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Intermolecular interaction in polymers and the physical network model

V I Irzhak, G V Korolev, M E Solov'ev

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Abstract. The current views on the nature of the intermolecular interaction and the interchain organisation of polymers in the rubber-elastic state are described. The possibility of representing the system of intermolecular interactions by an infinite network of physical links (the physical network model) is considered. Polymeric physical networks are compared with associated species formed in low-molecular-mass organic compounds containing localised intermolecular interaction centres. The principal physical properties of polymers are analysed on the basis of the physical network model. The bibliography includes 280 references.

I. Introduction

The science of the structures of amorphous polymers has a long history. The fundamental ideas about the nature of the elasticity of elastomeric networks, introduced in the 1930s by Mark, Guth and Kuhn [1] and based on the model of overlapping statistical coils,[2–4] made it possible to account for many thermodynamic and mechanical properties of elastomers. In the 1960s an attempt was made to re-examine the existing ideas about the structures of amorphous polymers on the basis of Frenkel's concept [5] of the existence of a quasi-crystalline short-range order in liquids. Kargin, Kitaigorodskii, and Sloninskii put forward the hypothesis of the 'packet' structure of amorphous polymers.[6] According to this model, the principal structural element of this system is not the macromolecule proper but an intermolecular packet consisting of several macromolecules in the uncoiled conformation arranged in parallel.[7–9] However, the packet model encountered extremely serious objections. Flory [2] demonstrated theoretically that the volume effects in the polymer vanish with increase in the concentration of the solution and that the macromolecule in a block has the form of an unperturbed statistical coil. Calculations by the Monte Carlo method yield the same result:[10–12] modelling of the conformations of nonintersecting chains showed that the gradual filling of a limited volume makes it possible to attain a packing density of the segments which corresponds to the density of the block polymer with retention of the Gaussian coil conformation. Conformational analysis of macromolecules on the basis of the rotational-isomeric model [3, 4, 13] also led to the conclusion that the macromolecule, having a Gibbs free energy minimum, should contain a fairly large number of bonds in the gauche-position. Convincing evidence in support of the amorphous polymer model, consisting of self-intersecting random coils, was obtained with the aid of the small angle neutron scattering technique.[14] Direct measurement of the neutron diffraction in deuterated specimens of vitreous polystyrene [15–17] and poly(-methyl methacrylate)[18] and also in a polyethylene melt [18–20] showed that the mean square dimensions of the macromolecules in a block and in dilute ideal solutions are the same within the limits of $\sim 10\%$.

All this led not only to the complete rejection of the 'packet' model but also to the denial by many investigators of the very possibility of the formation of any kind of structures in amorphous polymers. This conclusion cannot of course fail to give rise to objections. The set of accumulated experimental data shows that an ideal polymer, having the form of a structureless liquid consisting of self-intersecting random coils, is an exception rather than the rule. Indeed, the mechanical behaviour of network elastomers corresponding to this model occurs only under special conditions: when they are in a swollen state or for extremely small elongations.[21] In other cases, deviations from the predictions of the theory of rubber elasticity are observed. This is evidently associated not only with the imperfection of the theory itself [22–25] but also with the lack of correspondence between the structures of real networks and the structureless polymer model.[26–28]

It is essential to mention the structural inhomogeneity of polymers at the molecular (compositional),[29] topological, and supermolecular (inhomogeneity arising from fluctuations and morphological and microphase formations) levels. One should also bear in mind that the range of polymers employed in practice is extremely wide and includes systems such as thermoreversible gels, block copolymers, interpenetrating polymer networks, and polyelectrolytes.

In the present review, an attempt is made to describe the current ideas concerning the structures of polymer systems in the rubber-elastic state and to analyse on the basis of the physical network model the principal physical properties of polymers of this kind.

V I Irzhak, G V Korolev Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 35 88.
Tel. (7-096) 517 16 90 (V I Irzhak), (7-096) 517 10 89 (G V Korolev).
M E Solov'ev Yaroslavl' State Technical University, Moskovskii prosp. 88, 150053 Yaroslavl', Russian Federation

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II. Intermolecular interaction in a 'structureless' polymer system

First of all, we shall consider the structureless model of the structure of a polymeric body in which the only factor taken into account is the presence of long chains and the only form of intermolecular interaction (IMI) is repulsion due to their mutual impermeability.

1. The topological network model (entanglements network)

The simplest and at the same time the most evident feature of a 'structureless' system is the topological limitations induced by the fact that the chains cannot intersect. As early as 1944, it was observed that the modulus of elasticity of vulcanised butyl rubber differs from the values calculated on the basis of the kinetic theory of rubber elasticity.[30] This was attributed to the presence of three kinds of network defects: ends, loops, and entanglements. The latter exist in the network before cross-linking, cross-linking merely leading to their fixation and imparting to them the ability to be manifested as additional nodes.

The first studies on natural rubber already revealed the reversibility of its deformations, which is manifested when the period during which the specimen is maintained under load is fairly short.[31] This effect was explained by the intertwining of the molecules with formation of entanglements, which in the course of a short time act similarly to chemical cross-links. Later several characteristic features of the mechanical behaviour of polymers, caused by the interchain interaction, were observed. These include the characteristic inflection in the plots of the viscosity of polymer melts and solutions against their molecular mass and concentration, the existence on the thermomechanical curves of a plateau corresponding to the quasi-equilibrium rubber-elastic state, and the presence of a long-time region on relaxation time spectra. The terms 'entanglements' (coupling), 'temporary cross-linking and 'physical network' are employed in the literature for the description of these phenomena.

The first systematic studies on the physical network in elastomers were carried out by Tobolsky.[31–33] As early as 1946, a model was proposed for a network elastomer, according to which the nodes may be disrupted by thermal fluctuations and then reformed.[31] In this case, there is a possibility of a characteristic viscoelastic behaviour of the elastomer: an elastic response on rapid application of a load and viscous flow and relaxation of stress on slow application of a load. An attempt has been made in a monograph[33] to arrange systematically the viscoelastic properties associated with the appearance of an entanglements network and to estimate the length of the chains between the entanglements on the basis of the theory of rubber elasticity.

Several reviews have been devoted to the problem of entanglements as a specific form of intermolecular interaction in polymers.[34–37]

Although the existence of chain entanglements appears entirely evident, no one has succeeded in observing them directly. The deviation of the real elastic properties of an elastomer from those predicted by the classical theory of rubber elasticity is usually regarded as evidence for topological limitations. However, the existence of topological limitations does not yet imply that the entanglements are indeed in regions where the chains are entangled and intertwined. In this connection, several theoretical attempts were made to estimate the probability of the formation of an entanglement on the basis of the geometrical chain parameters. Thus Hoffmann[38] attempted to estimate the molecular mass of the chain section between entanglements. He suggested that the entanglements represent the type of intermolecular contacts in which one chain forms a loop around another. The calculation was performed for a polymethylene chain subject to the condition that the loops are formed by four–six methylene groups and taking into account the geometrical relations in a tetrafunctional node. According to the calculation, the number of bonds between entanglements should be 175, which agrees with experiment.

Other attempts to estimate the distances between the entanglements on the basis of geometrical considerations led to different results. Thus it has been found that in a chain comprising 700 units a loop may be formed by a sequence incorporating not less than 30 units.[39] The calculation of the density of the entanglements network in the form of loops, carried out using the van der Waals volumes of the molecules and the molecular packing coefficient, led to the conclusion that the effective distance between the loops must be such that the mass of this section would be several times greater than the mass-average molecular mass of the usual polymer.[40] It was also shown that the formation of loops is unfavourable on thermodynamic grounds as well. Frank-Kamenetskii and Vologodskii (see their review[41]) estimated the probability of the formation of loops and rings with a complex configuration. These results are especially important in the consideration of the topological structure of network polymers.

2. The properties of polymers associated with the topological limitations to chain conformations

Allowance for the topological limitations to conformations implies in the first place the abandonment of the hypothesis of phantom chains. The partition function of a network with non-intersecting chains cannot be calculated directly. Various models have therefore come to be widely employed. In particular, it has been suggested that account be taken of the limitations to the number of chain conformations by examining the statistical properties of the chain in the form of an external potential having the form of a 'box' or 'tube'[42,43] or by introducing the concept of sliding links.[34,44] It was proposed that the effect of neighbouring chains be modelled on the basis of the elastic potential of the attraction to the equilibrium position — channel.[45] Another version of the modelling of topological limitations is the approach,which may be called the 'chain in the entanglements lattice'.[25] It is usually assumed that the deformation of the surroundings of the chain, modelled by a tube, channel, or entanglements lattice, is of the affine type. The model parameter is as a rule the size of the tube linked in one way or another to the concentration of entanglements. When account is taken of topological limitations, one has in mind small deformations, which makes it possible to analyse the network elastic potential constant W in the form of the Mooney–Rivlin equation:

$$W = C_{100}(I_1 - 3) + C_{010}(I_2 - 3), \tag{1}$$

where C_{ijk} are elastic constants, I_k the invariants of the deformation tensor with $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and $I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2$, λ_i is the elongation of the specimen along the ith coordinate axis.

An attempt was also made to construct a theory of the elasticity of a chemical network with entanglements over a wide range of degrees of deformation.[46] The slip link and tube models have been used for the description of topological limitations under the conditions of small and large deformations respectively. The expression obtained for the free energy of deformation includes two terms:

$$\frac{F}{kT} = \frac{1}{2}N_c\left\{\frac{(1-\alpha^2)\sum_{i=1}^3\lambda_i^2}{1-\alpha^2\sum_{i=1}^3\lambda_i^2} - \lg\left(1-\alpha^2\sum_{i=1}^3\lambda_i^2\right)\right\} + \\ + \frac{1}{2}N_s\left\{\sum_{i=1}^3\left[\frac{\lambda_i^2(1+\eta)(1-\alpha^2)}{(1+\eta\lambda_i^2)(1-\alpha^2\sum_{i=1}^3\lambda_i^2)} + \lg(1+\eta\lambda_i^2)\right] - \right. \\ \left. -\lg(1-\alpha^2\sum_{i=1}^3\lambda_i^2)\right\}, \tag{2}$$

where N_c and N_s are the numbers of chemical cross-links and entanglements respectively and α and η are parameters characterising the extensibility and slip of the chains respectively.

The first term of Eqn (2) corresponds to the deformation of the chemical network and the second to that of the entanglements

network. The parameter N_s is determined from the rubber elasticity plateau modulus and the parameters α and η for real networks have values of about 0.1 and 0.2 respectively.

An attempt has been made to use the replica method to estimate the contribution of the inhomogeneity of the spatial distribution of the density of chemical cross-links to the free energy of the network [47] and it was concluded that the free energy and hence the mechanical properties of the polymer depend little on the microscopic details in the distribution of cross-links.

Flory proposed [48] that the entanglements be modelled as limitations to the number of fluctuations of the network nodes. In this model, it is assumed that the stress consists of the stresses due to the phantom chemical network (σ_c) and the stress associated with entanglements (σ_s). The ratio of the contribution of the entanglements to that of the phantom network is defined by the equation

$$\frac{\sigma_s}{\sigma_c} = \frac{\mu}{\nu}[\lambda K(\lambda_1^2) - \lambda^2 K(\lambda_2^2)]\,\frac{1}{\lambda - \lambda^{-2}}, \qquad (3)$$

where μ and ν are the concentrations of the entanglements and active chains respectively, $\lambda_1 = \lambda$, $\lambda_2 = \lambda^{-1/2}$, and

$$K(\lambda^2) = B\left[\frac{B}{B'+1} + \frac{(\lambda^2 B' + B)(x\lambda^{-2} + B^{-1})}{x}\right].$$

Here

$$B = \frac{(\lambda - 1)(\lambda + 1 - \xi\lambda^2)}{(1 + g')^2}, \quad g = \lambda^2[x^{-1} + \xi(\lambda - 1)],$$

$$B' = \frac{\partial B}{\partial \lambda^2}, g' = \frac{\partial g}{\partial \lambda^2},$$

x is the ratio of the mean square distance between the ends in the phantom network to the mean square fluctuations of the position of the node in the network with limitations, and ξ is a parameter determining the degree of nonaffinity of the change in the limitations domains on deformation.

Theories of the swelling of polymer networks with allowance for topological limitations [49] and birefringence [50] have been developed on the basis of Flory's model.[48] The experimental data on the mechanical properties, swelling, and birefringence of polydimethylsiloxane networks agreed satisfactorily with Flory's model.[51–54] This model has been used [55] to determine the contribution of the molecular parameters to the local deformation and orientation. Subsequently attention was turned to the fact that the nature of the topological limitations should depend on the way in which the network is formed. The proposed lattice model made it possible to take into account the influence of the cross-linking conditions.[56, 57]

The complexity of allowance for the topological limitations to the number of chain conformations stimulated interest in the construction of more rigorous models [58] and also in the investigation of network structures by means of a computer experiment. The influence of entanglements on the fluctuation of a network node has been investigated.[59] A rank 1 micronetwork with a node functionality of 3 and fixed ends having a length equivalent to 40 units was examined. Some of the predictions of Flory's model were confirmed, but the parameter x depended linearly on the number of units,whereas according to the above model a quadratic law should have held.

The Monte Carlo method has been used to model phantom networks and networks with nonintersecting chains in order to analyse the dependence of the number of elastically active chains, the form factor, and the cyclic rank on the structure of the network and their relation with the modulus of elasticity and the swelling parameters.[60–62] The topological limitations were taken into account by introducing δ-multipliers, which differentiate the permissible states of the network, into the integrated expressions for the partition functions and the probability of the Markov chains. It was found that in the region of extension the elastic behaviour of the model network obeys satisfactorily the Mooney–Rivlin equation.

It appears evident that the dynamic properties of polymers over a long time interval are controlled by the entanglements. For example, the relaxation of stress in uniaxially extended polystyrene has been investigated by the small angle neutron scattering method at a temperature above the glass transition temperature.[63] It was found that over a short time interval, the relaxation proceeds only on a small scale, in conformity with Rouse's model. If the time interval is long, the relaxation slows down but it is a large scale process. This is followed by the third stage, in which relaxation is independent of the degree of scattering. This stage is attributed to the unwinding of the entanglements.

The ideas concerning the presence of topological limitations have served as a basis of the 'tube' model — the reptation mechanism of the diffusion of macromolecules in concentrated systems.[64–66] The characteristic break in the curves relating the spin–spin and spin–lattice relaxation of protons to the molecular mass of polydimethylsiloxanes has been explained by the presence of entanglements.[34, 67] Detailed study of the curves for the decrease in free induction in linear and weakly cross-linked polymers [68, 69] also indicated, according to the authors, the presence of a network of entanglements for a molecular mass of the polymer of the order of 10^5. However, the mechanism of the diffusion of macromolecules was then interpreted within the framework of Rouse's theory: the 'tube' is not manifested in the time interval within which the NMR method operates.

The molecular mass of the chain section between the entanglements nodes (M_e) is usually estimated from the quasi-equilibrium modulus on the rubber elasticity plateau. These data have been presented in a series of books and reviews.[34, 70–74] We may note the existence of a correlation between M_e and the parameters of the chain rigidity, which are estimated, in particular, from the dimensions of the macromolecular coil in a θ-solvent.[72, 73]

In contrast to linear polymers, the topological entanglements in network polymers influence not only the dynamics but also the equilibrium mechanical properties of the specimens. The equilibrium modulus of shear consists of two components above the glass transition temperature: σ_x, determined from the classical theory of rubber elasticity, and σ_n, associated with the topology of the network.[22, 70] The fraction of the 'topological' component then depends on the degree of cross-linking for with low degree of cross-linking networks.[75] The contribution of trapped entanglements is manifested not only on deformation but also on swelling. Thus the dependence of the rate of transverse relaxation of protons δ in cross-linked polydimethylsiloxane on the degree of swelling q is divided into two characteristic regions.[76] In the region of low degrees of swelling, the main contribution to the $\delta(q)$ relation comes from the dispersion of the chains in the solvent. For high values of q, the rate of transverse proton relaxation begins to increase and tends to a limit. Effects associated with the presence of trapped topological entanglements are then manifested.

The study of the physical (mainly dynamic) properties of polymers and polymer blends from the standpoint of the reptation models is being continued.[77–80] A continuously growing number of results, which do not fully agree with the model of reptation diffusion and indicate the need to correct the structureless model of a polymeric body, are being accumulated in this connection. Thus as early as 1975 analysis of the rheological properties of monodisperse and polydisperse polymers led to the conclusion that 'the characteristic features of the viscoelastic properties of high-molecular-mass polymer blends are incompatible with the concept of a single network of randomly entangled macromolecules of different lengths'.[81]

Evidently it is necessary to take into account the real structure of the polymer, at any rate to the extent that the intermolecular interactions are manifested in liquids.

III. Localised intermolecular interactions and their role in low-molecular-mass liquids and polymers

1. Intermolecular interactions and their manifestation in low-molecular-mass systems

In order to elucidate the nature of the physical bonds arising from intermolecular interactions and promoting the formation of physical networks in polymer systems, it is possible to employ, as simple models, low-molecular-mass organic compounds in which there are strong intermolecular interaction centres, namely oxygen-containing (hydroxy-, carboxy-, ester, and other groups), nitrogen-containing (amide, amine, and other groups), halogen-containing, sulfur-containing, and other atomic groups capable of undergoing dipole–dipole interactions and of forming hydrogen bonds. Evidently in a condensed state the molecules of such organic compounds are linked to one another by a system of intermolecular interactions into associated species, the topology of which may be most diverse depending on the number (n) and functionality (F) of the IMI centres, their disposition (terminal, central), and the conformational features of the compounds (especially polyatomic ones), including the barriers to internal rotation. The functionality of an IMI centre should be understood as the number of bonds which may be formed one by such centre. For example, the hydroxy-group has the functionality $F = 2$, since it forms two hydrogen bonds — one at the O atom and the other at the H atom. Evidently for $F > 2$ the formation of associated species of the physical network type becomes probable,whereas for $F < 2$ only discrete structures with limited dimensions may arise.

