_i \Delta V_i\right)_l^0$ is the van der Waals volume of the repeating unit of the linear fragment.

Let us introduce the following designations: $\zeta = E_l/E_{c\text{-}l}$ and $\beta = \left(\sum_i \Delta V_i\right)_{c\text{-}l} \Big/ \left(\sum_i \Delta V_i\right)_l^0$, where E_l is the modulus of elasticity of a linear polymer and $E_{c\text{-}l}$ is the modulus of elasticity of a cross-linked polymer consisting of nothing but cross-link points. Then we obtain the following relationship:

$$\gamma = \frac{n}{n+\beta}.$$

Expression (46) can be transformed to the form

$$\frac{E_l}{E_c} = \gamma + (1-\gamma)\frac{E_l}{E_{c\text{-}1}} = \frac{n}{n+\beta} + \frac{\beta\zeta}{n+\beta}. \tag{47}$$

Since the polymer consisting of nothing but cross-link points has the modulus of elasticity many decimal orders of magnitude larger than that of the linear elastomer, then $\zeta \ll 1$ and for highly cross-linked networks $\zeta \ll \beta$. Hence the second term in expression (47) can be neglected, *i.e.*,

$$\frac{E_l}{E_c} = \frac{n}{n+\beta}. \tag{47a}$$

We revert now to the effective l_{ef}, q_{ef}, l_{ef}^d, and S_{ef} values. Taking into account the fact that the force constant of a rotational-isomeric subsystem is proportional to the mean-statistical number of the repeating units in the linear fragments between cross-link points (n), we can rewrite the relationship (42) in the form

$$E_l = \frac{l_{ef}RT}{(l_{ef}^d)^2 q_{ef} S_{ef} n},$$

and the modulus of elasticity of the rotational-isomeric subsystem of such a hypothetical polymer at $n_0 = 1$ and at temperature $T = T_0$ is

$$(E_l)_0 = \frac{l_{ef}RT_0}{(l_{ef}^d)^2 q_{ef}^0 S_{ef}}.$$

The ratio of these moduli is

$$\frac{E_l}{(E_l)_0} = \frac{T}{T_0}\,\frac{q_{ef}^0}{q_{ef} n}, \tag{48}$$

where $q_{ef} = \exp(\Delta E_{ef}/RT)$ and $q_{ef}^0 = \exp(\Delta E_{ef}/RT_0)$.

Substituting expression (48) in relationship (47a), we have

$$\frac{E_c}{(E_l)_0} = \frac{n+\beta}{n^2}\,\frac{T}{T_0}\,\frac{q_{ef}^0}{q_{ef}}. \tag{49}$$

For practical calculations account must be taken of the fact that the repeating network fragment consists of $n\Phi/2$ repeating units; therefore, with consideration of functionality Φ, expression (49) should be written as

$$\frac{E_c}{(E_l)_0} = \frac{2(n+\beta)}{\Phi n^2}\,\frac{Tq_{ef}^0}{T_0 q_{ef}}. \tag{50}$$

Let us analyse Eqn (50) in more detail and compare it with the equation given by the classical theory of rubber elasticity (39). It can be seen that these equations are similar and Eqn (50) describes the modulus of elasticity for both sparse and highly cross-linked networks. In fact, if we write $n = M_c/M_0$, then from Eqn (50) we obtain

$$E_c = (E_l)_0 \frac{2}{\Phi}\,\frac{M_c/M_0 + \beta}{(M_c/M_0)^2}\,\frac{T}{T_0}\,\frac{q_{ef}^0}{q_{ef}},$$

where M_0 is the molecular weight of the repeating unit.

For sparse networks, $\beta \ll M_c/M_0$, then

$$E_c = (E_l)_0 \frac{2}{\Phi}\,\frac{M_0}{M_c}\,\frac{T}{T_0}\,\frac{q_{ef}^0}{q_{ef}}. \tag{51}$$

Comparing formulae (39) and (51), we get

$$(E_l)_0 = \frac{3\rho R\Phi T_0 q_{ef}}{2M_0 q_{ef}^0}. \tag{52}$$

If the modulus of elasticity is measured at $T = T_0$, then $q_{ef} = q_{ef}^0$, and Eqn (50) simplifies and takes the form

$$E_c = (E_l)_0\,\frac{2(n+\beta)}{\Phi n^2}. \tag{53}$$

If chain fragments between cross-link points are long (sparse networks), the condition $\beta \ll n$ is fulfilled and Eqn (53) goes over into the following relationship

$$E_c = (E_l)_0\,\frac{2}{\Phi n},$$

and, with consideration of relationships $T_0/T = q_{ef}^0/q_{ef}$ and $M_0 n = M_c$, we obtain

$$E_c = \frac{3\rho RT}{M_c}, \tag{54}$$

i.e., Eqns (54) and (39) coincide.

Relationship (53) is convenient for practical calculations of the modulus of elasticity of highly cross-linked networks; the $(E_l)_0$ value can be either calculated using Eqn (52) or determined from experimental data on the equilibrium modulus of elasticity of sparse networks where $n \gg 1$.

Let us perform several additional transformations. At $T = T_0$ and $q_{ef} = q_{ef}^0$, expression (52) takes the form

$$(E_l)_0 = \frac{3\rho R\Phi T}{2M_0}. \tag{55}$$

From relationships (53) and (55) we get

$$E_c = \frac{3\rho RT(n+\beta)}{M_0 n^2}, \tag{56}$$

and from formula (56), taking account that $M_c = M_0 n$, we obtain

$$E_c = \frac{3\rho RT(n+\beta)}{M_c n}. \tag{57}$$

Let us divide the numerator and the denominator of formula (57) by n; then

$$E_c = \frac{3\rho RT(1+\beta/n)}{M_c} \tag{58}$$

or

$$M_c = \frac{3\rho RT(1+\beta/n)}{E_c}. \tag{59}$$

For a sparse network, $\beta \ll 1$ and $n \gg 1$; therefore, $\beta/n \to 0$ and the generalised equation (58) goes over into conventional Eqn (39).

In the case of highly cross-linked networks, the M_c value can be evaluated using formula (59). For the sake of convenience it can be transformed (considering that $n = M_c/M_0$) to the following form

$$E_c = \frac{3\rho RT(1+\beta M_0/M_c)}{M_c}.$$

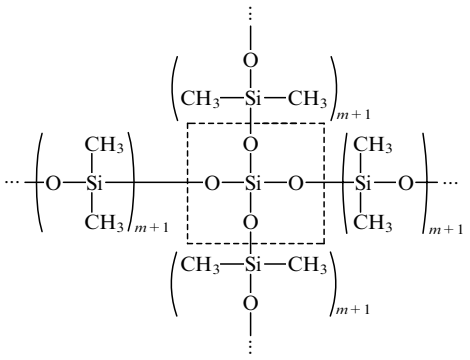
From this equation we get

$$M_c = \frac{3\rho RT + \sqrt{3\rho RT(3\rho RT + 4E_c M_0\beta)}}{2E_c}. \tag{60}$$

For sparse networks, $\beta \to 0$ and formula (60) goes over into Eqn (39).

2. The equilibrium rubbery modulus of model networks

Let us consider a model polydimethylsiloxane-based network studied by Mark and Sillivan [56] as an example. The network structure is shown below

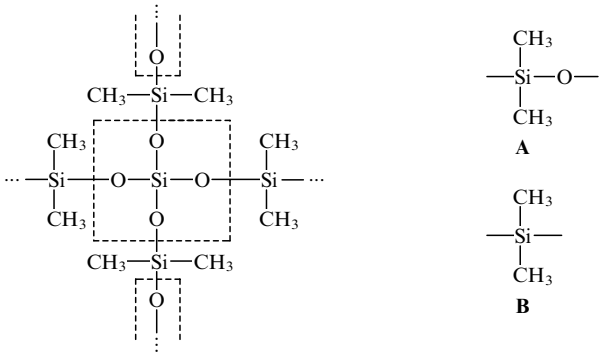


The cross-link point of the network is marked by dashed lines. For this network, we have

$$\left(\sum_i \Delta V_i\right)_{\text{c-1}} = 34.7\ \text{Å}, \quad \left(\sum_i \Delta V_i\right)_1^0 = 72.1\ \text{Å},$$

$$\beta = \frac{34.7}{72.1} = 0.481.$$

All details of the chemical structure of the network should be taken into account when calculating the equilibrium rubbery modulus of highly cross-linked networks using Eqn (53) and the glass transition temperature T_g using Eqn (6). The point is that at $m = 0$ this network has the following structure



In this case only a part of the unit **A** is a constituent of a linear chain fragment between neighbouring cross-link points of the network, since the oxygen atom of this unit is shared by the neighbouring cross-link point. For the quantity n defined as the $\left(\sum_i \Delta V_i\right)_1^* \Big/ \left(\sum_i \Delta V_i\right)_1^0$ ratio in which the numerator is equal to the van der Waals volume of the group **B**, we get $n = 0.99$. If $m = 1$, then $n = 1.99$, *etc*. Taking account of this fact is of prime importance when calculating the glass transition temperature T_g using Eqn (6). In this case Eqn (6) goes over into the following formula

$$T_g = \frac{\left(\sum_i \Delta V_i\right)_{\text{c-1}} + m\left(\sum_i \Delta V_i\right)_1^0 + \left(\sum_i \Delta V_i\right)_1^*}{\left(\sum_i K_i \Delta V_i\right)_{\text{c-1}} + m\left(\sum_i a_i \Delta V_i\right)_1^0 + \left(\sum_i a_i \Delta V_i\right)_1^*},$$

where the second and the third terms in the denominator are the sets of increments for the units **A** and **B**, respectively (note that in the case of the network considered $\sum_j b_j = 0$).

