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Relaxation properties of polymers and the physical network model

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Abstract. The role of the physical network in the dynamics of macromolecules is considered. It is shown that experimental data are often inconsistent not only quantitatively but also qualitatively with the results obtained in terms of the widespread reptation model based on the concept of network entanglement. Evidence is given indicating that the network of physical bonds is the governing factor in the dynamics of macromolecules. The bibliography includes 218 references.

I. Introduction

The condensed state of substances is determined by the nature of intermolecular interactions. This statement appears trivial; however, in the case of polymers the situation is not that simple. Indeed, below the glass transition temperature, the properties of a high-molecular body virtually do not differ from those of a low-molecular body (the latter may be brittle), whereas in the high-temperature range they differ rather substantially. This is primarily due to the chain nature of the molecules owing to which polymers display properties which allow one to speak about their specific (highly elastic) state; network structures are only possible in polymeric bodies; it is in the polymers that such a structural level as the topological one is the most important. Thus, intermolecular interactions in high-molecular-mass compounds cannot be reduced only to the formation of more or less strong bonds of an energetic nature. In order to understand and describe properties of polymeric substances, it is necessary to take into consideration topological features of their structures.

The use of the concept of physical networks [1] allows a more adequate description of polymers: energetic interactions are assumed to be localised at certain points regarded as nodes, whereas the topological aspects of the structure are interpreted with the aid of terminology used to describe covalent networks (*e.g.*, internodal chains, tails, gel and sol fractions, *etc.*).[2,3] Any polymeric system can be described as a network whose nodes have a finite lifetime. The concentration of nodes depends on external conditions: temperature, strain, the presence of a solvent.

Physical networks, usually called gels, are fairly well studied subjects.[4–7] According to Flory,[8] they can be classified as follows: well-ordered lamellar structures, including gel-like mesophases; totally disordered polymeric networks; polymeric networks formed by physical aggregation which are mostly disordered but comprise some ordered regions; and specific disordered structures.

This classification comprises covalent network polymers but does not include non-crosslinked polymers. This is due to the fact that in the cases under consideration the nodes of physical networks are represented by certain microphase structures. Common linear or branched polymers devoid of such structures, though not being called gels, exhibit, in definite temperature and time intervals, properties of gels, which are in particular exhibited in the relaxation of the elasticity modulus. Consequently, when considering all polymers, one can make recourse to the above-mentioned Flory classification complemented with disordered polymeric systems comprising the nodes whose nature differs from that of microphases.

At present, the most popular viewpoint is that the nodes of a physical network are entanglements, *i.e.*, units of topological and entropic rather than energetic origin.[9–13] However, it should be noted that in this case too, the concentration of nodes depends on temperature, although the heat of node formation is rather small, ~ 9 kJ mol^{-1}.[14]

The polymers containing functional groups capable of forming sufficiently strong energetic bonds (of the hydrogen bond type) can be regarded as an intermediate case, if these groups are distributed along the chain in a manner, which prevents the formation of 'zones of physical bonds'.[15] According to the Flory classification, the first group of physical networks is macromolecular in essence. Therefore, if the network polymers are excluded, then all the polymeric systems regarded as physical networks may be classified as follows:

(1) networks with nodes of a microphase type which have ordered or disordered structures;

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(2) networks with nodes formed by strong intermolecular bonding of the hydrogen bond type;

(3) networks with nodes of entropic (topological) nature.

The first group comprises systems which are commonly regarded as physical gels. Numerous papers and reviews have been devoted to the thermodynamic aspects of such systems and their phase structure.[4–8,15] The role of energetic intermolecular interactions in these systems has been established.

All other polymers may be included into the second and mostly the third groups. An important point here consists in estimating the contribution of the energetic component and intermolecular interactions to the properties of polymeric systems of these types.