The very fact of the association of organic liquids and in many instances also the topological characteristics of the associated species formed have long been established.[5,82] In the light of the problem of physical networks, the association of low-molecular-mass organic liquids is of definite interest: its study may help to discover a correlation between the parameters characterising the initial organic molecule as an elementary structural unit in a system of intermolecular bonds and the parameters of the system itself (the physical network). The nature of the IMI centres, their number and functionality, their positions, their intramolecular environment, and their mobility (the barrier to the internal rotation of an atomic group which is a carrier of the IMI centre) belong to the first group of parameters. The average concentration of intermolecular bonds v, formed at a given temperature T, the average lifetime of the bonds τ, the form of the function $v = f(T)$, and the topological type of the IMI system must be assigned to the second group.

Calculations based on the model of volume pair interactions, resorting to data on the frequencies of the atomic vibrations, the frequencies of pair collisions, and the heats of vaporisation, are used for the rough estimation of the parameters $v = f(T)$ and τ.[82,83]

The correlations observed in suitably selected comparison series, which include a large number of organic compounds, serve as the starting point for further systematic analysis of the physical properties of organic compounds. This results in the possibility of establishing which physical properties depend, and to what extent, on the IMI system (the physical network). Properties such as the boiling and melting points and the molecular packing coefficient K_p depend on the intermolecular interactions to the greatest extent. The molecular packing coefficient is determined by calculation[84] from data on the volume radii and interatomic distances in the molecule, the van der Waals volume of the molecules (V_v), and the molar volume (V_m) calculated from the density and the molecular mass of the substance.[40,74] By using different comparison series of organic compounds, it is possible to discover the regularities and characteristic features in the formation of the physical networks themselves from the regularities in the variation of the physical properties.[85,86]

The fundamental studies,[40,87–89] in which K_p and V_v were calculated and a comparative analysis of these parameters was carried out in relation to polymers and low-molecular-mass compounds, must be noted.

The results of the analysis of a representative set of data, including about 3000 organic compounds, are presented below.[85,86] This series includes the homologous series of mono-, di-, tri-, and, in isolated instances, also tetra-functional organic compounds with hydroxy-, carboxy-, nitrile, amide, ester, halide, and other functional groups,which occur in polymers to different extents.

a. Analysis of the set of data on the physical properties of low-molecular-mass organic compounds

Almost all the physical properties of organic compounds are related in one way or another to the strength of the intermolecular interaction. Evidently, the dependence of physical properties on the intermolecular interaction is multiparametric and, even in a series of organic compounds with isotypical IMI centres, for example in homologous series, the variation of several parameters at once is observed. The analysis of physical properties may therefore be successful only if the set of data is sufficiently representative to ensure the possibility of combining organic compounds into large systematic comparison series and of carrying out a multiprogram comparison.

The initial set should include at least several thousand compounds.[85] Only the boiling point T_b (as a rule at atmospheric pressure), the melting point T_m, and the density (in the vast majority of cases only at room temperature) have been determined for such a number of organic compounds. Other important physical properties, which depend on the intermolecular interactions just as strongly, for example, the viscosity η and the heat of vaporisation ΔH_e, have been measured for by no means all compounds. The quantities T_b, T_m, and K_p have therefore been used as the basic physical properties for systematic analysis,while the parameters η, ΔH_e, and others have been used only in those cases where this appeared possible.[85]

The quantities T_b and T_m are determined by the intensity of the intermolecular interaction at the opposite ends of the temperature range of the existence of organic compounds in the liquid state. The correlation between T_m and the IMI parameters is then complicated in many instances by crystallisation *i.e.* by the appearance of long-range order, which naturally may introduce errors into the analysis of the regularities in the intermolecular interaction unless this factor is specially taken into account. In this sense, the analysis of T_b is more correct.

When the coefficient K_p is employed, one must take into account its very high sensitivity to the shape of the molecules (conformational set). Therefore, in selecting the comparison series, it is essential to fix the shape factor and to compare only molecules with isotypical conformational characteristics.

The selection of the argument for the functions T_b, T_m, K_p or others plays a special role in the analysis of the set of data on physical properties. The van der Waals molecular volume V_v has been proposed as the universal argument.[85] This choice is justified in the following way. Strong intermolecular interactions of the type of dipole–dipole interactions and hydrogen bonds always occur against the background of weak dispersion forces, the overall energy of which is approximately proportional to V_v. Strong intermolecular interactions are localised strictly within the limits of a definite atomic group. For fairly high values of V_v, the contributions of the 'background' and localised intermolecular interactions are comparable. Therefore,in order to discover the correlations and regularities actually associated with the strong intermolecular interactions, it is necessary to differentiate the latter taking into account the 'background'. Such differentiation can be achieved by analysing relations of the 'physical properties (T_b, T_m, K_p, *etc.*) – V_v' type, provided that one assumes, to a rough approximation, that the magnitude of the 'background' is proportional to V_v and the contribution of strong intermolecular interactions for a fixed number of atomic carrier groups in the molecule is independent of V_v.

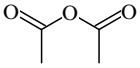
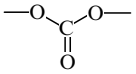
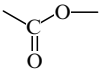
b. The role of the intermolecular interaction energy

The energy of the intermolecular interaction of functional groups (E), the values of which were estimated from the heats of vaporisation [90] (ΔH_e) of the corresponding organic compounds containing groups of the given type, are presented in Table 1. Figs 1–3 present the correlations of T_b, T_m, and K_p with V_v in homologous series of organic compounds having the corresponding functional groups. In order to reduce to a minimum the differences between the molecular shapes, only homologues with linear (unbranched) aliphatic chains and functional groups located at the ends of the chains are presented in the figures. Comparison of the data in Figs 1–3 and Table 1 permits the conclusion that the molecular packing density is the physical property which is most sensitive to the strength of the intermolecular interactions estimated in terms of the energy E. The disposition of the $T_b(V_v)$ curves in Fig. 1 is also consistent with the variation of E in Table 1.

The correlation between the $T_m(V_v)$ relation (Fig. 2) and the IMI intensity is complicated by a series of factors, the most important of which is the molecular shape and, for molecules of identical shape — their symmetry. The role of symmetry can be clearly seen on comparing the $T_m(V_v)$ relations for the even and odd members of homologous series: the even members are always characterised by higher T_m. This indicates a high significance of the contribution of the associative structures with a regular disposition of molecules to the establishment of long-range order on passing from the liquid to the solid state. The contribution of the IMI strength (Table 1) is manifested against this background only as a trend: alcohols, acids, and especially amides, characterised by the highest values of E, occupy a higher position also on the T_m scale. This trend can be seen more distinctly in the region of $V_v > 150$ Å^3, where the contribution of the molecular symmetry factor diminishes significantly, which may be inferred from the decrease in the amplitude of the T_m oscillations in the consecutive alternation of even and odd members of the homologous series.

When the molecules contain two functional end groups — carriers of localised IMI centres (see, for example, the data for glycols), the $T_m(V_v)$ curves are sharply displaced upwards relative

Table 1. The energies of the intermolecular interactions of functional groups of different types.

Group	E /kJ mol^{-1}	Group	E /kJ mol^{-1}
$-CONH_2$	60.6		
$-COOH$	45.1	CHO–	18.0
		–Br	15.9
	35.1		
			15.1
$-C_6H_5$	31.8 [a]		
$-OH$	30.5		
	27.6	$-NH_2$	15.1
		$-Cl$	13.2
		$-F$	7.3
$-CN$	26.3	–O–	6.3
$-I$	20.1		
	18.4		2.1

[a] The value which does not refer to localised intermolecular interactions but characterises the energy of the dispersion interaction.

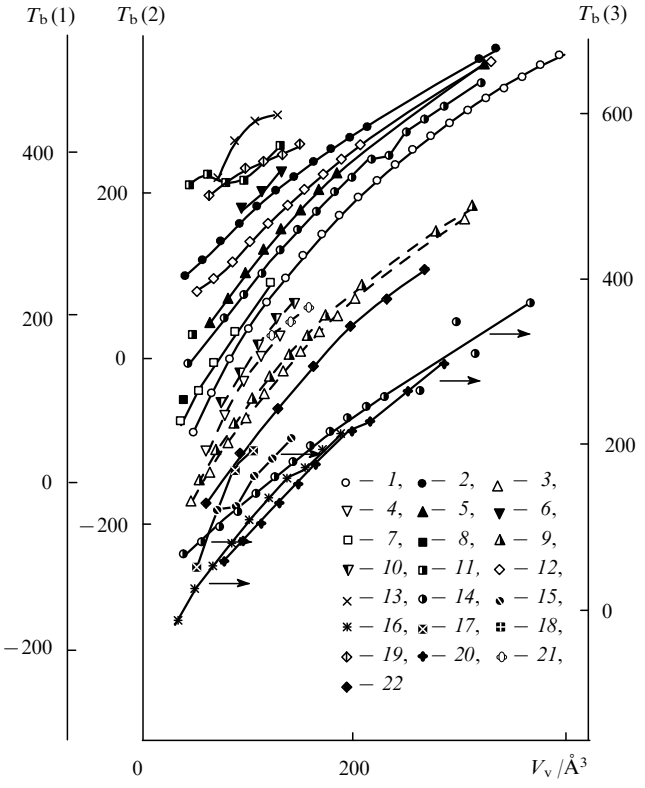


Figure 1. Dependence of the boiling point T_b (in °C) on the van der Waals volumes of the molecules of organic compounds: (*1*) aliphatic hydrocarbons; (*2*) monocarboxylic acids; (*3*) 1-chloro-compounds; (*4*) compounds dichloro-substituted at chain ends; (5) 1-iodo-compounds; (*6*) compounds diiodo-substituted at chain ends; (*7*) 1-fluoro-compounds; (*8*) compounds difluoro-substituted at chain ends; (*9*) 1-bromo-compounds; (*10*) compounds dibromo-substituted at chain ends; (*11*) amides; (*12*) nitriles; (*13*) dinitriles; (*14*) amines; (*15*) diamines; (*16*) aldehydes; (*17*) dialdehydes; (*18*) alcohols; (*19*) glycols; (*20*) monocarboxylic acid esters; (*21*) dicarboxylic acid esters; (*22*) ethers. The dashed curves refer to the $T_b(1)$ ordinate, the continuous curves without arrows refer to the $T_b(2)$ ordinate, and the continuous curves with arrows refer to the $T_b(3)$ ordinate.

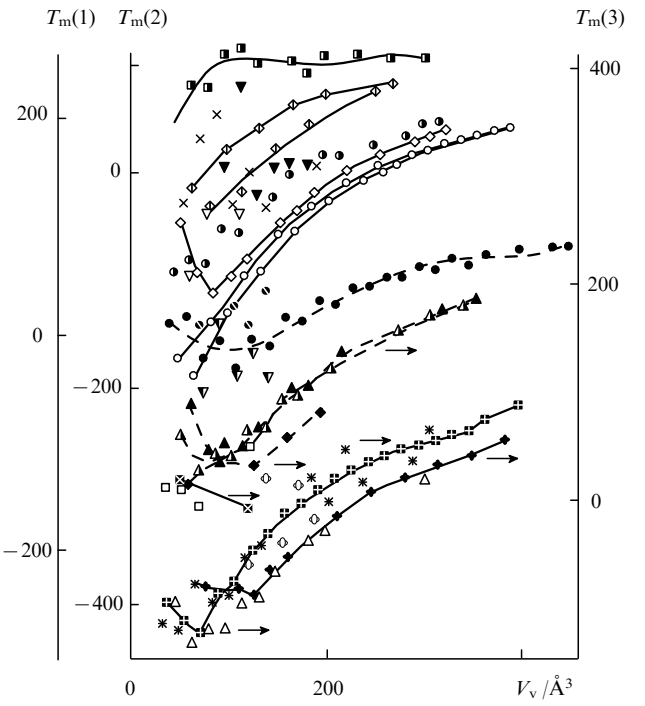


Figure 2. Dependence of the melting point T_m (in °C) on the van der Waals volumes of the molecules (for the designation of the curves, see Fig. 1). The dashed curves and points *7*, *10*, and *15* refer to the $T_m(1)$ ordinate, points *4*, *6*, *13*, and *14* refer to the $T_m(2)$ ordinate, and the continuous curves with arrows refer to the $T_m(3)$ ordinate.

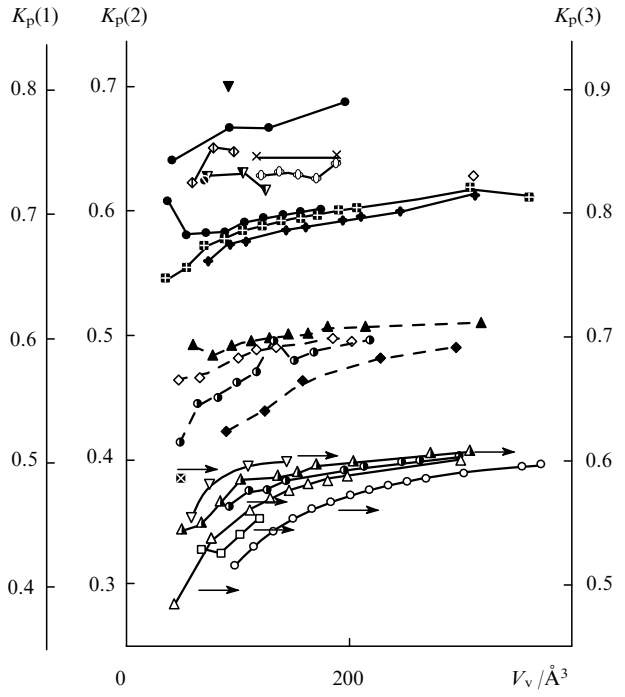


Figure 3. Dependence of the molecular packing coefficient K_p on the van der Waals volumes of the molecules (for the designation of the curves, see Fig. 1). The dashed curves refer to the $K_p(1)$ ordinate, the continuous curves without arrows refer to the $K_p(2)$ ordinate, and the continuous curves with arrows refer to the $K_p(3)$ ordinate.

to the curves for the monofunctional analogues. First of all, this is caused by the increase (doubling) of the average concentration of nodes. The sharp increase in the amplitude of the T_m oscillations for the even and odd compounds indicates the establishment of long-range order: the molecules are arranged in parallel and this arrangement is fixed by the strong terminal intermolecular bonds.

c. The role of molecular shape

Comparison of the IMI-dependent physical properties of molecules with similar values of V_v and E but having different shapes (conformational sets) makes it possible to estimate the contribution of this factor to the formation of the IMI system. As regards organic compounds containing one functional group in the molecule, the analysis leads to the following conclusions.

The molecular shape plays an important role in the formation of associated species both as a purely geometrical factor, promoting (or hindering) close packing and as an intramolecular factor which determines the degree of shielding of the IMI centre by 'inert' substituents. Comparison of the physical properties of isomers of the type $CH_3(CH_2)_2CH_2R$ (I) and $(CH_3)_3CR$ (II), where R = OH, COOH, Hal, or any other functional group is the carrier of the IMI centre, serves as the simplest illustration. The volumes V_v of different isomers are identical, while the equality of E for the pairs being compared holds owing to the identity of the functional groups. The type (I) linear isomers have a cylinder-like shape, while the type (II) branched isomers have a sphere-like shape. In all cases, the transition from (I) to (II) is accompanied by a sharp rise in T_m in the region of low temperatures, by a decrease in T_b in the region of high temperatures, and by a decrease in K_p in the intermediate region. The shape of type II molecules can exert a dual influence on K_p. On the one hand, it may act as a geometrical factor (the close packing of spheres is looser than that of cylinders). On the other hand, it may also prove to be an intramolecular factor: the shielding of the group R by CH_3 side groups prevents the optimum mutual approach of the groups R of neighbouring molecules, the associative linkages are weakened, and the packing becomes loosened owing to the decrease in the intensity of the field of intermolecular tightening forces. The occurrence of shielding is confirmed by an appreciable decrease in the heat of vaporisation ΔH_e on passing from form I to form II.

The role of molecular shape at low temperatures is determined by the ability of the system to form regular structures (long-range order). Cooperative intermolecular interactions in such structures lead to a sharp increase in their average lifetime τ up to values comparable to the observation times, which is interpreted as the transition from the liquid to the solid (nonfluid) state. Under these conditions, intramolecular energy barriers, *i.e.* barriers to the rotation of atomic groups around bonds (E_r), as well as the energy barrier to the dissociation of associative (intermolecular) bonds (E), contribute significantly to τ. In essence, the shape of a polyatomic molecule of an organic compound should be understood as a dynamic concept — as the set of conformations characteristic of the given molecule and controlled by the values of E_r.[91–95] The quantities E_r increase with increase in the number of branches and reach values comparable to E_r. For example, the $CH_3-C(CH_3)_3$ bond is characterised by the quantity $E_r = 19.6$ kJ mol^{-1}. In the light of this approach, factors associated with molecular shape, namely symmetry, regularity of the alternation of atomic groups in the molecule, and the values of E_r, should exert, together with E, a decisive influence on T_m. The transition from form I to form II is accompanied by an increase in E_r and in molecular symmetry, which is evidently the actual cause of the sharp increase in T_m.

The replacement of single by multiple bonds in the molecule of an organic compound causes a sharp depletion in the conformational set owing to the extremely marked increase in E_r, which actually leads to the prohibition of rotation about the multiple bond. This entails a corresponding change in the molecular 'shape' and in the physical properties sensitive to the given factor. Comparison of the properties of certain representatives of the classes of acids, alcohols, and aldehydes may serve as a typical illustration (Table 2). The values of E for these compounds are presented in Table 1.

The change in molecular shape in the examples presented, associated with the introduction of multiple bonds, leads to an increase in the molecular packing density: K_p increases on a scale

Table 2. Comparison of the properties of certain typical acids, alcohols, and aldehydes.