To calculate the equilibrium rubbery modulus E_c using Eqn (53), it is necessary first to evaluate the $(E_l)_0$ value. It has been mentioned above that this can be done in two ways. The first way is to use formula (55), *i.e*., the $(E_l)_0$ value is determined entirely by computation. Substituting $\rho = 1.169\ \text{g cm}^{-3}$, $\Phi = 4$, $M_0 = 74.15$, and $T = 293$ K in this formula, we obtain $(E_l)_0 = 230$ MPa.

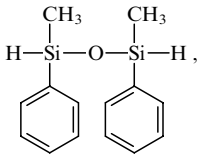
Table 2. Characteristics of polydimethylsiloxane networks.

m	n	β	E_c/MPa	T_g/K
0	0.99	0.482	148	183
1	1.99	0.241	61.5	166
2	2.99	0.160	38.2	161
3	3.99	0.120	27.6	158
4	4.99	0.096	21.6	156
6	6.99	0.069	15.0	154
9	9.99	0.048	10.3	153

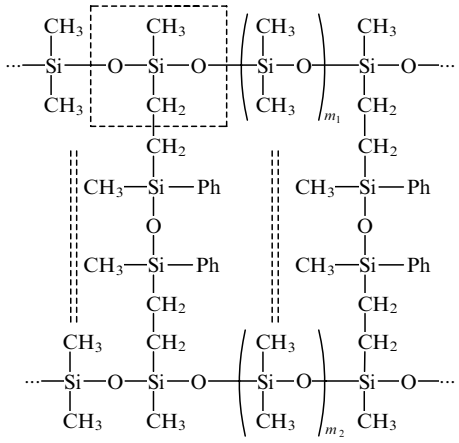
The second way is to use formula (53) and the experimental E_c value for a sparse network. Using the experimental E_c value obtained by Mark and Sullivan[56] and Eqn (53), we get $(E_l)_0 = 197$ MPa. The calculations of E_c using formula (53) and this $(E_l)_0$ value lead to the values of the equilibrium moduli listed in Table 2. It can be seen that the E_c value increases rapidly and for a very highly cross-linked network ($n = 1$) large E_c values are reached as the distance between adjacent cross-link points of the network decreases. It should be noted that the glass transition temperature remains below room temperature.

In the preceding section, we have considered the possibilities of evaluating the equilibrium rubbery modulus for highly cross-linked networks based on their chemical structure. However, the inverse problem, *viz*., the estimation of the composition of the microphase that forms effective cross-link points of the network, can also be solved.

In fact, if the chemical structure of the cross-linking agent differs essentially from that of chains subjected to cross-linking, microphase separation can occur. Let us analyse several systems. Considerable attention has been focused recently on the so-called bimodal networks.[57–59] The mechanical behaviour of such networks was studied by Sharaf and Mark.[60] These networks can be prepared by different methods, *e.g*., by random 'along-the-chain' cross-linking of polydimethylsiloxane chains containing reactive methylvinylsiloxane units. If the cross-linking agent has the chemical structure shown below,



then the following bimodal networks are formed:[61,62]



Tetrakisdimethylsiloxysilane is also used as cross-linking agent.[63–65] The mechanical properties of networks with this cross-linking agent have been studied[61–65] and it has been

shown [63–65] that the experimental data are in good agreement with the results obtained using the Flory–Erman theory.[66–68] However, Gottlieb *et al.*[61,62] have found that the values of the moduli of elasticity are considerably larger (by 10%–15%) than those predicted by the Flory–Erman theory based on the density of cross-links. The discrepancy can be due to neglecting the contribution of active entanglements.[60] With this contribution taken into account, the values calculated using the Flory–Erman theory and the experimental ones coincide.[61,62]

Other approaches explaining the discrepancy between the calculated and experimental data are also possible. For instance, the following explanation of the discrepancy mentioned is proposed. It is based on assumptions made by Sharaf and Mark [57–59] that short segments between cross-link points located along the molecule subjected to cross-linking can act as elastically effective chains by themselves. In accordance with this, it has been postulated that the length distribution of the network chains is bimodal.[57–59] Several investigators interpret large values of the modulus of elasticity obtained in the case of small deformations as a consequence of the contributions of short chains formed by the cross-linking agent (Fig. 18*a*).[60]

Another explanation of the experimental fact that the modulus of elasticity increases (all things being the same) due to the presence of short chains between cross-link points can be based on the approach described above. According to this approach, the equilibrium rubbery modulus is calculated using generalised Eqns (56) or (58). In this case, the definition of the cross-link point of the network given in the Introduction is used. However, when the chemical structure of linear chains and that of the cross-linking agent differ essentially, the concept of 'a cross-link point of the network' can become more complicated. According to the initial definition of 'a cross-link point of the network', which is valid when calculating glass transition temperatures, this cross-link point is marked by dashed lines. However, the possibility of microphase separation should be considered when analysing and calculating the equilibrium rubbery modulus. Here, one microphase is the polydimethylsiloxane microphase, while the other is that formed by the cross-linking agent. In this case (see Fig. 18*b*), the cross-link point of the network consists of the cross-linking agent with the adjacent CH_2 groups; this cross-link point is marked by double dashed lines.

In order that a microphase be able to act as a cross-link point, it must be rigid. Such a situation occurs in the case of block copolymers. For instance, in polystyrene–polybutadiene block copolymers the polystyrene domains act as cross-link points while the polybutadiene component plays the role of the rubber matrix. It is possible to calculate the possibility of microphase separation computationally from the difference of the surface energies of microphases. According to calculations of the surface energies for polydimethylsiloxane chains and for the complicated cross-link point (see Fig. 18*b*) using the method proposed in the literature,[69,70] the surface energy of polydimethylsiloxane chains is equal to 20.7 dyn cm^{-1} while that of the cross-linking agent is equal to 30 dyn cm^{-1}. The difference between these energies is quite sufficient for microphase separation.

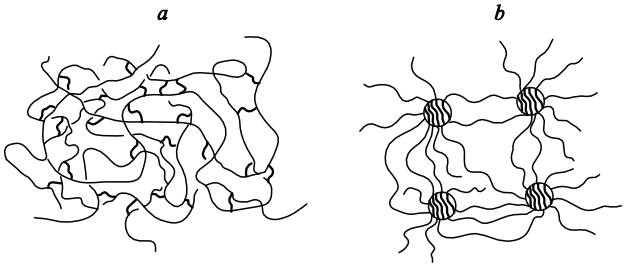


Figure 18. A scheme of a topological structure of polydimethylsiloxane networks cross-linked by a short-chain cross-linking agent.
(*a*) the formation of bimodal networks according to Sharaf and Mark;[60] (*b*) the topological structure of the same network in the case of microphase separation.

Assuming that rigid domains play the role of cross-link points, the van der Waals volume of such a cross-link point is equal to 315.8 $Å^3$. The van der Waals volume of the polydimethylsiloxane repeating unit is equal to 108.15 $Å^3$; therefore, the β value in Eqn (56) will be equal to 2.92. Now it is necessary to evaluate the $(E_l)_0$ value using Eqn (55). Substituting all the parameters required, we get that $(E_l)_0$ = 149 MPa at room temperature. Then, Eqn (56) can be written as follows:

$$E_c = 149\frac{2(173 - a2.92)}{3 \times 173^2},$$

where a is the number of the structures **1** in the complicated cross-link point.

Since the mole fraction of methylvinylsiloxane units was equal to 0.0057 (Ref. 56), a factor of 173 appears in the denominator of the last relationship. The fact that the experimental moduli are 15%–25% larger than those predicted by theory indicates that the complicated cross-link point contains 9–15 units of the cross-linking agent. This example shows that the approach described above also makes it possible to solve the inverse problem by comparing the calculated and experimental values of the equilibrium rubbery modulus, to assess the network structure, and to determine the structure of the cross-link point.

Thus, on going to highly cross-linked networks, when the linear fragment contains less than five repeating units, the account of the influence of the chemical structure of the cross-link point becomes necessary for a correct evaluation of the equilibrium rubbery modulus. Using this approach, one can eliminate the unpredictable front factor usually introduced into the classical equation of the rubber elasticity theory to obtain coincidence between the calculated and experimental values of the equilibrium rubbery modulus. The use of generalised Eqn (58) makes it possible to predict the equilibrium rubbery modulus value with a good accuracy, thus providing a way of designing the chemical structure of the network for the preparation of materials with unusual properties.

VI. Different-modulus and gradient-modulus polymers based on highly cross-linked networks

In this section we will consider the use of computational schemes that make it possible to evaluate the glass transition temperatures T_g and the equilibrium rubbery moduli E of highly cross-linked networks in designing polymeric materials with unusual properties. The case in point will be the design and preparation of two types of elastic different-modulus polymeric materials: (1) materials for which the modulus of elasticity is constant for each specimen but varies over a very wide range from one specimen to another, and (2) materials in which the modulus of elasticity changes gradually in a prescribed manner within the same specimen in which no layers and interfaces are present.

For example, gradual transition from rubber to plastic or *vice versa* is required within the same specimen. Such a transition will allow one to design complex different-modulus constructions without using traditional methods of joining, *viz.*, gluing, welding, *etc*. The problem of realisation of this idea is associated with two fundamental peculiarities of the behaviour of polymeric materials that require clarification.

The temperature dependence of the modulus of elasticity of a typical polymer is represented schematically in Fig. 19; unfortunately, in the glassy state region the modulus of elasticity depends slightly on the chemical structure of the polymer and varies within the limits $(2-3)\times10^3$ MPa. Therein lies the first problem of preparing different-modulus and gradient-modulus materials. Within the temperature zone of transition from the glassy to the rubbery state, the modulus of elasticity decreases sharply in the narrow temperature interval (ΔT = 20–30 °). In this connection, it may appear at first glance that the problem of obtaining polymers

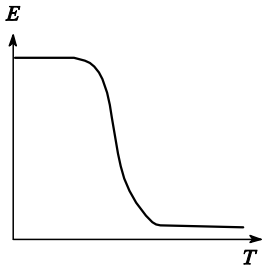


Figure 19. Temperature dependence of the modulus of elasticity.

with different moduli of elasticity varying, *e.g.*, in the interval from 3×10^3 to 3 MPa, is simple, *viz.*, it is merely necessary to obtain polymers with glass transition temperatures close to room temperature (if different-modulus materials must be used at room temperature). However, as is known, materials possess pronounced viscoelastic behaviour in the transition zone; in addition, their mechanical properties change sharply as the temperature either slightly decreases (transition to plastic) or increases (transition to rubber). Therein lies the second problem of obtaining different-modulus materials, which, in addition to the wide range of changes in the modulus of elasticity, must possess elastic rather than viscoelastic properties and retain the predetermined gradient of properties over a wide temperature range.

Theoretically, the materials free of plasticisers or fillers and possessing the moduli of elasticity varying over a wide range can be obtained by designing and preparing highly cross-linked network structures containing bulky rigid cross-link points connected by flexible linear chains of controlled lengths (Fig. 20). This follows from the generalised Eqn (58), which can be used for evaluating the equilibrium rubbery modulus E of cross-linked systems.

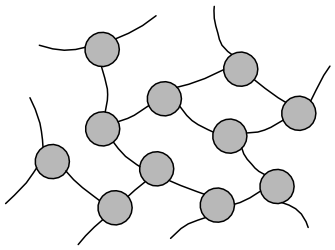
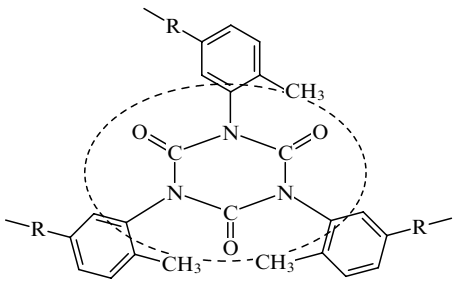


Figure 20. A scheme of a structure of a network containing bulky cross-link points and short and flexible linear chains.

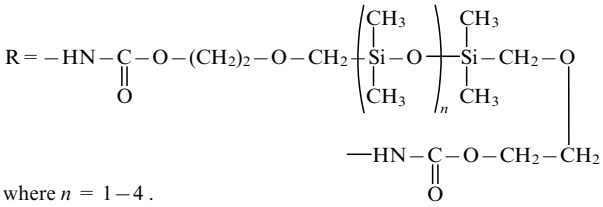
According to Eqn (58), large E value can be achieved on going to highly cross-linked networks with bulky cross-link points where $n \to 1$ and $\beta > 1$. In this case, linear fragments between cross-link points should be very flexible to retain the low glass transition temperature.

Cross-linked polyisocyanurates of the following chemical structure were synthesised [71–77] as structures containing rigid bulky cross-link points connected by flexible linear (–R–) chains:



The trifunctional isocyanurate ring plays the role of a cross-link point (outlined by dashes).

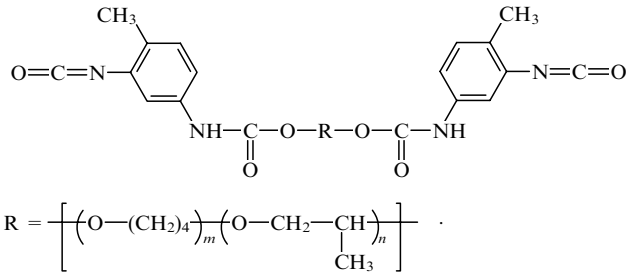
Short organosilicon chains with $n = 1-4$ were used as linear fragments.[71,72]



where $n = 1-4$.

In other studies, cross-linked copolymeric polyisocyanurates were obtained.[73–76]

Oligomeric diols were used as one of the initial components in the synthesis of these materials. Reactions of these diols with a diisocyanate (in particular, with toluylene 2,4-diisocyanate) resulted in macrodiisocyanates with urethane backbone



Commercial oligomeric rubbers with hydroxyl end groups (*e.g.*, the PF-OP-15 polyether, an oligomeric tetrahydrofuran–propene oxide copolymer) can be used as diols.

Macrodiisocyanates obtained from oligomeric rubbers undergo polycyclotrimerisation *in situ* and copolymerisation with diisocyanates of any structure (aromatic, alicyclic, or aliphatic) that are capable of forming cross-linked polyiso-cyanurates at a sufficient rate to yield cross-linked polymers. Actually, copolymers of mixed structures are prepared. The polymer simultaneously contains a network built of the products of homopolycyclotrimerisation of both the oligomer and the diisocyanate and a network with linear chains randomly distributed in the structure as a result of reaction of the oligomer with the diisocyanate.

The content of rigid cyclic structures in the network formed increases with the increase in the excess of diisocyanate with respect to the oligomeric macrodiisocyanate in the initial reaction mixture. Thus, the ratio of flexible (polyether) and rigid (isocyanurate rings with adjacent cyclic diisocyanates) fragments can be arbitrarily changed, which permits controlling the mechanical properties over a wide range. To check the possibility of controlling the properties of polymer networks in this way, glass transition temperatures of these cross-linked systems with variable chemical composition were calculated preliminarily using Eqn (6). Gradual decrease in T_g with an increase in the proportion of flexible rubber fragment can be seen in Fig. 21.