Formula	V_v/Å^3	$K_p^{20\,°C}$	T_m /°C	T_b/°C
$CH_3(CH_2)_2COOH$	89.5	0.585	−5.3	163.5
$CH_3CH=CHCOOH$	85.5	0.613	15.5	169
$CH_3CH(CH_3)COOH$	89.5	0.581	−46.1	154.7
$CH_2=C(CH_3)COOH$	85.4	0.600	16	163
$CH_3(CH_2)_2CH_2OH$	87.9	0.578	−89.5	112.4
$CH_3CH=CHCH_2OH$	83.9	0.597	< −30	121.2
$CH_3(CH_2)_2CHO$	82.2	0.550	−97.1	74.8
$CH_3CH=CHCHO$	78.2	0.569	−69.0	102.2

comparable to the effect associated with the replacement of the relatively 'weak' –CHO group ($E = 18.0$ kJ mol^{-1}) by the very strong –COOH group ($E = 45.1$ kJ mol^{-1}). The increase in packing density is apparently the main cause of the upward shift of both transition points, T_m and T_b, on the temperature scale.

The closure of the chain of functional organic compounds to form a ring also leads to the depletion of the conformational set. Organic compounds with linear and cyclic hydrocarbon chains are characterised by a higher molecular packing density than linear compounds (for V_v = const.). The introduction of multiple bonds into rings increases still further the compaction effect, evidently

owing to the development of additional conformational limitations.

Transition to aromatic cyclic compounds, the molecules of which have a disc shape, extremely favourable for the establishment of the closest packing, does indeed promote a still greater increase in K_p. As an example, one may compare benzene and pentane. Despite its somewhat smaller molecular volume (V_v), benzene has a significantly greater molecular packing density than pentane and hence higher values of T_m and T_b. Cyclopentane, the molecules of which have a similar volume ($V_v = 91.5 \pm 6$ Å^3), occupies, as should have been expected, an intermediate position between benzene and pentane as regards K_p, T_m, and T_b. On passing from pentane to benzene, ΔH_e increases by 6.3 kJ mol^{-1}.[90] Therefore, in order to discover the actual contribution of molecular shape it is necessary to include in the comparison series an organic compound the molecule of which has a shape similar to that of pentane and ΔH_e higher by 6.3 kJ mol^{-1} than in the case of the latter. Such a compound may be, for example, butyraldehyde (Table 2). It was found that the introduction of the aldehyde group ($E = 18$ kJ mol^{-1}), resulting in an increase in ΔH_e by 6.3 kJ mol^{-1} compared with pentane whilst retaining the linear molecular shape, does not lead to an increment in the packing density comparable to that arising on passing from the linear to the disc shape.

Thus the literature data on the properties of organic compounds make it possible to obtain important information for the understanding of the nature of the intermolecular interaction. A more complete study of the intermolecular interaction requires the application of a wide range of experimental methods, among which the traditional approaches occupy an important place:[5, 82] spectroscopy, measurement of relative permittivity, Rayleigh light scattering, X-ray diffraction, rheology, and thermophysical measurements. Certain new developments[83, 96, 97] have been designed for the direct experimental determination of the parameters of the IMI system as a physical network — both statistical and with elements of a regular structure. Among these, the main place is occupied by the EPR method in the spin-probe version, which makes it possible to infer from the form of the EPR spectra of nitroxyl radicals in the 3-cm range (without transfer of saturation) the degree of development of a physical network of short-lived associative bonds (τ is 5×10^{-11} to 10^{-7} s) and its evolution as a function of temperature. The spin–probe correlation time is regarded as a measure of the retardation by the physical network of the reorientation process in the magnetic field of the spin-carrying atomic group.

The precision thermomechanical method (sensitivity of 5×10^{-4} mm in terms of deformation), which makes it possible to record the abrupt thermal expansion of the substance at a temperature several degrees below T_m, is also used, provided that the possibility of the formation of a network of physical bonds arises in the system by virtue of the relatively high functionality of the test molecules.

2. Manifestation of intermolecular interactions in polymer systems

a. Molecular packing coefficient in polymer systems

The question of the role of molecular shape and barriers to internal rotation acquires special importance when the information about intermolecular interactions, obtained in the study of low-molecular-mass organic compounds, is transferred to polymer systems. Evidently the repeatability of the shape of the polymer unit as a factor influencing the packing density (and hence the intermolecular interactions and the properties of the polymer depending on the latter) is hindered by the limitation to mobility due to the linking of the units in the chain. This limitation is greater the higher the corresponding barriers to rotation. On the other hand, the limitation to mobility leads to the cooperation of the intermolecular interactions, to an increase in the stability of the IMI system (physical network), and ultimately to an increase in the molecular packing density. Comparison of the set of properties of polymeric and high-molecular-mass objects, modelling the individual fragments of the macromolecules, yields additional information about the cooperation between the intermolecular interactions in polymers.

In polymers, the units carrying localised IMI centres are linked by covalent bonds. This makes it possible to predict a series of differences between the physical networks in polymers and the similar networks in low-molecular-mass organic substances. Firstly, the degree of cooperativeness of neighbouring physical nodes is greater in polymers, which may be manifested by a sharp increase in their average lifetime τ (by an increase in stability). Secondly, as a result of the linkage of the IMI centres, steric hindrance to their mutual translational approach inevitably arises, which decreases the average concentration of nodes.

Consequently, for identical initial concentrations of the same IMI centres ($2v_0$) in low-molecular-mass organic compounds and in polymers, the nodes of the physical network formed in the latter are more stable (τ is greater), but their concentration v is reduced.

It is noteworthy that the volumes V_v of polymers listed in Table 3 refer to the repeat unit, so that the average volume of the macromolecule is equal to the product nV_v, where n is the average number of units in the polymer chains.

It follows from Table 3 that the molecular packing density of the polymer chains is influenced by the same factors as those influencing the packing density of low-molecular-mass organic compounds (it increases with increase in the IMI intensity and with increase in the barriers to internal rotation, responding to changes in the shape of the macromolecules), but to a much smaller extent. Indeed, the highest and lowest values of K_p [0.684 for poly(vinyl alcohol) and 0.627 for poly(dodecanyl methacrylate)] differ by only 5–6 units in the second digit after the decimal point. On the other hand, if polypropylene ($K_p = 0.669$), the macromolecules of which have exactly the same shape as those of poly(vinyl alcohol), and not the molecules of 'comb-shaped' poly(dodecyl methacrylate) with their outstanding shape, is chosen as the starting point for the calculation, then the difference between the values of K_p is not more than two hundredths.

For low-molecular-mass analogues, the difference between the molecular packing coefficients reaches 0.05 when the limiting value for a hydrocarbon ($K_p = 0.600–0.610$) is compared with $K_p = 0.662$ for a dihydric alcohol. If the dihydric alcohol is replaced by a trihydric alcohol, the difference between the values of K_p almost doubles.

It must be assumed that the contribution of the molecular shape factor to the molecular packing density of polymers is significantly greater than for monomers. For this reason, the monotonically constructed hydrocarbon chains $-(CH_2)-$ have a fairly dense packing ($K_p = 0.677$) even in the absence of large tightening forces ($E \approx 4.2$ kJ mol^{-1} per CH_2 group). The infringement of the monotonic construction as a result of the appearance of bulky side groups [$-CH_3$, $-Cl$, $-OCOCH_3$, $-COO(CH_2)_nH$] or the insertion of $-O-$ groups into the hydrocarbon chain, not compensated adequately by tightening forces ($E \leqslant 16$ kJ mol^{-1}), impairs the packing. The compensation phenomenon may be followed in the series of poly(alkylene oxides) (increase in K_p as the $-O-$ groups with $E = 6.3$ kJ mol^{-} accumulate) and on passing from the $-(CH_2)_n-$ polymer to macromolecules with $-CN$ and $-OH$ side groups ($K_p = 0.677$, 0.681, and 0.684 respectively). When the most bulky $-COO(CH_2)_nH$ substituents are introduced, the packing becomes looser with increase in n not only owing to the operation of the geometrical factor (the shape of the macromolecules) but also because of the characteristic features of the side fragment itself: in relation to low-molecular-mass analogues — dibasic acid esters — the role of the displacement of the IMI centre ($-COO-$) from its position at the end of the molecule to its centre, which leads to a significant increase in K_p, can be clearly traced.

The role of barriers to internal rotation is more marked in polymers than in their low-molecular-mass analogues. Thus, on passing from poly(alkyl acrylates) to poly(alkyl methacrylates), K

Table 3. Comparison of the properties of certain polymers and their low-molecular-mass analogues.

Polymers			Low-molecular-mass analogues		
Formula	V_v /Å^3	$K_p^{20\,°C}$	Formula	V_v /Å^3	$K_p^{20\,°C}$
$-[CH_2]_n-$	17.1	0.677	$H-[CH_2]_5-H$	97.7	0.510
			$H-[CH_2]_{10}-H$	183.2	0.568
			$H-[CH_2]_{30}-H$	525.2	0.605
$-[CH_2-CH(CH_3)]_n-$	51.3	0.669	$H[CH(CH_3)CH_2]CH(CH_3)H$	98	0.510
			$H[CH(CH_3)CH_2]_2CH(CH_3)H$	149	0.553
$-[CH_2-C(CH_3)_2]_n-$	68.5	0.673	$H[CH(CH_3)_2CH_2]_2H$	149	0.544
$-[CH_2-CH(Cl)]_n-$	49.1	0.661	$H[CH(Cl)CH_2]CH(Cl)H$	93	0.591
$-[CH_2O]_n-$	26.78	0.672			
$-[CH_2CH_2O]_n-$	43.94	0.679	$H[CH_2CH_2O]_2H$	90.2	0.523
$-[CH_2CH_2CH_2O]_n-$	61	0.633	$H[CH_2CH_2CH_2O]_2H$	124.4	0.540
$-[CH_2CH_2CH_2CH_2O]_n-$	78.1	0.640	$H[CH_2CH_2CH_2CH_2O]_2H$	158.6	0.564
$-[CH_2CH(OCOCH_3)]_n-$ (PVA)	79.65	0.662			
$-[CH_2CH(COOCH_3)]_n-$ (PMA)	79.65	0.662	$H[CH(COOCH_3)CH_2]H$	154.2	0.630
$-[CH_2CH(COOC_2H_5)]_n-$	96.75	0.652		188.4	0.618
			$H(CH_2)_mOC(O)(CH_2)_nCOO(CH_2)_mH$		
$-[CH_2C(CH_3)(COOCH_3)]_n-$	96.75	0.682	$n = 3, m = 1$	154.2	0.630
			$n = 1, m = 2$	154.2	0.611
$-[CH_2C(CH_3)(COOC_2H_5)]_n-$	113.85	0.676	$n = 4, m = 1$	171.3	0.628
			$n = 1, m = 2$	171.3	0.616
			$n = 0, m = 3$	171.3	0.603
$-[CH_2C(CH_3)(COOC_3H_7)]_n-$	130.95	0.664	$n = 5, m = 1$	188.4	0.640
			$n = 3, m = 2$	188.4	0.618
$-[CH_2C(CH_3)(COOC_4H_9)]_n-$	148.05	0.663	$n = 6, m = 2$	239.7	0.616
			$n = 4, m = 3$	239.7	0.609
			$n = 2, m = 4$	239.7	0.612
$-[CH_2C(CH_3)(COOC_6H_{13})]_n-$	182.25	0.650			
$-[CH_2C(CH_3)(COOC_8H_{17})]_n-$	216.45	0.639			
$-[CH_2C(CH_3)(COOC_{12}H_{25})]_n-$	284.85	0.627			
$-[CH_2CH(CN)]_n-$	54.0	0.681	$H[CH(CN)CH_2]CH(CN)H$	137	0.643
$-[CH_2CH(OH)]_n-$	41.6	0.684	$H[CH(OH)CH_2]CH(OH)H$	78	0.652
			$HCH(OH)CH(OH)CH(OH)H$ [a]	86	0.705

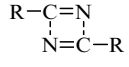
[a] Glycerol is not an exact structural analogue of the polymer chain fragment of poly(vinyl alcohol), demonstrating merely the role of the accumulation of hydroxy-groups in the molecule.

increases sharply (from 0.662 to 0.682 for the first members of the corresponding homologous series) owing to the appearance of the methyl side group, which inhibits internal rotation.

b. Network of localised physical bonds

If the polymer contains functional groups capable of forming strong intermolecular bonds, then the latter are a direct source of the appearance of a physical network. According to Flory's classification,[98] the networks formed by intermolecular physical bonds give rise to an unusual kind of polymer gels, although the difference between polymers with chemical and physical networks is in this instance purely quantitative. In particular, the classical polymer specimen with a chemical network — rubber vulcanised with sulfur at elevated temperatures — possesses the characteristic properties of a polymer with a physical network, namely the capacity for the relaxation of stress and creep, as a consequence of the occurrence of exchange reactions involving polysulfide bonds.[99, 100]

The dipole — dipole and inductive interactions of the $-CN$ groups in polyacrylonitrile and its copolymers — butadiene-nitrile rubbers — is an example of strong intermolecular interactions leading to the appearance of a physical network. The high dipole moment of nitrile groups makes them capable of forming dimers of the type



with an energy ranging from 19 to 38 kJ mol^{-1} according to various estimates.[101] In the low-molecular-mass analogue of polyacrylonitrile, namely acetonitrile, between 70% and 90% of the substance is in the associated state. By virtue of the presence of a network of dipole – dipole bonds, polyacrylonitrile has marked rubber-elastic properties above the glass transition temperature and the reversible deformation (before break) may reach 350%.[101] In butadiene – nitrile rubbers, an unusual relaxation π-transition corresponds to the disruption of the network of dipole – dipole interactions.[102, 103]

Another kind of strong intermolecular interaction in polymers is hydrogen bonding. The appearance of hydrogen bonds in polymers is usually caused by the presence of the following functional groups: amides ($-CONH$) (polyamides, polyesteramides, acrylamide or methacrylamide copolymers), urethane ($-COONH$) (polyurethanes, oligodiene urethaneepoxides, *etc.*), carboxy- ($-COOH$) (copolymers of acrylic and methacrylic acids), and hydroxy- ($-OH$) [poly(vinyl alcohol), cellulose]. The presence of hydrogen bonds in the polymer is deduced from the shift of the absorption frequencies in vibrational spectra,[104, 105] from the change in the chemical shifts and relaxation times in NMR spectra,[107] and also from the change in the relative permittivities and other indirect data,[108] including the deviation of certain characteristics of monomers from the additive values calculated from atomic group increments.[74]

Numerous studies devoted to polyamides [105, 106, 109] demonstrated the presence of a strong hydrogen bond in these polymers. Up to 99% of the amide groups form hydrogen bonds in polyamides of certain types. Hydrogen bonds have been detected also in polyurethanes.[110 – 112] According to a number of investigators,[113, 114] hydrogen bonds actually play a role as decisive factor in the mechanical and strength properties of these poly-

mers. Thus comparative study of the IR spectra and viscosities of oligourethane epoxides with different concentrations of urethane and epoxide groups demonstrated that hydrogen bonds are the most important factor responsible for their rheological properties, in particular for the anomalously high viscosity.[115,116]

The energy of hydrogen bonds depends on the geometry and nature of the substituents in the groups involved in their formation.[116–118] Thus it has been shown that aromatic substituents prevent the formation of hydrogen bonds.[116] Their replacement by aliphatic substituents leads to partial restoration of the interaction. The high energy of hydrogen bonds imparts to polymers, capable of forming them, all the characteristic features of polymers with a physical network. In particular, the occurrence of transitions in the temperature variation of the modulus of elasticity [119–121] and the ability to form physical gels [122–126] have been noted. The physical gels formed *via* hydrogen bonding possess quasi-equilibrium elasticity,[127] which may be described in terms of the theory of rubber elasticity for sufficiently short observation times. In this instance, the influence of gel formation conditions and of the type of solvent affects the elasticity constant of the gel. The application of a mechanical load leads to partial disruption of the hydrogen bonds, which is reflected in the IR spectra [108,121] and is manifested outwardly by the relaxation of stress. In those cases where the groups forming hydrogen bonds are located close to one another in the chain, as happens, for example, in segmented polyurethanes, there is a possibility of the appearance of associated species capable of giving rise even to microphase layer formation. The polyfunctional nodes of the physical network arising under these conditions are especially strong, which imparts the properties of a thermoelastoplastic to the polymer.

Associated species with similar properties may arise also when the polymer contains groups capable of forming bifunctional hydrogen bonds. Thus a polymer in which some of the units form bifunctional hydrogen bonds *via* the COOH- and NHCO-groups has been obtained by the interaction of polybutadiene with 4-(4′-carboxyphenyl)-1,2,4-triazine-3,5-dione.[125,126] The formation of associated species leads to the appearance on the corresponding plot of an equilibrium elasticity section with a positive temperature coefficient.

Polyelectrolyte complexes, obtained on mixing aqueous solutions of oppositely charged electrolytes, represent a special class of intermolecular interactions.[128,129] A characteristic feature of the thermoreversible gels formed under these conditions is that their modulus and degree of swelling depend on the pH of the medium and on the concentration of low-molecular-mass counterions. By altering the external conditions periodically, it is possible to vary the concentration of the intermolecular bonds and to induce either the contraction or elongation of the specimen,[130] *i.e.* it is possible to transform chemical energy directly into mechanical energy.

3. Local order and complementary sequences of units

A substance in the polymeric state may form a physical node not only as a result of strong intermolecular interactions, but, as mentioned above, also as a result of the cooperation of weak dispersion bonds. Such interaction leads to the appearance of a short-range order region in the polymer. Although numerous studies have been carried out on the problem of the ordering of polymers in the amorphous state (see, for example, Boyer [131]), this question continues to be controversial, mainly because many experimental results used to demonstrate the existence of local order are in principle susceptible also to a different interpretation. This applies mainly to studies on the electron microscopy of polymer films.[132–136] The existence of local order is indicated, according to a number of workers,[137–139] by the presence of several distinct 'intermolecular' maxima on wide angle X-ray diffractograms for both noncrystallising polymers above and below the glass transition temperature (T_g) and for crystallising polymers (polyethylene, poly-4-methylpent-1-ene) in the melt.[140,141] The anomalous variation of the heat capacities of polyethylene and polypropylene melts is attributed to the reversible disintegration and restoration of short-range order regions of the smectic type, characteristic of liquid crystals.[142] Convincing data supporting the existence of short-range segmental order in melts of different polymers have been presented in a series of studies.[143–146] Analysis of the differential curves for radial distribution functions, obtained by electron and X-ray diffraction methods, revealed the existence in melts of crystallising and noncrystallising polymers of sections with a quasi-parallel arrangement of segments with a structure of the liquid crystal type. The dimensions of these sections reach 20 Å in the direction of the long axis of the macromolecule and 30 Å in the perpendicular direction. This result has been confirmed by a careful analysis of the curve for the second moment of the radial distribution function plotted on the basis of X-ray diffraction measurements for a linear polyethylene melt.[147] Three well resolved intermolecular maxima with a periodicity of ~ 5 Å have been observed. Measurements of the osmotic pressures of the solutions and of the heats of solution of polyisobutylene in various solvents permitted the conclusion [148,149] that a residual order, corresponding to a degree of crystallinity of the order of $\sim 10\%$, exists in this X-ray-amorphous polymer.

Analysis of the dielectric properties of poly(ethylene terephthalate) in the rubber-elastic state and of polyisobutylene, as well as calculations of the conformations of the macromolecules of these polymers has shown that quantitative agreement between the theoretical dipole moments and other dielectric characteristics is achieved only on the assumption that ordered sections are present in the arrangement of chain segments with a quasi-crystallinee structure.[150,151] A characteristic feature of the dependence of the most probable relaxation time τ of the dipole-segmental polarisation on temperature is the fact that the slope of the $\lg\tau = f(1/T)$ curve changes within a comparatively narrow temperature range where $T \gg T_g$. This 'liquid–liquid' type transition, observed in many polymers,[152] apparently indicates the cooperative nature of the motion of the segments at $T > T_g$ and its loss above the transition temperature.

The presence of ordered structures has been observed by the light scattering method in vitreous poly(methyl methacrylate) [153] and by small angle X-ray diffraction in vitreous extended poly(-methyl methacrylate), polystyrene, and poly(vinyl acet-ate).[154] The density of the ordered sections is found to be close to that of the crystal.[153] Order among the chains in the amorphous regions of linear polyethylene can be observed by pulse ^{2}H NMR.[155]

The idea that highly dense fluctuations (clusters) occur in amorphous polymers served as the basis of the cluster model of the structure of vitreous bodies and of the vitrification process.[155–157]

A survey of experimental data on the structures of flexible-chain polymers in the amorphous state permitted the conclusion that the appearance of local order is a characteristic feature of the structures of amorphous polymers in the melt.[158,159] The approximate agreement between the experimental curve for neutron scattering by deuterated polymer chains and the theoretical curve calculated on the basis of the Gaussian model [16,18] does not conflict with the idea that small sections with an ordered arrangement of the segments are present subject to the condition that the distribution of such sections within a macromolecular coil is Gaussian. This claim appears entirely reasonable,particularly since experiment has shown that even strong local interactions, such as chemical cross-linking, do not give rise to an appreciable disturbance of the conformational state of the molecule as a whole.[14] However, this view is not generally accepted and the question of the structures of amorphous polymers remains controversial.[160–164]

At the same time the existence of local order in a whole series of polymers is unquestionable. For example, complementary syndiotactic sequences of one poly(methyl methacrylate) chain form stable stereocomplexes with isotactic sequences of another chain, which are so strong that this leads to the appearance of

strong physical network nodes,[165] although the bond energy corresponding to each interacting atomic group is only several kJ mol^{-1}.

We may note that the probability P_n of the formation of a complex of n linked groups (of a n-block) is significantly greater than the probability of its formation from isolated groups.[166] Indeed elementary calculation has shown that in the former case $P_n = 1-(1-\alpha)^n$, where α is the probability of the formation of a single bond (the complex exists so long as at least one bond remains unbroken), while in the latter case $P_n = \alpha^n$ (the complex exists provided that all n bonds have been formed). Since $\alpha < 1$, the difference is evident.

Similar stereocomplexes arise between the macromolecules of atactic polystyrene.[167] Solvent molecules may participate in their formation, which leads to the formation of thermoreversible gels in 'good' solvents. The structure of these complexes resembles that of a liquid crystal and their fusion is manifested as a temperature transition on differential thermal analysis curves. The temperature transitions in emulsion poly(vinyl chloride) above the glass transition temperature are apparently of a similar nature.[168] Sequences of stereoregular units participate in the establishment of local order, which gives rise to the appearance on the X-ray diffraction patterns of reflections corresponding to a degree of crystallinity of the order of several per cent.[169]

The formation of regions with local order in atactic polymers is a special case of the crystallisation of copolymers. As mentioned in a monograph,[170] chemically identical but isomeric units impart a distinct copolymeric character to the crystallisation behaviour of the macromolecule. For this reason, when the crystallisation temperatures of the components of a copolymer or of the isomers of a homopolymer differ sufficiently, then in the range between the melting points of the individual components the units of the higher-melting component exhibit a tendency towards ordering and hence towards the formation of a physical network. The degree of ideality of the crystal structure depends on the ability of the units of the copolymers to become arranged in the form of blocks.[171] The possibility of regulating the mechanical properties of the polymer over a wide range appears in this instance. In particular, it has been shown[172] that the thermoviscoelastic properties of ethene–propene polymers can be deliberately varied by altering the diameters of the nodes of the physical network formed by the microcrystallites of the ethene blocks.

The stability of the physical nodes and the mechanical behaviour of the system depend on the degree of local order and on the ideality of the local structure, which may consist of a wide range of formations — from fluctuation regions of the liquid crystal type up to fully regular microcrystallites. The temperature–time conditions in the preparation of specimens influence in their turn the ideality of the local structure and hence are capable of altering the relaxation characteristics of the physical network.[173]

4. Fluctuation inhomogeneity and microphase separation

The inhomogeneity of the supermolecular structure of polymers, understood in a broad sense, is an evident consequence of the molecular inhomogeneity of the polymers and copolymers themselves, arising in the stage involving their synthesis, modification, and cross-linking. First of all, the inhomogeneity is manifested as density and molecular mobility fluctuations, which is recorded by various structure-sensitive methods.[132,174–179] Microinhomogeneity can arise also in the stage involving the segregation of polymers as a consequence of the molecular mass distribution and spontaneous fractionation of the macromolecules on coagulation of the latex.[180]

Owing to the fluctuations in the concentration of the vulcanising agent, during the cross-linking of elastomers regions differing in the degree of cross-linking and hence in the mobility of their constituent chains appear. This can be detected, for example, by high-resolution ^3C NMR.[181,182] It has been suggested[183] that the cooperative relaxation of such densely cross-linked microregions of a network polymer is one of the slowest processes. It may be that similar processes have been observed in the study of polymer–oligomer blends:[179] according to pulse NMR data, a true equilibrium is established in such systems in the course of tens and perhaps hundreds of hours.

In those cases where the inhomogeneity is of fluctuation type and is not accompanied by microphase layer formation, the difference between the mobilities of chain sections belonging to different regions is small and the physical nodes produced have a comparatively low energy. Such inhomogeneities appear mainly in the form of small relaxation transitions on the temperature variations of the modulus and coefficient of mechanical losses.[184] The situation is different when one is dealing with block and graft copolymers.[113,114,185] The vitreous or crystalline domains of rigid blocks formed as a result of microphase separation represent a kind of polyfunctional physical nodes.Their energy is sufficiently high for the systems to behave like cross-linked rubbers below the melting points of the rigid blocks. Despite the fact that block copolymers are as a rule two-phase systems, the concept of a physical network is apparently applicable to them. At any rate, this claim is valid for a low content of rigid blocks when they still do not form a continuous phase. This is indicated, in particular, by the fact that below the melting points of the rigid blocks such systems have the characteristic properties of an elastomer and the principle of the temperature–time superposition is applicable to them,[185] extending also to temperatures above the melting point of the rigid blocks. However, the rigid blocks must then be characterised by employing an intrinsic reduction temperature. Since the dimensions of the domain are small, it can be regarded, subject to certain assumptions, as a polyfunctional physical node.

The concept of a physical network is used also in the analysis of the mechanical behaviour of more complex systems of block-copolymeric ionomers.[186] These thermoelastoplastics have two physical networks. In weakly sulfurised three-block copolymers of the 'styrene–(ethene–butene copolymer)–styrene' type, one network is made up of rigid polystyrene domains and the other consists of ionic clusters distributed within the polystyrene blocks. An intrinsic temperature transition is characteristic of each network. It is noteworthy that, by virtue of their ability to associate, ionomers exhibit a very distinct tendency to form a physical network. Thus the interaction of butadiene–2-methyl-5-vinylpyridine copolymers with monohalides yields, for a vinylpyridine group content as low as 6%, a product with the properties of a thermoelastoplastic, namely a high strength and elasticity,[27] which has been attributed to the association of the ionised vinylpyridine groups to form ionic clusters.

At high concentrations of rigid blocks in block copolymers, the domains form a continuous vitreous polymer phase, whereupon the concept of a physical network loses its significance. This applies also to systems such as interpenetrating polymer networks (IPN),[187,188] although the theory of rubber elasticity may be used for the analysis of the network structure in the IPN formation stage.

5. Physical gels. Models of the formation of physical gels

The most important characteristic of elastomers with a physical network, which differentiates them qualitatively from locally homogeneous elastomeric systems, is the ability to form thermoreversible physical gels. The range of questions related to the formation, structure, and properties of physical gels is extremely wide. A series of detailed reviews and monographs have been devoted to various aspects of this problem.[189–191] In the present section, we shall therefore confine ourselves to questions concerning mainly gels arising as a result of a local intermolecular interaction and which have a direct bearing on the topic of the present review.

There are various views on the causes of the transition of a polymer to a gel-like state. Thus Papkov's concept of gel formation[191] is based on the idea of the formation of a gel solely in the region of phase separation, the completion of which is prevented by the high viscosity of the concentrated polymer phase. The gel must therefore be regarded as a nonequilibrium

two-phase system with incomplete layer formation. However, it is difficult to agree with this view. Thermoreversible gels may be formed also under equilibrium conditions. Furthermore, there are fairly numerous examples of the existence of homogeneous physical gels.[192] It is well known that phase separation may occur in the course of the chemical cross-linking of the elastomer also in a thermodynamically good solvent (ν-syneresis).[22, 70]

Thus gel formation is caused by a local interaction between the macromolecules and phase separation should be regarded as its consequence and not conversely. The gel formation process may be divided into two stages.[192] In the first stage, the formation of weak bonds leads to the appearance of stable aggregates or 'swarms' of molecules.[192, 194] The second stage consists in the binding of the aggregates to one another in the course of their growth and in the formation of a three-dimensional structure. The appearance of hydrogen bonds between gelatin molecules may be the main cause of the formation of aggregates, but in gel formation the nodes are not local bonds but ordered chain sections linked by hydrogen bonds.[193] This mechanism apparently applies also to other biopolymers.[195]

At the same time, there is a region where Papkov's concept of gel formation is fully applicable. In particular, this concerns gels with a nonequilibrium structure formed *via* the spinodal decomposition mechanism. It has been shown [196] that there is a definite solution concentration above which a continuous phase, typical for the spinodal decomposition mechanism, may arise. Spinodal decomposition which has not been brought to the stage involving the complete separation of the system into two coexisting phases may be the cause of the polymer solution setting to a gel. Examples of the application of the theory of spinodal decomposition to gel formation have been published.[197–200] Thus, in aqueous solutions of poly(vinyl alcohol) [199] and in the poly(vinyl chloride) – γ-butyrolactone system,[200] gels are formed in the early stages *via* the spinodal decomposition mechanism.

A special case of the formation of thermoreversible gels is phase separation of the 'liquid – crystal' type, which proceeds *via* a mechanism involving the creation and growth of nuclei. The microcrystallites formed may become the nodes of the physical network of the gel. For example, there are experimental data on the formation of a poly(vinyl chloride) gel with nodes in the form of microcrystallites.[201] At the same time, it is essential to note that crystallisation as such is not a necessary condition for the formation of a gel. In particular, poly(vinyl alcohol) in an aqueous glycerol mixture affords crystalline gels, whereas in ε-methylpyrrolidone it gives rise to amorphous gels.

Single-phase gels are formed as a result of the appearance of the nodes of a three-dimensional network under the conditions of local interactions of the macromolecules with one another. Thus the formation of gels has been noted in cellulose triacetate – nitromethane and cellulose diacetate – tetrachloroethane systems at room temperature.[126] In the first case, the three-dimensional network arises as a result of the dipole – dipole interactions between the acetate groups, whilst in the second it is a consequence of the formation of hydrogen bonds between the hydroxy-groups.

Interest in the problem of the formation of gels as a result of local intermolecular physical bonds arose after gels of atactic polystyrene were observed in carbon disulfide below room temperature.[167, 202–204] It was found that the heat of gel formation in such systems is from 6 to 26 kJ mol^{-1} which is much less than the heat of formation of isotactic polystyrene gels (113 kJ mol^{-1}), which are known to be crystalline. The nature of the bonds ensuring the formation of gels in these systems has not been fully elucidated. A characteristic feature of such gels is that they are formed also in 'good' (in the thermodynamic sense) solvents. There is a view that gel formation is caused by the appearance of stable stereocomplexes involving solvent molecules.[167, 204]

Another view on the gel formation mechanism in polystyrene solutions [205] is that this transition is common to all atactic polymers and occurs as a result of the local 'fusion' of segment – segment contacts *via* the Frenkel' mechanism.[5] The formation of gels as a consequence of local intermolecular interaction has been demonstrated in relation to poly(butyl methacrylate).[206, 207] The network nodes in such gels consist of locally ordered regions in which 'suspended' butyl ester side groups participate. Comparison of the enthalpy of the physical cross-linking (37 kJ mol^{-1}) with the enthalpy of the intersegment contact (6 kJ mol^{-1}) shows that six segments participate simultaneously in the formation of a single cross-link. This transition has been recorded by dielectric spectroscopy also in the absence of a solvent.[206]

The formation of oligocarbamide gels in organic solvents is distinguished by interesting features.[208] Whereas the acceleration of the formation process on reduction of temperature is characteristic of other thermoreversible gels, in the given instance acceleration takes place when the temperature is increased. This is explained by the fact that the parallel arrangement of the molecules, treated as rigid rods the required increased mobility of which is attained at temperatures close to T_m, is the decisive stage of the process. In this case, the gel formation process is characterised by the competition between the decrease in the number of physical cross-links with increase in temperature and the appearance of new bonds as a consequence of a more ideal molecular packing.

Analysis showed that in most cases the gel formation process is based, regardless of the phase state, on intermolecular interactions promoting the appearance of a three-dimensional network structure. Many studies have been devoted to polymer gels as networks with nodes of a physical nature.[209–215] Particular attention was then turned to the nature of the node (microcrystal, another microphase formation, cluster comprising chain sections, *etc.*),[209, 210] its functionality,[211, 212] and the thermodynamics and kinetics of the formation of physical network nodes.[213–215]

Ferry was one of the first to attempt a theoretical description of the formation of a physical gel.[216] He began with the analogy between the formation of three-dimensional physical and chemical networks. The Flory – Stockmayer theory was applied to thermoreversible gels.[2] Assuming that the formation of an infinite three-dimensional network requires the formation of 1 – 2 bonds per macromolecule, Ferry showed (in good agreement with experiment [193]) that the critical concentration for the formation of a gelatin gel is 1%. A relation between the melting point of the gel and its concentration c was found:[217]

$$\ln c = -\frac{\Delta H}{RT} + \text{const}\,, \tag{4}$$

where ΔH is the enthalpy of formation of a bond in the gel network and T_m is the melting point.

This relation agrees well with experimental data for gelatin gels, but in the case of readily crystallising gels the relation between the melting point and the concentration is described better by the equation [2]

$$\frac{1}{T_m} = \frac{1}{T_{m0}} + \frac{R}{\Delta H}\,(V_1 - k_1 v_1^2)\frac{V_0}{V_1}\,, \tag{5}$$

where T_m and T_{m0} are the melting points of the polymer in the presence and absence of a solvent respectively, k_1 is the interaction parameter, V_1 and v_1 are the molar volume and the volume fraction of the solvent respectively, and V_0 is the volume of the monomer repeat unit.

A theory has been proposed for the description of the sol – gel transition.[218] Its essence is as follows. The free energy of the polymer – solvent system is represented by the sum of two terms: $F = F_h + F_b$, where F_h and F_b are the free energies of mixing and formation of the nodes respectively. The critical gel formation concentration is calculated with the aid of the Flory – Stockmayer criterion:

$$\varphi = \frac{1 + \exp(-kT\Delta F_b)}{lf^2}\,, \tag{6}$$

where l is the number of freely jointed segments in the polymer chain and f is the fraction of segments capable of forming a physical node.

The theoretical curve for the sol–gel transition, calculated from the equation presented, as well as the phase diagram plotted on the basis of the equation of state agree well with experimental data for gelatin gels.

The majority of modern theories of the formation of thermoreversible gels are based on the Flory–Rehner theory of the swelling of polymer networks,[2] according to which the free energy of the swollen network is represented by the sum of the free energy of mixing of the monomer with the solvent and the elastic energy of the network. According to this theory, the swelling pressure of the gel may be described by the equation

$$P = -\frac{RT}{V_1}[\ln(1 - v_2) + v_2 + \chi v_2^2] - \sigma_v(v_2), \quad (7)$$

where V_1 is the molar volume of the solvent, v_2 the volume fraction of the polymer in the swollen gel, χ the polymer–solvent interaction parameter, and $\sigma_v(v_2)$ the volume modulus of elasticity.