Calculations of the equilibrium modulus of elasticity using Eqn (53) have shown [74] that if T_g is below room temperature, the equilibrium modulus E_∞ can reach high values, intermediate between those of rubber and plastic. Such kind of preliminary calculations was carried out for networks with organosilicon linear fragments.[71,72] As a result, the following expression relating the T_g value of the network to the number of dimethyl–siloxane units (n) in the linear fragment was obtained for the structure in question

$$T_g = \frac{751 + 108.15n}{2450 + 721.5n} \times 10^3 . \qquad (61)$$

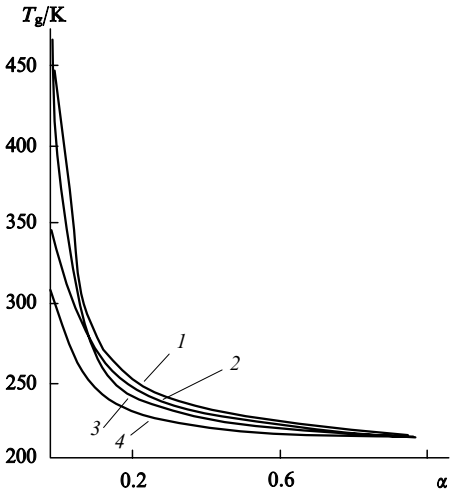
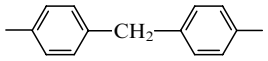
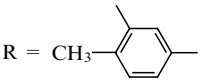
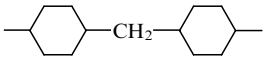


Figure 21. Dependence of the calculated glass transition temperature T_g of polyisocyanurate polymers based on diisocyanates of different structure on the mole fraction α of the PF-OP-15 rubber.

(*1*) R =  ; (*2*) R =  ;

(*3*) R =  ; (*4*) R = $-(CH_2)_6-$.

The results of calculations carried out using expression (61) are listed in Table 3. It can be seen that the T_g values are below room temperature and decrease as n increases approaching the glass transition temperature of polydimethylsiloxane.

The values of the equilibrium moduli which fall into the range from 3 to 886 MPa depending on the n value are also listed in Table 3.

Experimental studies of cross-linked polymers with the structure considered above confirmed the correctness of the assumptions made and calculations carried out.[71,72] Thus, the E_∞ values of the networks obtained with organosilicon linear fragments change over a range from 3 to 3×10^3 MPa (Fig. 22) depending on the length of the linear fragment.

Microphase separation due to considerably different surface energies of organosilicon chains ($\sim$21 dyn cm^{-1}) and iso-cyanurate cross-link points ($\sim$35 dyn cm^{-1}) is of great importance for such materials; its development was confirmed by X-ray photoelectron spectroscopy, electron microscopy, and dynamic mechanical analysis.[71,72]

The microphase separation can occur both in linear block copolymers (or polymer mixtures) and in polymer networks. Two clearly defined maxima are observed in these cases in the temperature dependence of the loss factor tan δ.

Table 3. Calculated and experimental characteristics of cured macrodiisocyanates.

n	T_g/K	E/MPa	
		Calculated	Experimental
0	310	–	–
1	271	884	886
2	268	249	283
3	232	123	149
6	206	40	43
9	193	22	24
19	174	8	7
43	161	3	3
∞	150	–	–

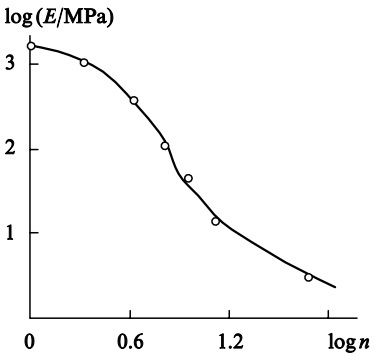


Figure 22. Dependence of the modulus of elasticity E on the number of dimethylsiloxane units n in linear fragments of polyisocyanurate networks.

The temperature dependence of the loss factor tan δ for block specimens of the polyisocyanurates under consideration with different lengths of linear organosilicon fragments is shown in Fig. 23. The low-temperature peak is shifted towards low temperatures as the length of the linear fragment increases approaching the glass transition temperature of poly(dimethylsiloxane). The high-temperature maximum associated with the glass transition of the entire system is virtually independent of n starting from $n = 2$.

Thus, there are two rather clearly defined transition temperatures, which can be considered as the glass transition temperature of the polydimethylsiloxane microphase in the polymer network and the glass transition temperature of the microphase containing isocyanurate cross-link points with adjacent spacers. This suggests that the microphase separation caused by incompatibility of the polydimethylsiloxane fragments and isocyanurate cross-link points with adjacent spacers exists in the system.

Taking into account the fact that the transition temperatures in both microphases are shifted towards each other, one can calculate the compositions of the microphases provided that the transition temperature coincides with the glass transition temperatures of microphases of given compositions. Since the transition temperature of the microphase formed mainly of organosilicon fragments is higher than that of polydimethyl-siloxane itself, it is obvious that the polydimethylsiloxane microphase contains neighbouring fragments.

What is the structure of these fragments? Glass transition temperatures of the following structures were calculated[72] to answer this question

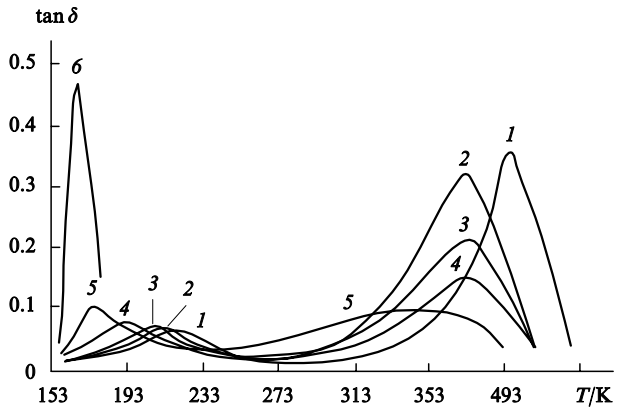
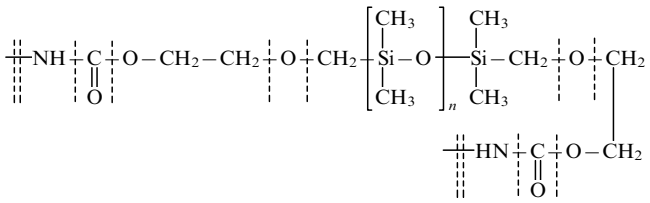


Figure 23. Temperature dependence of the loss factor tan δ for block specimens of polyisocyanurate networks with different lengths of linear organosilicon fragments. n: (*1*) 1.2; (*2*) 2.1; (*3*) 3.2; (*4*) 5.4; (*5*) 9.2; (*6*) 22.



Glass transition temperatures of polydimethylsiloxane fragments with adjacent chain fragments indicated by dashed lines were calculated stepwise for different n using formula (6). These fragments were 'elongated' until the calculated glass transition temperature coincided with the experimentally determined temperature of the first transition. It turned out that the calculated and experimental transition temperatures coincide when the polydimethylsiloxane domains contain chain fragments marked by double dashed lines, the structure of these fragments being independent of n, *i.e.*, of the length of the organosilicon chain. Such an approach to estimating the composition of microdomains can be extended to any objects characterised by microphase separation.

If microphase separation occurs in the system, then the concept of 'a cross-link point of the network' from the viewpoint of its chemical structure should be extended when calculating the equilibrium rubbery modulus. In fact, a rigid microphase (*e.g.*, consisting of isocyanurate cross-link points with adjacent spacers) plays the role of cross-link points provided that the glass transition temperature of this microphase is above room temperature. The presence of such a 'macro-cross-link point' leads to a considerable increase in the β value in Eqn (53), which favours the increase in the equilibrium rubbery modulus.

Such an analysis has been carried out for the system considered above [72] and it was found that T_g of rigid domains is equal to 306 K and that their van der Waals volume is equal to 751 Å^3.

Taking into account the van der Waals volume of the polydimethylsiloxane repeating unit (180.15 Å^3) we obtain $\beta = 751/180.15 \approx 4.2$.

The equilibrium rubbery moduli were determined experimentally [72] from the stress relaxation curves approximated using physically well-founded memory functions.[78–81]

The dependence of the modulus of elasticity of polyisocyanurate networks on the average number of repeating units in polydimethylsiloxane chains connecting the cross-link points is shown in Fig. 22. As was mentioned above, the range of numerical values of the moduli of elasticity for such networks exceeds the range characteristic of the zone of transition from the glassy to the rubbery state. However, despite this fact, these materials possess elastic mechanical behaviour characteristic of polymeric glasses rather than viscoelastic behaviour characteristic of all polymers in the transition zone. This is confirmed by the stress relaxation curves (Fig. 24). The first specimen was a conventional ED-20 epoxy resin cured with methyltetrahydrophthalic anhydride. This system has a glass transition temperature of 120 °C and is a glassy polymer at room temperature. Fast stress (σ) relaxation is observed in the initial period, then the drop in σ slows down, and the stress changes only slightly. The second specimen was an ED-20 epoxy resin cured with a mixture of poly(sebacic anhydride) and azelaic acid taken in such a proportion that the transition zone for this specimen was in the interval from −5 to 34 °C. The stress relaxation curve is characteristic of the transition zone, *i.e.*, fast stress relaxation virtually down to zero is observed.

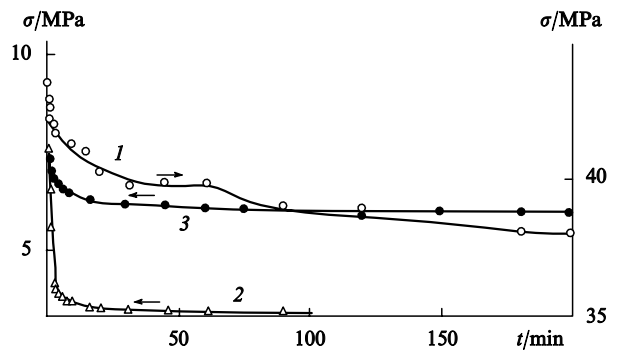


Figure 24. Stress relaxation curves for the ED-20 epoxy resin cured with methyltetrahyrophthalic anhydride (*1*) and a mixture of poly(sebacic anhydride) and azelaic acid (*2*), and for a polyisocyanurate network with linear organosilicon fragments with $n = 6.2$ (*3*).

The third specimen was a polyisocyanurate network with linear organosilicon fragments ($n = 6.2$). With this size of linear chains, the initial stress σ_0 is nearly equal to that of the viscoelastic material (7.5 MPa). However, the mechanical behaviour is fundamentally different, *viz.*, fast but small stress relaxation is observed in the initial period and then the stress virtually ceases to drop, *i.e.*, the material behaves as an elastic glassy polymer.§

Let us consider the properties of gradient-modulus materials based on the oligomeric PF-OP-15 rubber and toluylene 2,4-diisocyanate.

To obtain gradient-modulus materials, the initial components are gradually measured out thus achieving the targeted control of the chemical composition of the network within the same specimen.

This allowed one to prepare specimens in which the modulus of elasticity changed from 4.5 MPa (which is characteristic of rubbers) to 2000 MPa (which is characteristic of plastics).[75,76] The change occurred smoothly within the same material (with no interfaces and intermediate layers).

The dependence of the modulus of elasticity on the content of toluylene 2,4-diisocyanate in the initial reaction mixture is shown in Fig. 25 as an example. It can be seen that the modulus of elasticity changes linearly along the length of the specimen so that a gradual transition from rubber to plastic occurs with no interfaces, as was mentioned above.

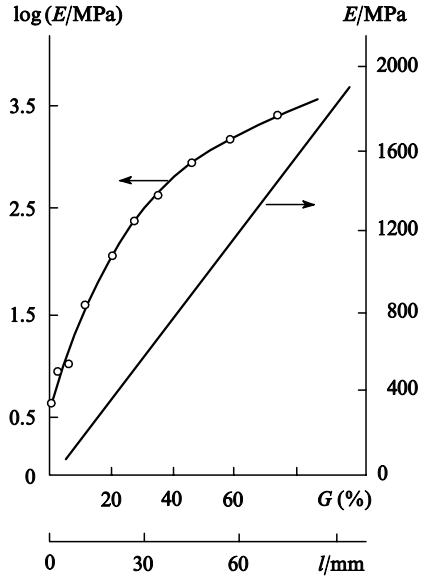


Figure 25. Dependence of the modulus of elasticity varying along the specimen length (l) on the content of toluylene 2,4-diisocyanate (G) in a mixture with oligomeric macrodiisocyanate.

To analyse the character of mechanical behaviour of the materials obtained, the stress relaxation curves were studied for

§ It is well to bear in mind that there are no absolutely elastic polymeric materials (except for ideal crystals). Therefore the terms 'elastic behaviour' and 'elastic material', as applied to the polymers, are conditional. The term 'elastic behaviour' is used in reference to such a behaviour where the stress relaxation occurs at a very slow rate.

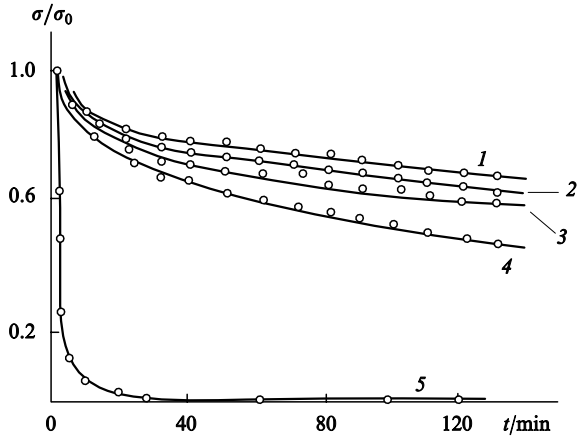


Figure 26. Stress relaxation curves for polyisocyanurate networks obtained from oligoether diisocyanate, toluylene diisocyanate at a content of the latter compound of 6% (*1*), 46% (*2*), and 27% (*3*); for the ED-20 epoxy oligomer cured with methyltetrahyrophthalic anhydride (*4*); and for an ED-20-based epoxy viscoelastic polymer cured with a mixture of poly(sebacic anhydride) (27.3%) and azelaic acid (13.8%) (*5*).

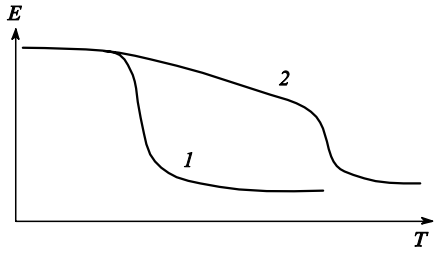


Figure 27. Temperature dependence of the modulus of elasticity for conventional polymers (*1*) and networks with bulky cross-link points and short and flexible linear fragments (*2*).

microspecimens cut from the initial macrospecimen in regions with different gradients of the modulus of elasticity (Fig. 26). For comparison, a stress relaxation curve for the viscoelastic material [ED-20 epoxy resin cured with poly(sebacic acid anhydride) in the presence of azelaic acid] is also shown in this figure. The glass transition temperature of this network is close to room temperature (the same temperature is characteristic of the material whose relaxation behaviour is illustrated by Fig. 24 [specimen (*2*)]. The stress relaxation curves were plotted in 'relative stress–time' coordinates; the relative stress was calculated as σ/σ_0, where σ is the current relaxing stress, and σ_0 is the initial stress developed at the instant of termination of 'instantaneous' initiation of the deformation.

Fast relaxation of the relative stress nearly down to zero is observed for the conventional viscoelastic material, while a slower drop in the stress characteristic of polymeric glasses or rubbers followed by a very slow rate of stress relaxation is observed for the cross-linked polymers synthesised.[75,76]

Thus, despite the fact that a part of the material within the same specimen is characterised by the modulus of elasticity corresponding to the transition zone, this part possesses elastic mechanical behaviour similar to that of glasses or rubbers rather than viscoelastic behaviour characteristic of all polymers in the transition zone.

The dynamic mechanical analysis of the networks obtained shows that they have very small tan δ values, like elastic materials, and that the value of the storage modulus E' is characteristic of the transition zone.

Films based on cross-linked polyisocyanurates with the gradient of the modulus of elasticity perpendicular to the film plane were obtained. These films formed by highly cross-linked polymer networks possess good mechanical properties (a strength of 50 MPa and a limiting elongation of 90%). Such gradient-modulus materials are devoid of brittleness, which is the major drawback of highly cross-linked polymer networks.

Thus, it is possible to obtain polymeric materials possessing new properties using the principles of the molecular design of polymer networks and performing targeted synthesis of the networks. The curves shown in Fig. 27 illustrate the mechanical behaviour of conventional and new polymeric materials over a wide temperature interval. As was mentioned above, irrespective of their chemical structure, conventional materials in the glassy state have approximately the same moduli of elasticity $[(2-3)\times 10^3$ MPa]. On heating of these materials to their glass transition temperatures, the moduli of elasticity decrease sharply in the narrow temperature interval $\Delta T \simeq 20-30^\circ$ and the materials undergo transition to the rubbery state.