Eqn (7) does not describe by itself the formation of a physical gel. Analysis of experimental data on the swelling of gel-forming polymers led to the conclusion [219] that the phase transition and the collapse of the physical gel may be described if the interaction parameter χ in Eqn (7) is assumed to depend on v_2:

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \ldots,$$

where χ_i are experimentally determined coefficients. In particular, $\chi = 0.505 + 0.37\, v_2 + 0.29\, v_2^2$ for a solution of polystyrene in cyclohexane. The postulate that the interaction parameter χ be expressed as a function of v_2 had been put forward also earlier.[220] However, on the whole the above theory must be regarded, despite its qualitative agreement with experimental data on the swelling and phase separation in physical gels, as semiempirical.

Tanaka's theory appears to be logically more complete.[221, 222] It considers a solution of a polymer each unit of which is capable of forming a physical bond with a unit of another molecule. The polydisperse molecular aggregate arising as a result of the interaction is called a cluster. The free energy of the system consists of the Flory–Huggins free energy of mixing ΔF_{mix}. and the free energy of formation of the clusters F_{cl}:

$$F = F_{cl} + \Delta F_{mix}, \quad (8)$$

$$F_{cl} = \sum_{m=1}^{\infty} N_m \mu_m^0, \quad (9)$$

where N_m is the number of clusters in which m molecules are bound and μ_m^0 is the chemical potential of the cluster.

By employing the standard Flory – Huggins procedure for a lattice model, Tanaka calculated the distribution with respect to the number of clusters and obtained an expression for the chemical potential of the solvent. The phase diagram of the system is qualitatively consistent with the experimental data for atactic polystyrene gels.

As a development of the above approach, the case where the gel is formed as a result not only of pair interactions but also as a result of the simultaneous interaction of the segments of several molecules was examined.[223] This permitted a better description of the weak dependence of the critical gel formation concentration on the molecular mass.

The next step was the formulation of a theory, by Khokhlov,[224] of the swelling of polymer networks in a large amount of solvent, taking into account long range interactions. It was suggested that the free energy of a defect-free network be described by the following expression:

$$F = \frac{NT}{m}\left[\frac{dx^2 + dy^2 + dz^2 - 3}{2} - \frac{2}{f}\ln(dx\,dy\,dz)\right] + NT\left[\frac{Bn_0}{dx\,dy\,dz} + \frac{Cn_0}{dx^2\,dy^2\,dz^2}\right], \quad (10)$$

where N is the total number of units in the network, m the average number of units in the chain between two neighbouring branching points, n_0 the average concentration of the polymer under the initial (θ-state) conditions, B and C are the second and third virial coefficients for the interaction of monomer units, f is the functionality of the branching points, and dx, dy, and dz are the relative deformations of the network along the x, y, and z axes compared with the state at the start of the readings.

The first term describes the free energy of the deformation of the network and the second the free energy of the interaction of the monomer units. In essence, this formula differs from the corresponding formula in Flory's classical theory only by the choice of the start of the readings: here the θ-state was selected as the initial state, whereas in Flory's theory the state of the network in the absence of a solvent is assumed to be the initial state.

Within the framework of Khokhlov's theory, an explanation was obtained for the phenomenon of the collapse of polymer networks, first observed experimentally in 1978 in relation to polyacrylamide gels swelling in an acetone–water mixture.[225] This phenomenon consists in a sharp, frequently abrupt, decrease in the size of the specimen on reducing the temperature or on improving the quality of the solvent. Analysis of the collapse of uncharged networks [225] has shown that it is a consequence of a coil–globule transition in the subchains constituting the network. Such a transition may be both a discrete jump (if the chains are sufficiently rigid or if the specimen is subjected to uniaxial extension) or it may be continuous but extremely sharp.

Experimental and theoretical studies of the collapse phenomenon were developed further.[226–233] Examination of the elastic properties of swollen polymer networks led to the conclusion that the extension of collapsed networks can induce their transition to the swollen state.[234] An expression was obtained for the stress in a swollen deformed network:

$$\tau = \frac{n_0 T}{m}\left(\sigma - \frac{\alpha^2}{\sigma}\right), \quad (11)$$

where σ is the relative deformation along the z axis and α the relative deformation along the x and y axes.

On slow extension, a jump is observed in the $t(\sigma)$ relation. An experimental test showed,[235] that, for a certain solvent composition and temperature, the gel sucks in spontaneously an enormous amount of the solvent during the extension process and that in an uncharged gel the dependence of the degree of swelling on the applied stress is continuous, whereas in a charged gel the transition to the swollen state takes place abruptly.

6. The properties of polymers in the presence of an effective intermolecular interaction

As already stated above, the deformation of polymer systems does not alter the internal energy if the only type of intermolecular interaction is repulsion due to the mutual in penetrability of the chains. Other types of intermolecular interaction may induce a change in the internal energy on deformation.

In the simplest case, the intermolecular interaction potential may be represented as the sum of the potentials of the central and orientation interactions. The orientation interaction potential is then described by the expression [236]

$$P(\upsilon) = \frac{B}{2}(3\cos^2\upsilon - 1), \quad (12)$$

where υ is the angle between the directions of the interacting segments and B is a constant.

The interaction of segments of this type can be most simply taken into account by the average field method.[237] The expression obtained for the corresponding elastic potential has the form of a

series in powers of N^{-1} Calculations have shown [238] that the deviations from the predictions of the theory of entropic elasticity for not unduly open networks can be explained precisely by orientation effects. A quantitative procedure for the determination of the parameters of the orientation of elastomers using the wide angle scattering of X-rays has been proposed.[239] An approach which makes it possible to estimate the contribution of the intermolecular interaction to the relation between orientation and deformation was developed in the same study. Apart from the traditional double refraction method, pulse NMR [240] and ^{1}H NMR (molecular probe spectroscopy)[241, 242] are also used to estimate the degree of orientation order. An important feature of the orientation order on extension is the orientation phase transition of the liquid crystal type induced by the extension.[243–249]

In contrast to the orientation interaction, local intermolecular interactions of the physical network type are disrupted in the deformation process. The relaxation of stress in deformed elastomers has been accounted for [102, 250, 251] by the disruption process and subsequent rearrangement of the physical network. It was assumed that the dependence of the lifetime of a physical node on the stress is described by the familiar Zhurkov disruption law.

A simple mathematical model, based on the physical network concept, which makes it possible to describe qualitatively a wide class of phenomena, including equilibrium and non equilibrium properties, has been proposed.[247, 248] It is assumed that the concentration of physical nodes diminishes exponentially in the deformed state:

$$v = v_e + (v_0 - v_e)\exp(-kt), \tag{13}$$

where ν_0 and ν_e are the initial and equilibrium concentrations of the physical nodes. The constant k is expressed by Eyring's procedure taking into account the force due to the deformation of the chains. In this sense, the approach is close to Bartenev's idea, because Eyring's equation may serve as a formal justification of Zhurkov's equation.

Despite the semiempirical nature of the model described, the results obtained with its aid agree well qualitatively with a whole series of experimental facts.

A more rigorous model [249] describes the influence of the rearrangement the physical network in a chemically cross-linked elastomer on its equilibrium elasticity and mechanical losses. This model presupposes that the chains contain singular points, between which operate attractive forces with a small radius of action. The calculation of partition functions taking into account additional approximations, associated with the low concentrations of the interacting points, yields the following expression for the stress tensor:

$$\sigma_{kn} = \sigma_{kn}^{(0)} + \frac{3kT}{V}\sum_{i<j} W_{ij}\frac{r_{ijk}^0 r_{ijn}^0}{b_{ij}^2}, \tag{14}$$

where $\sigma_{kn}^{(0)}$ is the stress tensor of the Gaussian network in the absence of physical bonds, r_{ijk}^0 are components of the radius-vector between the ith and jth points in the Gaussian network in the absence of interaction, b_{ij}^2 is the square of the deviation, averaged over the network, of the reciprocal radius-vectors of the interacting points from their positions in the network without interaction, and W_{ij} is the probability of entanglement between the ith and jth points:

$$W_{ij} = q\frac{P_{ij}}{1 + qP_{ij}}, \tag{15}$$

where P_{ij} is the Gaussian distribution of the radius-vectors and q is a characteristic of the intensity of the interaction.

Analysis of Eqn (14) for uniaxial deformation showed that the model examined describes qualitatively the known deviations of the experimental relations from the predictions of the classical theory of rubber elasticity.

IV. Thermodynamic model of the deformation of elastomers in the presence of a physical network

As shown above, ideas concerning the physical network are widely used for the qualitative explanation of the processes associated with the alteration of the supermolecular organisation of polymers due to intermolecular interaction. Here the intermolecular interaction is modelled by physical nodes — formations similar to chemical cross-links but with such a low disruption energy that they can be disrupted and reformed as a result of thermal motion. The average concentration of such nodes may vary during the deformation of the specimen, in contrast to chemical nodes.

In the rubber-elastic state, such systems have specific properties determined, on the one hand, by the presence of entropic elasticity and, on the other hand, by the possibility of a change in the parameters of the equation for rubber elasticity on deformation. The existence of quasi-equilibrium rubber elasticity in systems with a physical network constitutes a most important experimental fact, indicating the occurrence in the systems of at least two kinds of fluctuations of the thermodynamic parameters with different time scales.

The first short-term type of fluctuations corresponds to the establishment of equilibrium in the chains constituting the physical network; the second, long-term type of fluctuations is associated with the rearrangement of the physical network itself. The marked difference between the time scales of thermal fluctuations makes it possible to employ a two-level thermodynamic model for a qualitative analysis of the behaviour of such a system.

Knowing the thermodynamic characteristics of the two-level system, it is possible to determine the thermodynamic properties of this system for constant values of the parameters of the second level and when additional information is available about the second level. One can also take into account the process involving the rearrangement of the supermolecular organisation,provided that the thermodynamic properties of the system with a constant supermolecular structure are known.

Such an approach constitutes the basis of the thermodynamic model of the deformation of polymers developed by the authors of the present review.[252–261]

1. A two-level model of the physical network

In the formulation of the problem of the deformation of a polymer system, a logical difficulty arises, associated with the fact that the deformation of the physical network may entail not only a change in the concentration of the physical nodes but also a rearrangement of the network at constant concentration. If there are no chemical nodes, a change in the size of the undeformed specimen, *i.e.* plastic deformation, is observed. The components of the specimen deformation tensor cannot therefore play the role of external parameters in this instance.

When the state of a physical network is examined in terms of equilibrium statistical thermodynamics, it is postulated that the deformation of the physical network chains remains constant regardless of the way in which the deformation of the specimen varies under these conditions.

However, it is natural to suppose that when extension from the undeformed state takes place over a period sufficiently short compared with the characteristic times of the rearrangement of the network, then the chain deformation parameters actually coincide with the specimen deformation parameters. The justification of this hypothesis follows from the following simple considerations. The rearrangement of the physical network results in a nonaffine migration of the centres of mass of the macromolecules, compared with the deformation of the specimen as a whole. By virtue of the close packing and the mutual impermeability of the chains, the latter occurs as a result of reptation, the characteristic time of which is known to exceed greatly the time required to attain conformational equilibrium.[65] Thus, if the lifetime of the physical node is short and the rate of extension is

fairly high, then the equilibrium concentration of the nodes is established for a specified deformation of the chains, which differs little from the deformation of the specimen.

When elastomers contain both chemical and physical nodes, the processes involved in the rearrangement are 'frozen' by the chemical network, as a result of which the chain and specimen deformation parameters must be regarded as identical.

These hypotheses made it possible to obtain an expression for the free energy of a deformed network with a constant number of nodes and also expressions for the average number of nodes of the ith type (having an energy E_i) and an arbitrary stress.

The concentration of nodes g is defined by the following equation:[252, 259, 261]

$$g = nY(D) = n\,\frac{D\exp D - \exp D + 1}{(\exp D - 1)^2}, \tag{16}$$

where n is the maximum possible concentration of physical nodes and

$$D = \frac{\Delta E}{kT}. \tag{17}$$

Here ΔE is the free energy of formation of a node, including also the free energy $\psi(\lambda)$ of the deformation of the chains attached to the given node.

The form of the $Y(D)$ relation is illustrated in Fig. 4. Evidently the fastest decrease in the concentration of nodes occurs within a narrow region near $D = 0$, *i.e.* when the free energy of the deformed chains and the energy required to disrupt a node are equal. This condition determines the characteristic temperature of the disruption of nodes for a given deformation and the characteristic deformation on disruption at a given temperature.

The conventional stress is described by the equation

$$\sigma(\lambda) = 2nY(D)\,\frac{\mathrm{d}\psi(\lambda)}{\mathrm{d}\lambda}. \tag{18}$$

The qualitative form of this relation for a network without chemical nodes is shown in Fig. 5 (curve *1*). The point λ_0, at which the stress decreases rapidly, corresponds to the condition $D = 0$ in Fig. 4.

The curve $\sigma(\lambda)$ corresponding to equilibrium conditions has an extremum and bounds the region of the permissible non-equilibrium states of the system for which

$$\sigma > \frac{\mathrm{d}\psi}{\mathrm{d}\lambda}.$$

In other words, the specimen can exist only in states which correspond to points which are not located below curve *1* in Fig. 5. The boundary points on the ascending section of the curve then refer to equilibrium states and those on the section of the curve with $\lambda > \lambda_k$ refer to pseudoequilibrium states.

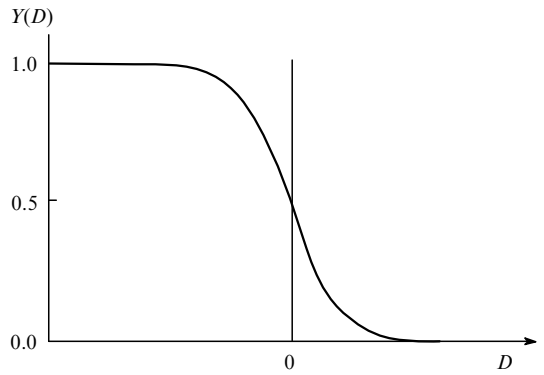


Figure 4. The form of the function $Y(D)$ [Eqn (16)].

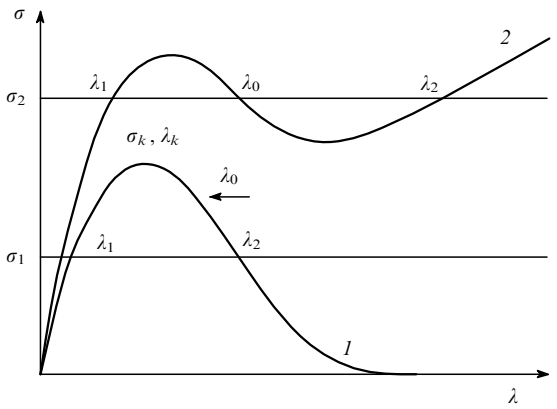


Figure 5. Dependence of σ on λ for noncross-linked (*1*) and cross-linked (*2*) polymers (for the explanation, see text).

As can be seen from the figure, the region of permissible states for a specified stress consist of two sections: $[1, \lambda_1]$ and $[\lambda_2, \infty]$. In the absence of thermodynamic fluctuations, the deformation process would end with transition to the equilibrium state λ_1, since the transition to the non equilibrium region $[\lambda_2, \infty]$ requires that an energy barrier be overcome. However, by virtue of the fluctuations, small fragments of the medium can receive an amount of heat sufficient for transition to the state λ_2, which leads to irreversible deformation. If the relaxation time of the material to the equilibrium state λ_1 is short compared with the characteristic lifetime of the fluctuations, then in the course of a certain period the specimen is in a state close to equilibrium with a deformation λ_1 and possesses virtually irreversible elasticity. On the other hand, if the external stress exceeds the value corresponding to the maximum on the curve ($\sigma > \sigma_k$), then plastic deformation arises immediately after the application of a load.

Thus the equilibrium theory makes it possible to separate two qualitatively different levels of loads for an elastomer in which there is a physical network. At the first level, for $\sigma < \sigma_k$, there is a possibility of quasi-equilibrium elasticity, while at the second, for $\sigma > \sigma_k$, the disruption of the physical network begins immediately during the deformation process. This feature has become the basis of a method for the determination of the thermodynamic parameters of the physical network nodes from the temperature dependence of their concentration. The concentration of the nodes is calculated from the quasi-equilibrium stress for $\sigma < \sigma_k$, found in experiments on extension at a constant rate or in experiments involving the measurement of creep.

This method has been used in the study of the deformation of elastomers of two classes differing in the mechanism of the formation of physical nodes. The elastomers of the first class consisted of copolymers with functional groups capable of forming fairly strong intermolecular hydrogen bonds.[259, 261, 262] The objects of study were poly(nonyl acrylate) and its copolymers with acrylamide.[263] The possibility of the formation of physical network nodes in these polymers is attained as a result of the formation of strong hydrogen bonds between the acrylamide or acrylic acid units.

Stereoregular polybutadiene, in which physical network nodes may be formed as a result of the interaction of complementary sequences of stereoregular units, is a representative of elastomers of the second class. Noncross-linked industrial stereoregular SKD polybutadiene and a rubber cross-linked with tetramethylthiuram disulfide were chosen for study.[257, 261, 264] Acrylamide copolymers were tested under creptation conditions, acrylic acid copolymers were tested in a stress relaxation regime and a regime with extension at a constant rate, while polybutadiene copolymers were tested in a regime 'extension at a constant rate – relaxation at temperatures from -40 to 160 °C'.

It was established that, as the concentration of functional groups increases, there is some increase in the energy of the

physical node due to the change in the nature of the distribution of the functional groups in the chain. Studies by the ^{13}C NMR method showed that the probability of the formation of blocks increases with increase in concentration. The energy of the physical nodes also increases after the additional chemical cross-linking of the elastomer. It was found by ^{13}C NMR relaxometry that this is induced by the decrease in the mobility of fragments of the polymer chains.