A fundamentally different picture is observed for new materials. At low temperatures, the new materials (like conventional ones) are also in the glassy state. However, on heating to the temperature of the first relaxation transition the modulus of elasticity decreases very slowly (up to the temperature of the second relaxation transition). Only after passing this temperature a sharp decrease in the modulus of elasticity occurs and the material undergoes transition to ordinary rubbery state. In this case the temperature interval, in which the slow drop in the modulus of elasticity is observed, is ~200 degrees. This interval is the major operating range for these materials. Despite the fact that within this interval the moduli of elasticity take the values characteristic of the zone of transition from the glassy to the rubbery state, the materials possess elastic rather than viscoelastic behaviour. It is possible that in this case a new physical state is observed different from the glassy and rubbery states. It is needless to say that this assumption is tentative, though the distinction in the mechanical behaviour of conventional materials and those under consideration is beyond doubt.

VII. Optical sensitivity of highly cross-linked networks

The stress-optical coefficient C_σ, *i.e.*, the coefficient of proportionality between birefringence Δn and the mechanical stress σ that induces birefringence, is one of the characteristics of the optical sensitivity of materials

$$\Delta n = C_\sigma \sigma .$$

The stress-optical coefficient C_σ is a fundamental characteristic of the materials used in the photoelasticity method of stress investigation. In this method, a model of an actual construction made of transparent, optically sensitive materials is loaded as required. As a result, birefringence appears in the material the model is made of and the stress-strain state of the construction can be judged from the birefringence pattern. In the case of three-dimensional models, the deformation freezing method is rather efficient. A model is heated to the temperature at which the constituent material undergoes transition to the rubbery state; it is then loaded and cooled under load to room temperature, which is about $80-100^\circ$ lower than the glass transition temperature for conventional optically sensitive materials. The deformations and optical anisotropy appearing upon loading the model are frozen. Then the model is sliced and these specimens are investigated thereafter.

Without dwelling on other modifications of the photoelasticity method of stress analysis, we should note that their progress is only possible as new polymeric materials with desired optico-mechanical properties have become available. Two types of materials (elastic and viscoelastic ones) are required to solve different problems. Different-modulus polymeric materials with the ratio of the moduli of elasticity from 2 to 10 and possessing elastic properties both under static and under dynamic loads are

required for studying the stress fields in laminated elastic media by the dynamic photoelasticity method. Such materials have come into use in dynamic photoelastic studies recently.[71] The problem of their preparation is that all polymeric glasses irrespective of their chemical structure have nearly the same moduli of elasticity ($\sim 10^3$ MPa).

It might seem that different-modulus materials could be prepared if polymers were synthesised that possess the behaviour characteristic of the zone of transition from the glassy to the rubbery state at the test temperature (*e.g.*, at room temperature). Since the modulus of elasticity decreases sharply in this zone, it is always possible to choose a material with the desired modulus of elasticity. However, materials in the transition zone possess extremely high viscoelasticity, whereas elastic materials are required for solving this problem by the photoelasticity method of stress analysis. Polymer networks of specific chemical structure (highly cross-linked networks possessing extremely large rubbery moduli have low glass transition temperatures much below room temperature) fulfil these two incompatible requirements. The present state-of-the-art studies in the field of predicting the properties of such systems makes it possible to predict the structure of highly cross-linked networks that would meet these two contradictory requirements.[72, 82]

Using the above approach, the glass transition temperatures and the moduli of elasticity of cross-linked carbofunctional organosilicon polyisocyanurates with short linear fragments of different lengths were predicted.[71, 72] The structure of these networks is shown in page 705. The relaxation properties of these materials have already been compared to those of the viscoelastic material. Let us consider mechanical and optical properties of the networks under creep conditions.

The time dependences of mechanical and optical creep are shown in Fig. 28. It can be seen that a gradual increase in the compliance values is observed after loading the viscoelastic material, whereas fast creep relaxation is observed for silicon-containing cross-linked polyisocyanurates in contrast to typical viscoelastic polymer.

Thus, it can be pointed out that elastic behaviour, complicated only by weak indications of viscoelasticity, is characteristic of carbofunctional organosilicon polyisocyanurates.[71, 72]

Table 4 lists the values of the equilibrium moduli of elasticity (E_∞) found by fitting the stress relaxation curves using new memory functions,[78] which make it possible not only to obtain high correlation coefficients but also to calculate such physical characteristics of a material as the number of microdefects, the initial entropy of the system, *etc*. The stress-related values of material strip $\sigma_0^{1.0}$ are also given in this table. As can be seen from the table, the stress-optical sensitivity ($\sim 1/\sigma_0^{1.0}$) in the series of polyisocyanurates differing only in the number of dimethylsiloxane units between cross-link points of the network increases as the length of the linear fragment n increases. It seems most likely that the increase in optical sensitivity, despite the decrease in the concentration of the groups possessing high anisotropy of polarizability (isocyanurate ring, aromatic rings), is associated with an increase in the mobility of the macrochain, which depends both on the concentration of cross-link points in the network and on the number of dimethylsiloxane units with low potential energy barrier to rotation about the Si–O–Si bond.[83]

Table 4. Optico-mechanical characteristics of cross-linked macrodiisocyanates.

n	Static load		Dynamic load		
	E_∞/MPa	$\sigma_0^{1.0}$/ MPa (295 K)	v_p/ m s^{-1}	E_d/MPa	$\sigma_0^{1.0}$/MPa
1.2	866	1.26	1980	4822	2.6
2.5	283	1.14	1700	3454	2.3
3.8	149	1.08	1270	1897	2.1
5.4	–	0.80	1000	1140	1.8
6.2	43	0.69	800	727	1.6
9.2	24	0.41	570	357	1.0

Dynamic characteristics of optico-mechanical properties of the polymers can differ appreciably from the static ones because of the influence of the time factor. Thus, the duration of the processes that occur under the action of short-term impulse loads and are recorded in the optical birefringence pattern model are from several to hundreds of microseconds. In this case conventional quasi-static creep and stress relaxation tests cannot reproduce the essence of the phenomena occurring in the polymeric material upon dynamic action.

The photogram analysis shows that longitudinal and transverse waves propagate along the rods made of cross-linked polyisocyanurates at a constant velocity. The values of the velocity of propagation of longitudinal waves C_p and the dynamic moduli of elasticity E_d calculated using the following equation

$$E_d = \rho C_p^2 ,$$

where ρ is the density of the material, are listed in Table 4. As can be seen, the velocities of propagation of longitudinal waves C_p and

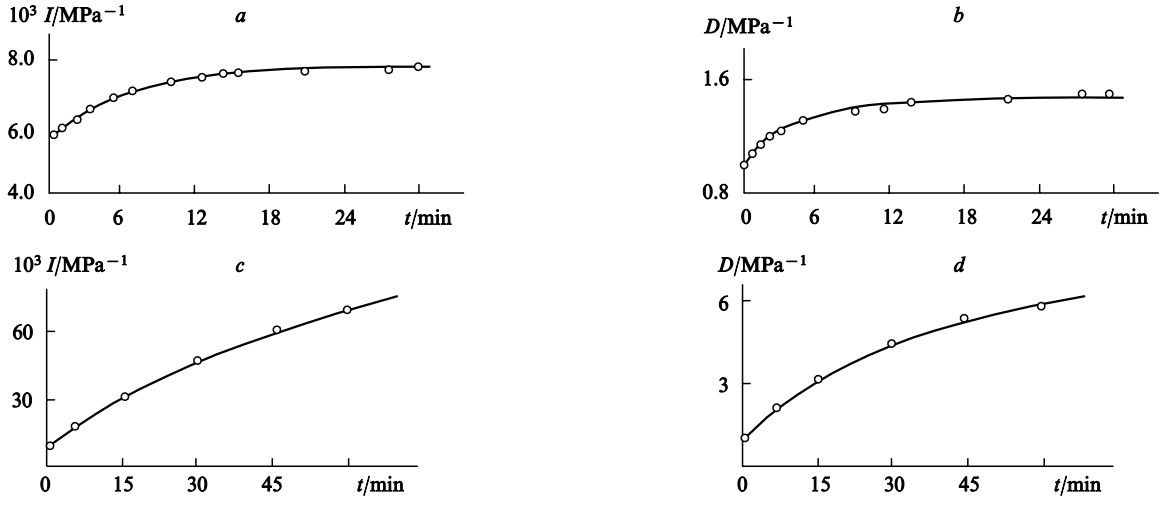


Figure 28. The mechanical $I(t)$ (a, c) and optical $D(t)$ (b, d) creep curves for polyisocyanurate networks with $n = 6.2$ and $\sigma = 1.4$ MPa (a, b) and for the viscoelastic polymer based on the ED-20 epoxy oligomer cured with a mixture of poly(sebacic anhydride) (27.3%) (c, d) and azelaic acid (13.8%).

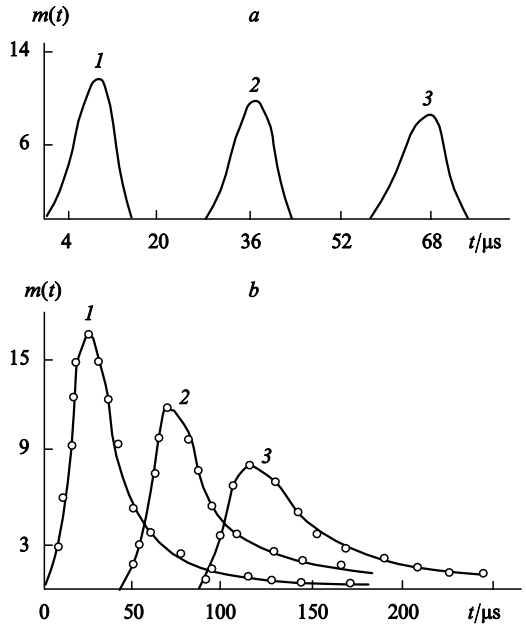


Figure 29. Changes in impulse birefringence pattern $m(t)$ at different cross-sections l of the rods made of a cross-linked polyisocyanurate with $n = 2.5$ for $l = 50$ (*1*); 100 (*2*); and 150 (*3*) mm (*a*); those for an ED-20-based viscoelastic polymer cured with a mixture of poly(sebacic anhydride) (27.3%) and azelaic acid (13.8%) for $l = 60$ (*1*); 110 (*2*); and 160 (*3*) mm (*b*).

the dynamic moduli of elasticity E_d of the materials presented vary over a wide range.

Thus, optically sensitive materials based on the cross-linked polyisocyanurates with short chains between cross-link points differ substantially from the traditional ones. The latter have different static moduli of elasticity but virtually the same dynamic moduli of elasticity, which limits the field of their application when solving certain dynamic problems.

To evaluate the viscoelastic properties of cross-linked polyisocyanurates under conditions of dynamic action, let us consider the birefringence patterns under the impulse loading $m(t)$ at different cross-sections l of the rods.[82] For comparison, the impulse values $m(t)$ are plotted on the same graph (Fig. 29) with the shift in time, which takes account of the velocity of wave propagation in the materials. In contrast to the typical viscoelastic polymer, slight changes in the shape of impulses and their durations observed with increasing distance covered in the rods are characteristic of specimens of cross-linked polyiso-cyanurates with $n = 1-9$; this indicates their weak viscoelasticity under impulse loading. Hence, optically sensitive cross-linked polyisocyanurates are suitable for studying the stress-strain state of laminated media by the dynamic photoelasticity method.

Previously, we have considered elastic polymeric materials. However, optically sensitive materials possessing viscoelasticity are required for solving a number of problems. It is natural that viscoelastic behaviour is mostly characteristic of the zone of transition from the glassy to the rubbery state.

The currently available methods of creep simulation by the photoelasticity method (the photocreep method) are based on a specific selection of materials possessing both high optical sensitivity and pronounced viscoelastic properties. To solve this problem, it is necessary to have polymer networks for which the test temperature falls into the zone of transition from the glassy to the rubbery state. Viscoelasticity of the materials will increase as the test temperature approaches the glass transition temperature. Therefore, it is necessary to have a set of polymeric materials with preset glass transition temperatures not equidistant from the test temperature. The preparation of such materials has been reported in the literature.[84–88]

In addition to physical characteristics considered above [density (the molar volume), the glass transition temperature, and the equilibrium rubbery modulus], the molar (or specific) heat capacity, the coefficient of volume expansion in the glassy and in the rubbery states, the dielectric constant, the refractive index, the energy of intermolecular interaction, *etc*., can also be calculated for highly cross-linked polymer networks. These properties are calculated using the same relationships as for linear polymers with account of the fact that in the case of networks their repeating fragments rather than the 'monomer' units of the polymers play the role of the repeating units.

The ability to calculate the characteristics mentioned above makes it possible to solve the inverse problem, *viz*., to judge the structure of a network (especially of a complex network) from the experimental characteristics. Analysis of the structure of phenol–formaldehyde resins is an example of such an approach.[89]

VIII. Analysis of the structure of cross-linked polymers (taking cured phenol–formaldehyde resins as an example)

Phenol–formaldehyde (PF) resins belong to the oldest representatives of highly cross-linked polymer networks; however, interest in their structure and properties has persisted up to the present.[90] Numerous studies have been dedicated to the analysis of the structure and properties of PF resins; however, there is no agreement concerning the chemical structure of the network formed by these resins as yet. This is probably due to the fact that the network may have different structures depending on the course of curing of PF resins. In addition, OH groups capable of forming hydrogen bonds are present in the network structure. Hydrogen bonds can be formed both due to intermolecular interaction of the OH groups in the neighbouring chains of PF resins and due to interaction between the OH groups within the same repeating unit.

It is convenient to clarify the sense of such concepts as the inter- and intramolecular interaction from the viewpoint of the approach presented using a simplified scheme (Fig. 30). Figure 30*a* illustrates the case of intermolecular interaction resulting in the formation of a network of physical (hydrogen) bonds between the chains. It is natural that the formation of this network favours an increase in the glass transition temperature. Figure 30*b* illustrates the case where two OH groups are within the same unit of a linear fragment of PF resin; the hydrogen bonding occurs within this unit while no formation of a network of physical bonds between the neighbouring chains occurs. Of course, different types of intermolecular interaction (hydrogen bonding) can actually coexist and appreciably affect the properties of PF resins (see below).

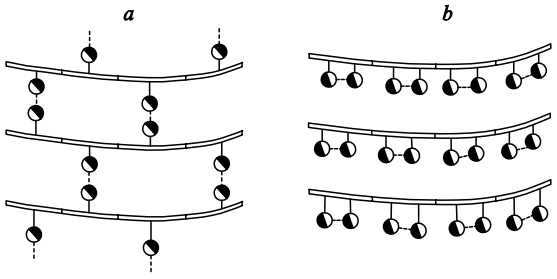
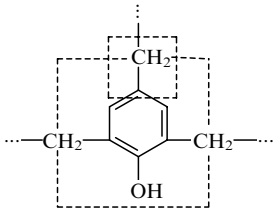
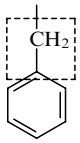


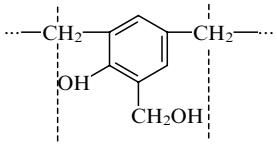
Figure 30. A scheme of a network of hydrogen bonds; (*a*) hydrogen bonding between neighbouring chains; (*b*) hydrogen bonding within the same repeating unit.

The cured PF resin can contain the following structures (the cross-link point is shown near the structure **20a**):

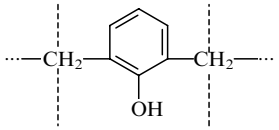


20a

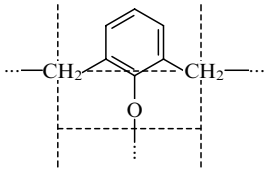




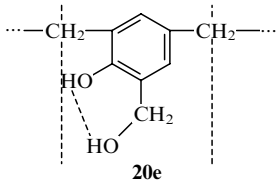
20b



20c



20d



20e

The structure **20a** constitutes only the network, the repeating fragment of which is marked by dashed lines. The cross-link point is specified within the repeating fragment (in accordance with our definition of the chemical structure of the cross-link point).

Let us calculate the glass transition temperature of the network using Eqn (6). It is reasonable that the entire cross-link point contains three of these sets of atoms. The data for structure **20a** are given in Table 1.

Substituting the values of the parameters for the ideal structure **20a** in Eqn (6), we get

$$T_g = \frac{101.1}{21.5 \cdot 3 + 71.6} \times 10^3 = 743\,\text{K}.$$

The calculated T_g is much higher than the experimental T_g values. The experimental values of the parameters are listed below: T_g = 343–433 K, ρ = 1.24–1.33 g cm^{-3}, n = 1.57–1.63, α = (18.0–22.5) $\times 10^{-5}$ K^{-1}, C_p^s = 29–48 cal mol^{-1} deg)$^{-1}$.

Hence, the actual network differs in structure from the ideal one.

The possible structure **20b** of PF resins corresponds to a linear polymer (the repeating unit is marked by dashed lines). The data for this structure are listed in Table 1.