An anomalous deformation behaviour is characteristic of elastomers with a physical network: when they are extended at a constant rate, the increase in deformation is sharply retarded after the attainment of a certain deformation up to its complete cessation. In certain cases, the stress can actually fall. In this region, the initial structure is disrupted, which is accompanied by a series of effects such as the appearance of turbidity, a decrease in the Poisson coefficient and the formation of a 'neck', and the appearance of 'string'. On further extension, the stress begins to increase so long as the specimen does not disintegrate, provided that a sufficient number of chains bound in a network retained in the elastomer.

In the presence of chemical nodes, the equation for a conventional stress in the physical network assumes the form

$$\sigma = 2\,[nY(D) + n_{\text{chem}}]\frac{d\psi}{d\lambda}, \tag{19}$$

where n_{chem} is the concentration of chemical network nodes.

As can be seen from Fig. 5 (curve *2*), the deformation curve has two extrema — a maximum and a minimum. This means that in a certain region two stable states may arise with deformations λ_1 and λ_2 and one pseudo-equilibrium state with a deformation λ_0 for identical values of the conventional stress. Consequently, under these conditions there is a possibility of the separation of the system into regions with different concentrations of the physical nodes and with different degrees of deformation, which is characteristic of a first-order phase transition.

The phase separation arising on deformation of an elastomer with a physical network may explain the characteristic form of the relation $\sigma(\lambda)$ for such systems under the conditions of extension at a constant rate. The section corresponding to a retarded growth of stress on the experimental curves may be compared with the section of the theoretical relation $\sigma(\lambda)$ located between points λ_1 and λ_2, on which a constant stress should be retained as a consequence of the phase separation on equilibrium deformation.

Under real conditions at a constant rate of deformation, phase separation does not go to completion. For this reason, only a retardation of the growth of stress and not the attainment of a plateau are observed on the experimental curves in most cases. Nevertheless, the observation of the deformation-induced separation into layers with formation of 'string' or a 'neck' in many real polymers in the region corresponding to the section $\lambda_1 < \lambda_0 < \lambda_2$ in Fig. 5 is evidence in support of the validity of the approach under discussion. Furthermore, it is apparently possible to draw an analogy between the deformation-induced separation and the well known phenomenon of the forced elasticity of vitreous polymers. A vitreous polymer can be regarded in a certain sense as a dense-network polymer with physical nodes, because the mobility of chain elements not exceeding in size the kinetic segment is retained below the glass transition temperature. These short chains, whose length corresponds to several units, possess mainly energetic and not entropic elasticity. At the same time, it is quite possible to select for them an expression describing the potential $\psi(\lambda)$. Since it has been shown that the specific form of the potential is unimportant, the relation illustrated in Fig. 5 is qualitatively preserved. The role of the chemical network can be assumed in this case by the network of entanglements, the lifetime of which exceeds by a large factor the lifetime of the low-energy physical nodes constituting the quasi-network of the vitreous polymer. The condition $n > n_{\text{chem}}$ is then known to hold.

The phenomenon of forced elasticity is best illustrated by the deformation-induced layer formation effect. In the first place, the deformation curve itself, corresponding to forced elasticity, has a distinct horizontal section and sometimes even a bend,[265, 266] which is fully consistent with Fig. 5. The reversibility of forced elasticity also fits well within the theoretical framework. Finally, the appearance on the $\lambda_1 < \lambda_0 < \lambda_2$ section of 'silver' cracks, which are not cracks in the usual sense but represent layered microregions in the polymer, is also consistent with the concept of deformation-induced separation. In the 'silver' cracks, there is a loosened material with extended chains and a deformation λ_2, which actually represents a new phase. The chains of the remaining material belong to another phase with a deformation λ_1. In the course of the cold drawing process, the phase volumes virtually undergo a redistribution: the fraction of the material with the deformation λ_1 diminishes and that of the material with the deformation λ_2 increases. This process continues until the 'neck' has grown by the overall length of the specimen; the phase with the deformation λ_1 then vanishes. Next follows a process in which the chain deformation in the oriented phase increases The deformation remains fully reversible and, after heating, the specimen again assumes its initial shape.

Naturally, forced elasticity is strictly speaking a nonequilibrium process and all the considerations quoted above must be regarded not as a rigorous theoretical justification but only as an analogy. At the same time, the possibility of an adequate description of the observed phenomena with the aid of this type of extension of the equilibrium theory indicates that it is entirely reasonable.

2. The form of the thermomechanical curve in the region of the rubber elasticity plateau

The proposed equilibrium theory of the deformation of elastomers has served as the basis of the description of thermomechanical curves for linear polymers in the temperature range $T > T_g$.[267]

The thermomechanical curves for polymers are traditionally analysed on the basis of the concept of a spectrum of relaxation times and their temperature dependence.[251, 268] An important relation, namely the Williams – Lundell – Ferry (WLF) formula, is actually based on this. The relation between the extent of the rubber elasticity plateau (the temperature range between the glass transition temperature T_g and the flow temperature T_f) and the molecular mass, first obtained by Kargin and Slonimskii[269] as early as 1948, can also be accounted for on the basis of a fairly simple model of the relaxation of polymer chains. However, this approach has not so far made it possible to interpret even qualitatively the influence of the molecular mass distribution (MMD) on the form of the thermomechanical curve.[270, 271] When the WLF equation is used, the temperature dependences of the rates of deformation of polymers with any MMD are of the same kind and the thermomechanical curves differ only in the derivative of deformation, which depends on the average molecular mass.[267] Indeed, it has come to be assumed[268] that the viscosity of polymer solutions and melts depends on the weight-average molecular mass (or even the molecular mass averaged with respect to higher MMD moments). At the same time, experiment shows that the difference between the deformation curves of polymers with different MMD is qualitative.[267]

The concept of a network of physical nodes has been used[267] for an adequate description of the temperature dependence of the deformation of the polymer in the region of the transition from vitrification to flow.

The theory of the relation between the molecular mass of the polymer and T_f has been based on the dependence of the viscosity on the molecular mass.[272] The start of the increase in the derivative of deformation as a function of temperature ($d\varepsilon/dT$) is believed to be a characteristic indication of the transition from the rubber-elastic to the viscofluid state. The application of this feature to a network of physical bonds leads to the conclusion that the increased $d\varepsilon/dT$ is caused by the sharp diminution of the network modulus induced by the disruption of its nodes as a consequence of a rise in temperature. The flow of a polymer

system (at a definite rate of application of a load) begins when the cross-linking index becomes 1.

According to Eqn (16), the concentration of the physical network nodes in the polymer system depends on temperature and the applied force. If the number of nodes is referred to the number of chains N and account is also taken of the fact that the breakdown of the network occurs for fairly large values of D in absolute magnitude, then we obtain the following expression for the critical cross-linking index with respect to physical nodes, *i.e.* for the criterion of the transition to flow:

$$\ln M = D. \tag{20}$$

Bearing in mind that the flow temperature T_f is the same as the glass transition temperature T_g when the molecular mass of the chain is equal to the mass of the segment M_0, we obtain from Eqns (17) and (20)

$$\ln M = \ln M_0 + \frac{\Delta E}{RT_g}\frac{X}{1+X}, \tag{21}$$

where

$$X = \frac{T_f - T_g}{T_g}.$$

We may recall that the energy term in Eqn (21) takes into account also the intensity and duration of the application of a force to the system. Thus the equation obtained makes it possible to analyse the relation between the temperature of the transition of the system to the viscofluid state, the nature of the load applied to it, and the molecular mass of the polymer.

The relation between the flow temperature and the molecular mass for a series of polymers in terms of the variables of Eqn (21) is presented in Fig. 6. Evidently the equation describes satisfactorily the experimental data. The intercept on the ordinate axis slightly depends on the nature of the polymer (polybutadiene, polyurethanes, polyacrylonitrile) and is close to 3. This means that the molecular mass of the chain section between the physical network nodes is approximately the same and equal to the value for the Kuhn segment in the vicinity of the glass transition temperature of any polymer.[74, 273] This conclusion is fully consistent with the physical significance of the α-transition: the segmental motion of polymer chains ceases to be inhibited when the length of the chain section between the nodes of the network of physical bonds becomes greater than the Kuhn segment. At the same time the multiplier

$$A \approx \frac{\Delta E}{RT_g}$$

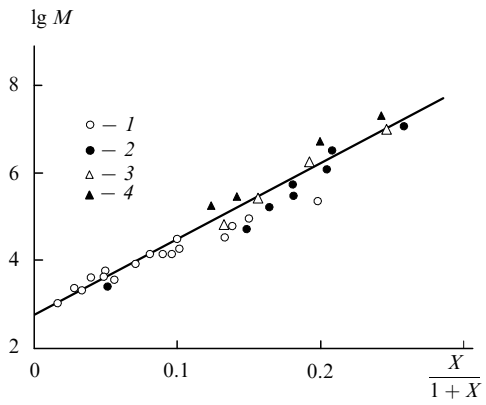


Figure 6. Relation between the flow temperature and the molecular masses of linear polymers in terms of the variables of Eqn (21): (*1*) polybutadiene; (*2*) and (*3*) polyurethanes with different structures; (*4*) polystyrene.

in Eqn (21) proves to be constant [272, 273] and almost independent of the type of polymer (the glass transition temperature): $A \approx 17$. Thus Eqn (21) is universal.

Figure 7 presents thermomechanical curves for polybutadienes with different polydispersity parameters.[267] Evidently the temperature dependence of the deformation is extremely sensitive to the nature of the MMD. In conformity with the considerations presented above, an increase in temperature induces a decrease in the cross-linking index of the polymer chains and an increase in the fraction of elastically inactive chains of the physical network and in the sol fraction. If the system consists of chains with one length only, then the gel – sol transition occurs at the flow temperature T_f. In this case, the dependence of the proportion of the sol fraction (more precisely of the fraction of elastically inactive chains) φ on temperature can be conveniently described using the Dirac δ-function, the integral of which is zero for negative values of the argument and unity for $T - T_f > 0$. Taking this factor into account in the case of a polymer consisting of a set of polymer chains characterised by a distribution function $\omega(M)$, the temperature dependence of the fraction of the elastically active chains φ can be described by the equation

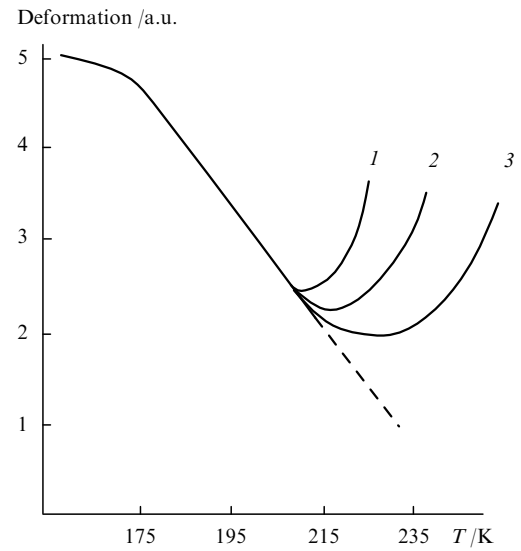


Figure 7. Thermomechanical (dilatometric) curves for polybutadienes with different polydispersities characterised by $M_w/M_n = 1.24$ (*1*), 3.50 (*2*), and 9.50 (*3*). $M_n = 1.45 \times 10^5$.

$$\varphi(T) = \int_0^{\infty} \omega(M)\mathrm{d}M \int_{-\infty}^{\Delta M} \delta(t)\mathrm{d}t\,, \tag{22}$$

where $\Delta M = T - T_f(M)$.

The function $\varphi(T)$ varies from 0 for $T < T_f$ in the lowest-molecular-mass fraction in the given polymer system to 1 for T_f in the highest-molecular-mass fraction. Thus $\varphi(T)$ is an integral function of the MMD when it is constructed not in terms of temperature but in terms of the corresponding molecular masses. We may recall that the relation between temperature and molecular mass is defined by condition (21). Accordingly, the derivative $\mathrm{d}\varphi(T)/\mathrm{d}T$ becomes a differential function of the MMD.

Eqn (22) makes it possible to relate the MMD function to the thermomechanical curve for the polymer if the model is based on the concept of a network of physical bonds. This relation can be formulated in the simplest case as the equation

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \frac{\sigma - [1 - \varphi(T)]E\varepsilon}{\eta} \tag{23}$$

or, when account is taken of the linear increase in temperature as a function time,

$$\frac{d\varepsilon}{dt} = \frac{\sigma - [1 - \varphi(T)]E\varepsilon}{q\eta} = \frac{\sigma/E - [1 - \varphi(T)]\varepsilon}{\tau q}, \quad (24)$$

where ε is the deformation, σ the stress, E the modulus of a hypothetical polymer with an infinitely large molecular mass, η the viscosity, $\tau = \eta/E$ the relaxation time, and q the rate of scanning the temperature.

So long as $\varphi(T) < 1$, the deformation occurs in a stationary regime, provided that its rate is sufficiently low. On the other hand, if the rate of deformation is high, a deformation-induced inhomogeneity of the system arises, as mentioned above, which requires a more complex analysis.

Thus the stationary deformation ε_{st} is a measure of the change in the quantity $\varphi(T)$, which increases with increase in temperature:

$$\varepsilon_{st} = \frac{\sigma}{E[1 - \varphi(T)]}. \quad (25)$$

As soon as $\varphi(T)$ reaches unity, the increase in deformation begins to be determined by the differential equation (24), in which the part of the second term enclosed in brackets is 0. At this instant, the decisive factor becomes the temperature dependence of the relaxation time (viscosity) of the system. Thus Eqn (25) establishes a direct relation between the deformation of the polymer system and the integral MMD function $\varphi(T)$.

This conclusion is illustrated by the experimental data in Refs 267 and 275. The approach described made it possible to put forward a method for the determination of the MMD based on the analysis of the temperature variation of the deformation of polymers in the region of the rubber elasticity plateau.[275]

V. Conclusion

As shown by numerous studies on the structures and properties of polymer systems, a very broad spectrum of intermolecular interactions, ranging from a weak dispersion interaction to a strong dipole–dipole interaction, may be manifested in them. A feature especially characteristic of polymers is that the interaction may involve a fairly large number of bonds (chain units). The presence of long chains predetermines the possibility of the formation of a network of physical bonds, which is reflected in most diverse ways in the properties of polymers.

The physical network model is applicable to the description of the properties not only of systems in which the nodes are formed *via* hydrogen bonds or a dipole–dipole interaction but also of the properties of crystallising polymers in the rubber-elastic state and also polymers with a complex phase structure, where very dense fluctuations (clusters) may play the role of the microphase. All these formations may serve as physical nodes. Thus the physical network model is in essence applicable to any polymers and polymer systems.

As in any model approach, certain properties of the system are in this instance treated as absolute, their role is over estimated, and other properties are not taken into account. A criterion of the validity of this approach may be its successful application in the solution of the relevant problems. Certain examples of the use of the physical network model in the equilibrium variant have been described.[255, 258, 259, 276–278] Evidently the theory should answer the question how the structure and properties of the physical network itself vary with time and on what basis one can describe the time variations of the properties of polymer systems. The reptation model of the diffusion of polymer chains is extremely fruitful in this sense. However, it does not take into account the entire diversity of the types of intermolecular interactions in polymers. Certain attempts to take into account this factor theoretically in the study of the dynamic characteristics of polymer systems have been undertaken.[261, 279, 280] However, on the whole the problem formulated still awaits its solution.

References

1. L Treloar *The Physics of Rubber Elasticity* (Oxford: Pergamon Press, 1953)
2. P J Flory *Principles of Polymer Chemistry* (New York: Cornell University Press, 1953)
3. P J Flory *Statistical Mechanics of Chain Molecules* (New York: International Pbl., 1969)
4. M V Vol'kenshtein *Konfiguratsionnaya Statistika Polimernykh Tsepei* (Configurational Statistics of Polymer Chains) (Moscow: Izd. Akad. Nauk USSR, 1959)
5. Ya I Frenkel' *Kineticheskaya Teoriya Zhidkostei* (Kinetic Theory of Liquids) (Leningrad: Nauka, 1975)
6. V A Kargin, A I Kitaigorodskii, G L Slonimskii *Kolloid. Zh.* **19** 131 (1957) [a]
7. V A Kargin *Sovremennye Problemy Khimii Polimerov* (Current Problems in Polymer Chemistry) (Moscow: Izd. Mosk. Gos. Univ., 1962)
8. V A Kargin, G L Clonimskii *Kratkie Ocherki po Fizikokhimii Polimerov* (Shot Essays on the Physical Chemistry of Polymers) (Moscow: Khimiya, 1967)
9. A I Kitaigorodskii *Poryadok i Besporyadok v Mire Atomov* (Order and Disorder in World of Atoms) (Moscow: Nauka, 1966)
10. J G Curro *J. Chem. Phys.* **61** 1203 (1974)
11. E De Vos, A Bellemans *Macromolecules,* **8** 651 (1975)
12. A A Sariban, T M Birshtein, A M Skvortsov *Dokl. Akad. Nauk SSSR* **229** 1400 (1976) [b]
13. V G Dashevskii *Konformatsionnyi Analiz Makromolekul* (Conformational Analysis of Macromolecules) (Moscow: Nauka, 1987)
14. J Allen, in *Strukturnye Issledovaniya Makromolekul Spektroskopicheskimi Metodami* (Structural Investigations of Macromolecules by Spectroscopic Methods) (Ed. A L Buchachenko) (Moscow: Khimiya, 1980) p. 304
15. H Hayashi, F Hamada, A Nakajima *Macromolecules* **9** 543 (1976)
16. G D Wignall, D G H Ballard, J Schelten *Eur. Polym. J.* **10** 861 (1974)
17. J Schelten, G D Wignall, D G H Ballard, W Schmatz *Colloid Polym. Sci.* **252** 749 (1974)
18. R G Kirste, W A Kruse, K Ibel *Polymer* **16** 120 (1975)
19. G Leieser, E W Fischer, K Ibel *J. Polym. Sci., Polym. Lett.* **13** 39 (1975)
20. J Schelton, D G H Ballard, G D Wignal *Polymer* **17** 751 (1976)
21. K Dusek (Ed.) *Polymer Networks* (Berlin: Springer, 1982)
22. K Dusek, W Prins *Adv. Polym. Sci.* **6** 1 (1969)
23. L S Priss, in *Issledovaniya v Oblasti Stroeniya i Svoistv Kauchukov i Rezin* (Investigations in the Field of Structure and Properties of Rubbers) (Moscow: Research Institute of Tire Industry, 1977) p. 9
24. A J Staverman, in *Polymer Networks* (Ed. K Dusek) (Berlin: Springer, 1982) p. 74
25. A Yu Grossberg, A R Khokhlov *O Nereshennykh Problemakh Statisticheskoi Fiziki Makromolekul* (Unsolved Problems in the Statistical Physics of Macromolecules) (Pushchino: The All-Union Research Centre of the Academy of Sciences of the USSR, 1985)
26. A A Dontsov *Protsessy Strukturirovaniya Elastomerov* (Processes of Structuring in Elastomers) (Moscow: Khimiya, 1978)
27. B A Dogadkin, A A Dontsov, V A Shershnev *Khimiya Elastomerov* (The Chemistry of Elastomers) (Moscow: Khimiya, 1981)
28. M F Bukhina *Tekhnicheskaya Fizika Elastomerov* (Technical Physics of Elastomers) (Moscow: Khimiya, 1984)
29. V A Myagchenkov, S Ya Frenkel' *Kompozitsionnaya Neodnorodnost' Sopolimerov* (Composition Heterogeneity of Copolymers) (Leningrad: Khimiya, 1988)
30. P J Flory *Chem. Rev.* **35** 51 (1944)
31. A V Tobol'skii *Svoistva i Struktura Polimerov* (Properties and Structure of Polymers) (Moscow: Khimiya, 1964)
32. M S Green, A V Tobolsky *J. Chem. Phys.* **14** 80 (1946)
33. H Mark, A Tobolsky *Physical Chemistry of High Polymeric Systems* (New York: Interscience, 1950)
34. R S Porter, J F Jonson *Chem. Rev* **66** 1 (1966)
35. W W Graessley *Adv. Polym. Sci.* **16** 1 (1974)
36. W W Graessley *Adv. Polym. Sci.* **47** 67 (1982)

37. J E Mark, A Eisenberg, W W Graessley, L Mandelkern *Physical Properties of Polymers* (Washington, DC: American Chemical Society, 1984)
38. M Hoffmann *Rheol. Acta* **6** 377 (1967)
39. A E Tonelli *J. Polym. Sci., Polym. Chem. Ed.* **8** 656 (1970)
40. A A Ackadskii, Yu I Matveev *Khimicheskoe Stroenie i Fizicheskie Svoistva Polimerov* (Chemical Structure and Physical Properties of Polymers) (Moscow: Khimiya, 1983)
41. M D Frank-Kamenetskii, A V Vologodskii *Usp Fiz. Nauk* **139** 641 (1981) [c]
42. S F Edwards, K F Freed *J. Phys. A, Math. Gen.* **2** 145 (1969)
43. R Collins, A Wragg *J. Phys. A, Math. Gen.* **2** 151 (1969)
44. V F Popov, V I Mudruk, in *Matematicheskie Metody dlya Issledovaniya Polimerov (Materialy II Vsesoyuznogo Soveshchaniya)* [Mathematical Methods for Investigation of Polymers (Proceedings of the Second All-Union Meeting)] (Pushchino: The All-Union Research Centre of the Academy of Sciences of the USSR, 1982) p. 22
45. L S Priss *Teoriya Vysokoelastichnosti. Sostoyanie i Tendentsii ee Razvitiya* (The Theory of Viscoelasticity. Current State and Tendencies of Its Development) (Pushchino: Nauka, 1981)
46. S F Edwards, T A Vilgis *Polymer* **27** 483 (1986)
47. T A Vilgis *Macromolecules* **25** 399 (1992)
48. P J Flory *Br. Polym. J.* **17** 96 (1985)
49. J P Queslel, J E Mark *Polym. Bull.* **10** 119 (1983)
50. B Erman, P J Flory *Macromolecules* **16** 1601 (1983)
51. B Erman *Br. Polym. J.* **17** 140 (1985)
52. B Erman, P J Flory *Macromolecules* **16** 1607 (1983)
53. R W Brotzman, J E Mark *Am. Chem. Soc., Polym. Prepr.* **27** 292 (1986)
54. R W Brotzman, J E Mark *Macromolecules* **19** 667 (1986)
55. B Erman, in *Proceedings of the Symposium of National American Chemical Society Meeting, Chicago, 1985* (New York, 1986) p. 279
56. R Ulman, in *Proceedings of the Symposium of National American Chemical Society Meeting, Chicago, 1985* (New York, 1986) p. 291
57. R Ulman *Macromolecules* **19** 1748 (1986)
58. T Tanaka *J. Phys. Soc. Jpn.* **53** 2205 (1984)
59. D B Adolf, J G Curro *Macromolecules* **20** 1646 (1987)
60. A M El'yashevich, I Ya Lodyzhenskii *Vysokomol. Soedin., Ser. B* **27** 137 (1985) [d]
61. I S Remeev, A M El'yashevich *Vysokomol. Soedin., Ser. A* **27** 629 (1985) [d]
62. A M El'yashevich, I Ya Lodyzhenskii *Vysokomol. Soedin., Ser. A* **29** 2372 (1987) [d]
63. F Boue, M Nierlich, K Osaki, in *Symposium on Molecular Basis of Viscoelasticity, 1983* (Faraday Symp. Chem. Soc., **18**, 1983) p. 83
64. P G de Gennes *Scaling Concept of Polymer Physics* (New York: Cornell University Press, 1978)
65. A Yu Grossberg, A R Khokhlov *Statisticheskaya Fizika Makromolekul* (Statistical Physics of Macromolecules) (Moscow: Nayka, 1989)
66. M Doi, S F Edvards *Theory of Polymer Dynamics* (New York: Academic Press, 1986)
67. R Kimmich, G Schnur, M Kopf *Progr. Nucl. Magn. Reson. Spectrosc.* **20** 385 (1988)
68. T P Kulagina, V V Marchenkov, B N Provotorov *Statisticheskaya Teoriya YaMR Spektrov v Amorfnykh Gibkotsepnykh Polimerakh* (Statistical Theory of Nuclear Magnetic Resonance Spectra in Amorphous Flexible Chain Polymers) (Chernogolovka: Institute of Chemical Physics of the Academy of Sciences of the USSR, 1985)
69. T P Kulagina, in *The IIth European Symposium on Polymer Spectroscopy,Valladoid, Spain, 1994* p. 107
70. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery* (Polymer Networks) (Moscow: Nauka, 1979)
71. Yu S Lipatov, A E Nesterov, T M Gritsenko, R A Veselovskii *Spravochnik po Khimii Polimerov* (Handbook on the Chemistry of Polymers) (Kiev: Naukova Dumka, 1971)
72. K K Chee *J. Appl. Polym. Sci.* **33** 1067 (1987)
73. A V Sidorovich *Vysokomol. Soedin., Ser. A* **38** 2020 (1995) [d]
74. D W Van Krevelen *Properties of Polymers Correlations with Chemical Structure* (New York: Elsevier, 1972)
75. M Kluppel, in *Physics of Polymer Networks. The 29th Europhysics Conference* (Alexisbad: European Physical Society, 1991) p. 85
76. J P Cohen-Addad, M Domard, G Lorentz, J Herz *J. Physique (France)* **45** 575 (1984)
77. C M Ylitalo, J A Kornfeld, G G Fuller *Macromolecules* **24** 1991 (1991)
78. K L Ngai, D J Plazek, C A Bero *Macromolecules* **26** 1065 (1993)
79. D K Potter, A Rudin *Macromolecules* **24** 213 (1991)
80. U Seidel, R Stadler, G G Fuller *Macromolecules* **27** 2066 (1994)
81. G V Vinogradov *Mekh. Polim.* 160 (1975)
82. M I Shakhparonov *Metody Issledovaniya Teplovogo Dvizheniya Molekul i Stroeniya Zhidkostei* (Methods of Investigation of Heat Movement of Molecules and Structure of Liquids) (Moscow: Izd. Mosk. Gos. Univ., 1963)
83. G V Korolev, M P Berezin *Mekhanizm Assotsiativnykh Protsessov i Metodika ikh Issledovaniya s Pomoshch'yu Spin-zonda* (Mechanism of Associative Processes and the Procedure of Its Investigation by Spin Probe) (Chernogolovka: Institute of Chemical Physics in Chernogolovka of the Russian Academy of Sciences, 1994)
84. A I Kitaigorodskii *Organicheskaya Kristallokhimiya* (Organic Crystal Chemistry) (Moscow: Izd. Akad. Nauk SSSR, 1955)
85. G V Korolev, A A Il'in *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekh.* (in the press) (1997)
86. G V Korolev, A A Il'in *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekh.* (in the press) (1997)
87. G L Slonimskii, A A Askadskii, A I Kitaigorodskii *Vysokomol. Soedin., Ser. A* **12** 494 (1970) [d]
88. A A Askadskii, G L Slonimskii, A I Kitaigorodskii *Vysokomol. Soedin., Ser. A* **16** 424 (1974) [d]
89. A A Tager, A A Askadskii, M V Tsilipotkina *Vysokomol. Soedin., Ser. A* **17** 1346 (1974) [d]
90. A A Abramson *Poverkhnostno-aktivnye Veshchestva* (Surfactants) (Leningrad: Khimiya, 1981)
91. E B Wilson, in *Advances in Chemical Physics* Vol II (Ed. I Prigogine) (New York: Interscience, 1959) p. 367
92. E B Wilson *Proc. Natl. Acad. Sci. USA* **43** 816 (1957)
93. L Pierce *J. Chem. Phys.* **34** 498 (1961)
94. J M O'Reilly, L Pierce *J. Chem. Phys.* **34** 1176 (1961)
95. J P Lowe *Prog. Phys. Org. Chem.* **6** 1 (1968)
96. G V Korolev, M P Berezin *Vysokomol. Soedin., Ser. A* **29** (in the press) (1997) [d]
97. G V Korolev, M M Mogilevich, M M Golikov *Setchatye Poliakrilaty: Mikrogeterogennye Struktury, Fizicheskie Svoistva, Deformatsionno-prochnostnye Svoistva* (Network Polyacrylates: Microheterogeneous Structures, Physical Properties, Deformation and Strength Properties) (Moscow: Khimiya, 1995)
98. P J Flory *Faraday Discuss. Chem. Soc.* **57** 7(1974)
99. S M Kavun, in *Khimicheskaya Relaksatsiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii. Struktura i Svoistva Kauchukov i Vulkanizatov* (Chemical Relaxation and Technology of High-Molecular Compounds. Structure and Properties of Rubbers and Vulcanisates) (Moscow: Izd. VINITI, 1975) Vol. 6, p. 149
100. O K Kornilova, V V Dubrovskaya, M I Shepelev *Struktura Sernykh Vulkanizatov Kauchukov i Metody ee Issledovaniya* (The Structure of Sulfur Vulcanisates of Rubbers and Methods for Its Investigation) (Moscow: TsNIITENeftekhim, 1973)
101. G Henrici-Olive, S Olive *Adv. Polym. Sci.* **32** 123 (1979)
102. G M Bartenev *Struktura i Relaksatsionnye Svoistva Elastomerov* (The Structure and Relaxation Properties of Elastomers) (Moscow: Khimiya, 1979)
103. L A Akopyan, N A Ovrutskaya, E V Gronskaya, G M Bartenev *Vysokomol. Soedin., Ser. A* **26** 436 (1984) [d]
104. T I Novikova, L A Bakalo, T E Lipatova in *Fiziko-khimicheskie Svoistva i Struktura Polimerov* (Kiev: Naukova Dumka, 1977) p. 71
105. M V Shablygin, P M Pakhomov *Vysokomol. Soedin., Ser. B* **21** 612 (1979) [d]
106. M A Kuznetsov, A L Smolyanskii *Zh. Prikl. Spektrosk.* **20** 672 (1974)
107. J Homer, in *Nuclear Magnetic Resonance* Vol. 7 (Oxford: Alden Press, 1978) p. 318
108. F Cangelosi, M T Shaw *Polym.-Plast. Technol. Eng.* **21** 13 (1983)
109. V M Pozdnyakov, A N Savitskaya, N V Klimenko *Vysokomol. Soedin., Ser. B* **11** 649 (1969) [d]
110. V N Vatulev, N I Litsev, L A Yurok *Zh. Prikl. Spektrosk.* **14** 667 (1971)
111. O M Kutsenko, V A Khranovskii, T M Gritsenko *Vysokomol. Soedin., Ser. B* **20** 579 (1978) [d]
112. G K Romanovskii, V A Tsitokhtsev, L Ya Rappoport *Vysokomol. Soedin., Ser. A* **17** 2512 (1975) [d]
113. Yu S Lipatov, Yu Yu Kercha, L M Sergeeva *Struktura i Svoistva Poliuretanov* (Structure and Properties of Polyurethanes) (Kiev: Naukova Dumka, 1970)