If both OH groups are involved in the formation of the hydrogen bonds between the chains (see Fig. 30), then

$$\sum_j b_j = 2b_h + b_m;$$

$$\sum_j b_j = (-139.6 \times 2 + 16.0) \times 10^{-3} =$$

$$= -263.2 \times 2 \times 10^{-3}\,\text{Å}^3\,\text{K}^{-1}.$$

Substitution of the values of all parameters in Eqn (5) gives the following T_g value of the ideal linear structure **20b**:

$$T_g = \frac{123.05}{505.4 - 263.2} \times 10^3 = 508\,\text{K}.$$

As for the structure **20a**, this value is beyond the experimental temperature interval in which the α-transition for PF resins is observed.

The structure **20c** forms only linear chains; their repeating unit is enclosed by dashed lines. The following relationship is valid for such a structure

$$\sum_j b_j = b_h + b_m = (-139.6 + 16.0) \times 10^{-3} =$$

$$= -123.6 \times 10^{-3}\,\text{Å}^3\,\text{K}^{-1}.$$

By substituting the values of the parameters in Eqn (5) we can obtain T_g of the ideal structure **20c**.

$$T_g = \frac{99.05}{331.9 - 123.6} \times 10^3 = 476\,\text{K}.$$

This value is somewhat higher than the observed temperature interval of α-transition for PF resins.

The structure **20d** forms a network the repeating fragment of which is shown by dashed lines (the cross-link point of the network is enclosed by dashed lines). All parameters for the structure **20d** are given in Table 1. Substituting the values of the parameters in Eqn (6), we get the T_g value of an ideal network based on the structure **20d**

$$T_g = \frac{91.25}{56.5 + 120.7} \times 10^3 = 515\,\text{K}.$$

Thus, the glass transition temperature of such a highly cross-linked polymer network is rather high.

The structure **20e** has the same molecular formula as the structure **20b**; however, hydrogen bonding occurs within the same repeating unit. Such a structure was described by Nikolaev.[91]

If hydrogen bonds are formed between the neighbouring OH groups within the same repeating unit, then no formation of the physical network between the chains due to the hydrogen bonds occurs. Then the following should be taken into account when determining the $\sum_j b_j$ value for calculating the glass transition temperature: the fact that the structure **20e** is linear requires the introduction of the b_m increment to account for the *m*-substitution in the aromatic ring; in addition, there are two branchings from the aromatic ring, which requires introducing two b_d increments. Then

$$\sum_j b_j = b_m + 2b_d = 16.0 - 2 \times 55.4 =$$

$$= -94.8 \times 10^{-3}\,\text{Å}^3\,\text{K}^{-1}.$$

Substituting the values of all parameters of the structure **20e** in Eqn (6), we obtain

$$T_g = \frac{123.05}{505.4 - 94.8} \times 10^3 = 300\,\text{K}.$$

This T_g value is below the temperature interval of α-transition for cured PF resins.

None of the calculated glass transition temperatures of possible ideal structures of PF resins fall into the interval in which experimental values are observed. This suggests that the cured PF resin has a more complex structure than the ideal structures considered above, which has been noted by most investigators. It is most likely that the actual structure of PF resins consists of a set of the considered ideal structures.

To establish the most plausible actual structure of PF resins, let us calculate, in addition to T_g, such characteristics of cured PF resins as density ρ, the refractive index n, the coefficient of volume

Table 5. Calculated characteristics of ideal structures of cured PF resins.

PF structure	T_g/ K	ρ/ g cm^{-3}	n	$10^4\,\alpha$/ K^{-1}	C_p^s/ kcal mol^{-1} deg^{-1}
20a	743	1.253	1.621	1.30	31.9
20b	508	1.250	1.583	1.89	42.4
20c	476	1.205	1.604	2.02	31.4
20d	515	1.301	1.645	1.86	26.1
20e	300	1.250	1.583	3.20	42.4

expansion α_G, and the molar heat capacity C_p^s. These characteristics were chosen with account of their sensitivity to the changes in the structural formula of the substance and of the fact that both the increase and decrease in the values of other characteristics can be observed for different ideal structures of PF resins with the increase in the glass transition temperature. The latter is of importance for searching the most plausible structure of PF resins using the experimental design method.

The calculated densities of PF resins for structures **20a**–**20e** are listed in Table 5.

The refractive index n was calculated using the following equation [7]

$$\frac{n^2-1}{n^2+2} = \frac{kR_f}{N_A\left(\sum_i \Delta V_i\right)_f}, \qquad (62)$$

in which the molar refraction of the repeating fragment R_f is the sum of the refractions R_i of particular atoms and increments for different types of bonds (double and triple bonds).

The n values for different structures found using Eqn (62) are listed in Table 5.

The calculations of the molar heat capacity C_p^s in the glassy state of the polymer were carried out using the following relationship [92]

$$C_p^s = \sum_i C_{p,i}^s \Delta V_i - 0.77\,,$$

where $C_{p,i}^s$ are the partial heat capacities characteristic of each atom and ΔV_i are the van der Waals volumes of the atoms.

The coefficient of volume expansion α is related to the glass transition temperature by the following relationship [7]

$$\alpha = \frac{0.096}{T_g}\,.$$

Comparison of calculated and experimental values of the characteristics of possible ideal structures of PF resins (see Table 5) allows one to conclude that a cured PF resin represents a set of structures rather than an ideal network. The experimental design method of construction of simplex lattices and polynomial 'composition–property' models was applied to multicomponent systems to find such a set of structures.[89]

It has been found [89] that one possible relation between the relative content of ideal structures corresponding to the permissible set of network structures has the form $\alpha_1 = \alpha_5 = 0.345$, $\alpha_3 = 0.2$, and $\alpha_4 = 0.11$, where α_1, α_3, α_4, and α_5 are the mole fractions of the structures **20a**, **20c**, **20d**, and **20e**, respectively.

The following values have been found for the actual network, *viz*., $T_g = 429$ K, $\rho = 1.248$ g cm^{-3}, $n = 1.6057$, $\alpha = 2.238 \times 10^{-4}$ K^{-1}, and $C_p^s = 34.8$ cal mol^{-1} deg^{-1}. All these values fall into the range of experimental values (see Table 5).

Taking into account the narrow limits of the permissible set of ideal structures of cured PF resin, it is possible to conclude that the actual network structure considered is close to the most plausible one.

Thus, comparing the experimental and calculated characteristics of complex highly cross-linked network systems allows one to draw certain conclusions on their structure.

IX. Conclusion

The study of the influence of the chemical structure of highly cross-linked polymer networks on their properties shows that the passage from sparse networks to highly cross-linked networks occurs when the number of the repeating units between the cross-link points is reduced to 4–5. Changes in the properties become particularly noticeable as the number of repeating units is reduced to 1–2 or becomes less than 1. Changes in the chemical structure of a highly cross-linked network to an extent that it only vaguely resembles that of the initial network is the main reason for principal changes in the network properties.

Numerous studies of the structure and properties of highly cross-linked networks have shown that the classical theory of rubber elasticity becomes inapplicable to the description of the dependence of the equilibrium rubbery modulus on the distance between the cross-link points. The same is also valid when solving the inverse problem (estimation of the distance between the cross-link points from the experimentally measured equilibrium rubbery modulus). This required the development of altogether new approaches and methods for assessing the structure and properties of highly cross-linked polymer networks. An analysis of the potentialities of the equations and computational schemes proposed has shown that the distance between the cross-link points can be estimated with a good accuracy by comparing experimental and calculated glass transition temperatures. The proposed generalised equation for evaluating the equilibrium rubbery modulus makes it possible to perform calculations with a good accuracy for both highly cross-linked and sparse networks. All the relationships considered in this review require no fitting parameters and allow one to analyse the properties on the basis only of the chemical structure of the network. Mention should be made of yet another important circumstance, *viz*., any change in the network topology (the appearance of dangled chains, branchings, isolated loops, and cycles) results in changes in its chemical structure and, as a consequence, in changes in the physical properties.

This approach is of fundamental importance for designing cross-linked polymers with unusual properties. Primarily it concerns gradient-modulus polymeric materials in which the modulus of elasticity changes by a factor of 1000–10 000 within the same specimen in a prescribed manner. In this case it has been possible to eliminate the major drawback of the polymers in the zone of transition from the glassy to the rubbery state and possessing pronounced viscoelasticity. In addition to the moduli of elasticity characteristic of the transition zone, the new materials obtained possess elastic behaviour rather than viscoelastic behaviour.

Yet another example is the use of this approach for predicting the unusual properties of cross-linked polymers followed by the synthesis of these materials that have found application in the photoelasticity method.

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