114. J Buist (Ed.) *Developments in Polyurethanes-1* (London: Appl. Sci. Publ., 1978)
115. G K Romanovskii, L Ya Rappoport, N G Pavlov *Vysokomol. Soedin., Ser. A* **14** 2241 (1972) [d]
116. O M Fedorenko, D P Kochetov, A V Barantseva *Vysokomol. Soedin., Ser. B* **30** 606 (1988) [d]
117. A A Tager, A I Suvorova, Yu S Bessonov *Vysokomol. Soedin., Ser. A* **13** 2454 (1971) [d]
118. E G Atovmyan *Vysokomol. Soedin., Ser. B* **26** 691 (1984) [d]
119. H Ohno, E Tshuchida *Am. Chem. Soc., Polym. Prepr.* **20** 1055 (1979)
120. V A Bershtein, L G Razgulyaeva, V M Gal'perin *Vysokomol. Soedin., Ser. A* **20** 1885 (1978) [d]
121. V A Bershtein, M Z Pyatkevich, L G Razgulyaeva *Vysokomol. Soedin., Ser. A* **20** 2682 (1978) [d]
122. L Z Rogovina, G L Slonimskii, L S Gembitskii *Vysokomol. Soedin., Ser. A* **15** 1256 (1973) [d]
123. M A Mateesku, N D Scbell, M Dimonie *Polym. Bull.* **12** 421 (1984)
124. C Hilger, R Stadler, L de Lucca Freitas *Polymer* **31** 818 (1990)
125. R Stadler, L de Lucca Freitas *Polym. Bull.* **15** 173 (1986)
126. G I Timofeeva, A S Buntyakov, V M Aver'yanova *Vysokomol. Soedin., Ser. B* **17** 685 (1975) [d]
127. J Gyorgyi-Edelenyi, M Nagy *Acta Chim. Acad. Sci. Hung.* **102** 341 (1979)
128. A B Zezin, V B Rogacheva, in *Uspekhi Khimii i Fiziki Polimerov* (Advances in the Chemistry and Physics of Polymers) (Moscow: Khimiya, 1973) p. 3
129. V A Kabanov *Vysokomol. Soedin., Ser. A* **36** 183 (1994) [d]
130. N Ise, I Tabusi (Eds) *Polimery Spetsial'nogo Naznacheniya* (Polymers for Special Purposes) (Translated into Russian; Moscow: Mir, 1983)
131. R F Boyer, in *Order in the Amorphous State of Polymers* (New York: Plenum, 1987)
132. J H Wendorff, E W Fischer *Kolloid. Z., Z. Polym.* **251** 876 (1973)
133. A L Renninger, G G Wicks, D R Uhlmann *J. Polym. Sci., Polym. Phys. Ed.* **13** 1247 (1975)
134. A L Renninger, D R Uhlmann *J. Polym. Sci., Polym. Phys. Ed.* **13** 1481 (1975)
135. D R Uhlmann, A L Renninger, G Kritschevsky, J Van der Sande *J. Macromol. Sci., Phys.* **12** 153 (1976)
136. R M Gleaser, in *Physical Aspects of Electron Microscopy and Microbeam Analysis* (Eds B M.Siegel, D R Beaman) (New York: Wiley, 1975) p. 474
137. H G Kilian, K Boucke *J. Polym. Sci.* **58** 311 (1962)
138. R Hosemann, J Loboda-Cackovie, H Cackovic *Z. Naturforssh., A, Phys. Sci.* **27** 478 (1972)
139. S M Wecher, T Davidson, J B Cohen *J. Mater. Sci.* **7** 1249 (1972)
140. S Krishnamurthy, D McIntyre *J. Polym. Sci., Polym. Phys. Ed.* **8** 647 (1972)
141. G E Wilkes, M H Lehr *J. Macromol. Sci., Phys.* **7** 225 (1973)
142. P P A Smit *Kolloid Z., Z. Polym.* **250** 27 (1972)
143. Yu K Ovchinnikov, G S Markova *Vysokomol. Soedin., Ser. A* **9** 449 (1967) [d]
144. Yu K Ovchinnikov, G S Markova, V A Kargin *Vysokomol. Soedin., Ser. A* **11** 329 (1969) [d]
145. G S Markova, Yu K Ovchinnikov, E B Bokhgan *J. Polym. Sci., Polym. Symp.* **42** 671 (1973)
146. Yu K Ovchinnikov, E M Antipov, G S Markova *Vysokomol. Soedin., Ser. A* **17** 1806 (1975) [d]
147. G W Longman, G D Wignall, R P Sheldon *Polymer* **17** 475 (1976)
148. S H Maron, C A Daniels *J. Macromol. Sci., Phys.* **2** 463 (1968)
149. S H Maron, C A Daniels *J. Macromol. Sci., Phys.* **2** 591 (1968)
150. A Tanaka, K Sawada, Y Ishida *J. Polym. Sci., Polym. Phys. Ed.* **12** 2157 (1974)
151. A Tanaka, Y Ishida *J. Polym. Sci., Polym. Phys. Ed.* **12** 1283 (1974)
152. B I Sazhin, A M Lobanov, O S Romanovskaya *Elektronnye Svoistva Ppolimerov* (Leningrad: Khimiya, 1986)
153. Yu S Sereda, B P Shtarkman, S A Arzhakov *Dokl. Akad. Nauk SSSR,* **214** 1358 (1974)
154. A V Sidirovich, Yu S Nadezhin *Dokl. Akad. Nauk SSSR* **227** 400 (1976) [b]
155. V N Belousov, G V Kozlov, A L Mikitaev, Yu S Lipatov *Dokl. Akad. Nauk SSSR* **313** 630 (1990) [b]
156. D S Sanditov, G V Kozlov, V M Belousov, Yu S Lipatov *Ukr. Polym. J.* **1** 241 (1992)
157. G V Kozlov, D S Sanditov *Angarmonicheskie Effekty i Fiziko-mekhanicheskie Svoistva Polimerov* (Anharmonic Effects and Physical Mechanical Properties of Polymers) (Novosibirsk: Nauka, 1994)
158. V P Privalko, in *Strukturnye Osobennosti Polimerov* (Structural Features of Polymers) (Kiev: Naukova Dumka, 1978) p. 3
159. V P Privalko *Molekulyarnoe Stroenie i Svoistva Polimerov* (Molecular Structure and Properties of Polymers) (Leningrad: Khimiya, 1986)
160. V A Marikhin, L P Myasnikova *Nadmolekulyarnaya Struktura Polimerov* (Supermolecular Structure of Polymers) (Leningrad: Khimiya, 1977)
161. S A Arzhakov, N F Bakeev, V A Kabanov *Vysokomol. Soedin., Ser. A* **15** 1154 (1973) [d]
162. Yu I Matveev, A A Askadskii *Vysokomol. Soedin., Ser. A* **28** 1365 (1986) [d]
163. R W Miller, R F Boyer *J. Polym. Sci., Polym. Phys. Ed.* **22** 2043 (1984)
164. Yu I Matveev, A A Askadskii *Vysokomol. Soedin., Ser. A* **31** 617 (1989) [d]
165. J Gons, E J Vorenkamp, G Challa *J. Polym. Sci., Polym. Phys. Ed.* **15** 3031 (1977)
166. T F Irzhak, N I Peregudov, M L Tai, V I Irzhak *Vysokomol. Soedin., Ser. B* **28** 1921 (1996)
167. J M Guenet, M Klein *Makromol. Chem., Makromol. Symp.* **39** 85 (1990)
168. N Motosuke, O Akira *Polymer* **25** 75 (1984)
169. B P Shtarkman *Plastifikatsiya Polivinilkhlorida* (Plasticisation of Polyvinyl Chloride) (Moscow: Khimiya, 1975)
170. L Mandelkern *Crystallisation of Polymers* (New York: McGraw-Hill, 1964)
171. A G Sirota *Modifikatsiya Struktury i Svoistv Poliolefinov* (Modification of Structure and Properties of Polyolefins) (Leningrad: Khimiya, 1984)
172. B J R Scholtens *Br. Polym. J.* **17** 134 (1985)
173. N P Zoloteev, G M Bartenev, O I Zateeva *Vysokomol. Soedin., Ser. A* **26** 681 (1984) [d]
174. Bacon Ke (Ed.) *Newer Methods of Polymer Characterisation* (New York: Wiley-Interscience, 1964)
175. E G Moisya, in *Novye Metody Issledovaniya Polimerov* (New Methods for Investigation of Polymers) (Kiev: Naukova Dumka, 1975)
176. A T Bulloch *Electr. Spin Reson.* **7** 280 (1982)
177. A M Vasserman, A L Kovarskii *Spinovye Metki i Zondy v Fiziko-khimii Polimerov* (Spin Labels and Probes in Physical Chemistry of Polymers) (Moscow: Nauka, 1986)
178. H-K Roth, F Keller, H Schneider *Hoch-frequenz-spektroskopie in der Polymerforschung* (Berlin: Academie-Verlag, 1984)
179. S M Mezhikovskii *Vysokomol. Soedin., Ser. A* **29** 1571 (1987) [d]
180. V K Antchak, G Yu Shchekaturov, G L Inikhov *Zh. Vses. Khim. O-va im. D I Mendeleeva* **28** 114 (1983)
181. D J Patterson, C M Shields, A Cholli, J L Koenig *Am. Chem. Soc., Polym. Prepr.* **25** 358 (1984)
182. A M Zaper, J L Koenig *Rubber Chem. Technol.* **39** 179 (1986)
183. G M Bartenev, B I Revjakin, N M Ljalina *Acta Polym.* **36** 331 (1985)
184. G M Bartenev, V P Dushchenko, N I Shut *Vysokomol. Soedin., Ser. A* **27** 405 (1985) [d]
185. J A Manson, L H Sperling *Polymer Blends and Composites* (New York: Plenum, 1976)
186. R A Weis, A Sent, L A Pottic, C L Willis *Polym. Commun.* **31** 220 (1990)
187. Yu S Lipatov, L M Sergeeva *Vzaimopronikayushchie Setki* (Interpenet-rating Networks) (Kiev: Naukova Dumka, 1979)
188. L K Sperling *Interpenet-rating Polymer Networks and Related Materials* (New York: Plenum, 1981)
189. H C Haas, R D Moreau, N W Shuler *J. Polym. Sci., Polym. Chem. Ed.* **2** 915 (1967)
190. L Z Rogovina, G L Slonimskii *Usp. Khim.* **43** 1102 (1974) [*Russ. Chem. Rev.* **43** 503 (1974)]
191. S P Papkov *Studneobraznoe Sostoyanie Polimerov* (Jelly-like State of Polymers) (Moscow: Khimiya, 1974)
192. Yu S Lipatov *Kolloidnaya Khimiya Polimerov* (Colloidal Chemistry of Polymers) (Kiev: Naukova dumka, 1984)
193. H Boedtker, P Doty *J. Phys. Chem.* **58** 968 (1954)
194. G Beyer *J. Phys. Chem.* **58** 1050 (1954)
195. M A V Axelos, M Kolb *Makromol. Chem. Makromol. Symp.* **45** 23 (1991)
196. J J Aarsten *Eur. Polym. J.* **7** 919 (1970)

197. V I Andreeva, A A Tager, I S Takova, L F Golenkova *Vysokomol. Soedin., Ser. A* **19** 2604 (1977) [d]
198. S Wellinghoff, I Shaw, E Baer *Macromolecules* **12** 932 (1979)
199. M Komatsu, T Inoue, K Miyasaka *J. Polym. Sci., Polym. Phys. Ed.* **24** 303 (1986)
200. K Kawanishi, Y Takeda, T Inoue *Polym. J.* **18** 414 (1986)
201. S J Guerrero, A Keller, P L Sony *J. Macromol. Sci., Phys.* **20** 161 (1981)
202. A Hiltner, E Baer *Am. Chem. Soc. Polym. Prepr.* **27** 207 (1986)
203. B Koltisko, A Keller, M Litt *Macromolecules* **19** 1207 (1986)
204. J Francois, J Y S Gan, J M Guenet *Macromolecules* **19** 2755 (1986)
205. F R Boyer, E Baer, A Hiltner *Macromolecules* **18** 427 (1985)
206. L M Jelich, S P Nunes, E Paul, B A Wolf *Macromolecules* **20** 1943 (1987)
207. S P Nunes, B A Wolf, H E Jeberien *Macromolecules* **20** 1948 (1987)
208. L Z Rogovina, A I Feofanova, V G Vasil'ev, G L Slonimskii *Vysokomol. Soedin., Ser. A* **30** 528 (1988) [d]
209. A Keller, in *The 35th International Symposium on Macromolecules* (Akron, USA: American Chemical Society, 1994) p. 2
210. A Keller, in *Europhysics Conference on Gels* (Balatonzeplak, Hungary: European Chemical Society, 1995) L. 13
211. K Te Nijenhuis, H U Winter *Macromolecules ,* **22** 411 (1989)
212. K Te Nijenhuis, in *Europhysics Conference on Gels* (Balatonzeplak, Hungary: European Chemical Society, 1995) L. 15
213. H Bergmans, F Deberdt *Trans. R. Soc. Can.* **L348** 117 (1993)
214. F Deberdt, H Bergmans *Polymer* **10** 2192 (1993)
215. J Arnaults, H Bergmans, R Koningsveld *Makromol. Chem.* **94** 77 (1993)
216. J D Ferry *Adv. Polym. Chem.* **1** 1 (1948)
217. J E Eldridge, J D Ferry *J. Phys. Chem.* **58** 992 (1954)
218. T Tanaka, G Swislow, I Ohmine *Phys. Rev. Lett.* **49** 1556 (1979)
219. B Erman, P J Flory *Macromolecules* **19** 2342 (1986)
220. B E Eichinger, P J Flory *Trans. Faraday Soc.* **64** 2053 (1968)
221. F Tanaka *Macromolecules* **22** 1988 (1989)
222. F Tanaka, A Matsugama *Phys. Rev. Lett.* **62** 6367 (1989)
223. W H Stockmayer *Macromolecules* **24** 6367 (1991)
224. A R Khohlov *Polymer* **21** 376 (1980)
225. F Tanaka *Phys. Rev. Lett.* **40** 820 (1978)
226. F Tanaka *Polymer* **20** 1404 (1979)
227. J Steyskal, M Gordon, J A Tornigton *Polym. Bull.* **3** 621 (1980)
228. S Katayama, J Hirokawa, T Tanaka *Macromolecules* **17** 2641 (1984)
229. S G Starodubtsev, N R Pavlova, V V Vasilevskaya, A R Khokhlov *Vysokomol. Soedin., Ser.,* **27B** 485 (1985) [d]
230. M Ilavsky *Polymer,* **3** 1687 (1981)
231. M Ilavsky, J Hrouz, K Ulbrich *Polym. Bull.* **7** 107 (1982)
232. M Ilavshy, J Hrouz *Polym. Bull.* **8** 387 (1982)
233. V V Vasilevskaya, V A Ryabina, S G Starodubtsev, A R Khokhlov *Vysokomol. Soedin., Ser. A* **31** 713 (1989) [d]
234. A R Khokhlov *Vysokomol. Soedin., Ser. A* **22** 736 (1980) [d]
235. A R Khokhlov, V V Vasilevskaya, S G Starodubtsev *Protsessy Studneobrazovaniya v Polimernykh Sistemakh* (Processes of Jelly Formation in Polymer Systems) (Saratov: Saratov State University, 1985)
236. B J R Scholtens *Br. Polym. J.* **17** 134 (1985)
237. A Ziabicki, J Walasek *Br. Polym. J.* **17** 116 (1985)
238. S S Abramchuk, A R Khokhlov *Dokl. Akad. Nauk SSSR* **297** 385 (1987) [b]
239. G R Michell *Br. Polym. J.* **17** 111 (1985)
240. T Nishi, T Chikaraishi *J. Macromol. Sci. Phys., Phys.* **19** 445 (1980)
241. D Andre, D Bertrand, H Jean *Polymer* **25** 1405 (1984)
242. M M Jacobi, R Stadler, W Gronski *Macromolecules* **19** 2884 (1986)
243. M R Kuzma *Mol. Cryst. Liq. Cryst.* **101** 351 (1983)
244. V V Rusakov, in *Strukturno-mekhanicheskie Issledovaniya Kompozitsionnykh Materialov i Konstruktsii* (Structural Mechanical Investigations of Composite Materials and Constructions) (Sverdlovsk: Ural Research Centre of the Academy of Sciences of the USSR, 1984) p. 37
245. Yu Ya Gotlib, V G Baranov, A V Maksimov *Vysokomol. Soedin., Ser. B* **27** 312 (1975) [d]
246. S S Abramchuk, I A Nyrkova, A R Khokhlov *Vysokomol. Soedin., Ser. A* **31** 1759 (1979) [d]
247. J Furukawa *Polym. Bull.* **10** 336 (1983)
248. J Furukawa *Polym. Bull.* **12** 547 (1984)
249. I B Borodin, T N Khazanovich, in *Matematicheskie Metody dlya Issledovaniya Polimerov (Tr. II Vsesoyuz. Soveshchaniya)* [Mathematical Methods for Investigation of Polymers (Proceedings of the Second All-Union Meeting)] (Pushchino: The All-Union Research Centre of the Academy of Sciences of the USSR, 1982) p. 38
250. G M Baptenev, Yu V Zelenev *Fizika i Mekhanika Polimerov* (Physics and Mechanics of Polymers) (Moscow: Vysshaya Shkola, 1983)
251. G M Bartenev, S Ya Frenkel' *Fizika Polimerov* (Physics of Polymers) (Leningrad: Khimiya, 1990)
252. M E Solov'ev, A B Raukhvarger, V I Irzhak *Vysokomol. Soedin., Ser. B* **28** 106 (1986) [d]
253. M E Solov'ev, A B Raukhvarger, V I Irzhak, N S Enikolopyan *Dokl. Akad. Nauk SSSR* **290** 661 (1986) [b]
254. M E Solov'ev, A B Raukhvarger, V I Irzhak *Vysokomol. Soedin., Ser.* **29B** 293 (1987) [d]
255. M E Solov'ev, T K Ivashkovskaya, A B Raukhvarger, V I Irzhak *Vysokomol. Soedin., Ser. B* **29** 731 (1987) [d]
256. M E Solovyov, A B Raukhvarger, V I Irzhak, in *The 31st IUPAC Macromolecular Symposium Macro'87 (Abstracts of Reports) (GDR, Microsymposium IV) 1987* p. 172
257. A R Basaev, N A Budanov, M E Solov'ev, Yu E Shapiro *Vysokomol. Soedin., Ser. B* **30** 570 (1988) [d]
258. M E Solov'ev, T K Ivashkovskaya, A B Raukhvarger, V I Irzhak *Vysokomol. Soedin., Ser. B* **30** 144 (1988) [d]
259. M E Solov'ev, A B Raukhvarger, L I Makhonina, G V Korolev, V I Irzhak *Vysokomol. Soedin., Ser. B* **31** 485 (1989) [d]
260. A B Raukhvarger, M E Solovyov, V I Irzhak *Chem. Phys. Let.* **155** 455 (1989)
261. M E Solov'ev, Doctoral Thesis in Physical Mathematic Sciences, Semenov Institute of Chemical Physics, Moscow, 1994
262. M E Solov'ev, A R Basaev, A N Privalov *Vysokomol. Soedin., Ser. B* **31** 938 (1990) [d]
263. L I Makhonina, A A Baturina, V P Grachev, G V Korolev *Izv. Vyssh. Uchebn. Zaved., Khim Khim. Tekhnol.* **36** 70 (1993)
264. N A Budanov, A R Basaev, M E Solov'ev, Yu E Shapiro *Vysokomol. Soedin., Ser. B* **30** 510 (1989) [d]
265. V E Gul', V V Kovriga, E G Eremina *Vysokomol. Soedin., Ser. A* **3** 1616 (1960) [d]
266. E M Solov'ev, Yu B Kitaev, V E Gul', N D Zakharov *Vysokomol. Soedin., Ser. A* **22** 297 (1980) [d]
267. Yu A Ol'khov, S M Baturin, V I Irzhak *Vysokomol. Soedin., Ser. A* **38** 849 (1996) [d]
268. G V Vinogradov, A Ya Malkin *Reologiya Polimerov* (Rheology of Polymers) (Moscow: Khimiya, 1977)
269. V A Kargin, G L Slonimskii *Dokl. Akad. Nauk SSSR* **62** 239 (1948) [b]
270. A Ya Malkin, A E Teishev *Vysokomol. Soedin., Ser. A* **29** 2230 (1987) [d]
271. A Ya Malkin, A E Teishev *Vysokomol. Soedin., Ser. A* **30** 175 (1988) [d]
272. Yu I Matveev, A A Askadskii *Vysokomol. Soedin., Ser. A* **33** 1251 (1991) [d]
273. V A Bershtein, V M Egorov *Differentsial'naya Skaniruyushchaya Kalorimetriya v Fizikokhimii Polimerov* (Differential Scanning Calorimetry in Physical Chemistry of Polymers) (Leningrad: Khimiya, 1990)
274. Yu I Matveev, A A Askadskii *Vysokomol. Soedin., Ser. A* **35** 63 (1993) [d]
275. Russ. P. 2 023 255 (1984); *Byull. Izobr.* (21) 142 (1984)
276. M E Solov'ev, T K Ivashkovskaya, V I Irzhak *Vysokomol. Soedin., Ser. B* **31** 510 (1990) [d]
277. M E Solov'ev, T K Ivashkovskaya, V I Irzhak *Vysokomol. Soedin., Ser. B* **34** 36 (1992) [c]
278. G V Korolev, M L Bubnova *Vysokomol. Soedin., Ser. A* **36** 2000 (1994) [d]
279. M E Solov'ev, A B Raukhvarger, A R Basaev, V I Irzhak *Vysokomol. Soedin., Ser. A* **34** 127 (1992) [d]
280. V I Irzhak, S E Varyukhin, T F Irzhak, in *Europhysics Conference on Gels* (Balatonzeplak, Hungary: European Chemical Society, 1995) p. 69

[a] — *Russ. Colloid. J. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Physics-Uspekhi (Engl. Transl.)*
[d] — *Polym. Sci. (Engl. Transl.)*