II. The role of topological factors. The reptation model

A distinctive feature of polymeric systems consists in the existence of the highly elastic state which is manifested in that they exhibit properties of an elastic body over definite time and temperature intervals: above the glass transition temperature and below the flow temperature, one observes a high-elasticity plateau in the relaxation curves. In this range, the real part of the elasticity modulus is slightly dependent on the temperature and time (frequency of measurements) of the experiment; consequently, the plateau is of the entropic rather than energetic origin. It is noteworthy that the above-mentioned weak dependence is relative, because in the interval of low temperatures and high frequencies (short times) the high-elasticity plateau is superimposed on the glass transition region. For this reason, it is sometimes difficult to establish whether the changes in the elasticity modulus are associated with this circumstance, or this parameter depends *per se* on the temperature and time of the experiment in the plateau region.

Evidence in favour of the entropic nature of intermolecular interactions which determine properties of the polymeric systems is provided by the dependences of the range of the high-elasticity plateau and the viscosity of melts and concentrated solutions of polymers on their molecular masses (MM).

The theories which substantiate the above dependences (see, *e.g.*, Refs 10, 13, 16–18) are based on the concepts of crucial role of the network of physical (topological) nodes, while the network connectivity (critical conditions of the network appearance) depends on the length of the chains that are cross-linked the correlation between theoretical predictions of basic regularities of diffusion and relaxation in such systems and experimental results requires that some refinements of the type of 'constrain release' and 'tube relaxation or tube renewal' are introduced.[19,20]

The simplest version[13] of the reptation model describes the dynamic properties of a polymer melt in terms of the Rouse theory (R) if MM is smaller than a certain critical value M_c. In this case, the viscosity η should be proportional and the diffusion coefficient D inversely proportional to MM; hence, the product ηD is independent of MM. The dynamics of a macromolecule is determined by two characteristic scaling parameters: the segment length l and the mean square radius of the macromolecule coil $\langle R^2\rangle^{1/2}$. The dependence of the squared displacement of the central segment of the chain on time $g_m(t)$ obeys the following relations:

$$g_m(t) \propto \begin{cases} t \text{ if } g_m < l^2, \\ t^{1/2} \text{ if } l^2 < g_m < \langle R^2\rangle, \\ t \text{ if } g_m > \langle R^2\rangle. \end{cases} \quad (1)$$

At MM $> M_c$, the crucial role is played by the third scaling parameter, *i.e.*, the mean square radius of the chain between entanglements or the 'tube' radius $\langle R_e^2\rangle^{1/2}$. The dependence of viscosity and maximum relaxation time on MM should be exponential with the exponent equal to 3. The diffusion coefficient decreases proportionally to the squared MM; consequently, the product ηD is proportional to MM. The squared displacement of the central segment of the chain as a function of time $g_m(t)$ is determined by the following relations:

$$g_m(t) \propto \begin{cases} t \text{ if } g_m < l^2, \\ t^{1/2} \text{ if } l^2 < g_m < \langle R_e^2\rangle, \\ t^{1/4} \text{ if } \langle R_e^2\rangle < g_m < \langle R^2\rangle, \\ t^{1/2} \text{ if } \langle R^2\rangle \frac{N}{N_e} > g_m > R^2, \\ t \text{ if } g_m > \langle R^2\rangle \frac{N}{N_e}. \end{cases} \quad (2)$$

where N is the chain length and N_e is the chain length between entanglements.

Predictions of the dynamics of macromolecules have been the subject of both numerous experimental studies[10,14–23] and computer simulations.[24–38] In the latter case, the energy factor was not, as a rule, taken into account, since it was believed that only the excluded volume (the 'repulsive' part of the interaction potential) and impermeability of chains are significant. Unfortunately, there are virtually no studies (except for the investigations[29–32] on the behaviour of low-molecular chains of the type of paraffin oligomeric chains) in which the 'attractive' part of the interaction potential has been estimated. In short, '...the reptation hypothesis and models built thereon give an extremely good qualitative description of a broad range of experimental observations; in many cases, the agreement is quantitative. ...If it is more important for a good model to explain a wide variety of phenomena reasonably well than to be in precise agreement with a restricted set of observations, then reptation-based models must be viewed as extremely successful'.[19]

The existence of topological nodes in the structure of polymers is proved by their fixation upon cross-linking of linear polymers.[33] At a sufficiently high degree of cross-linking, the total number of nodes as determined from physical measurements exceeds the number of nodes calculated from the conditions of a chemical experiment by an amount which presumably corresponds to the number of entanglements (topological nodes) in a non-cross-linked system.[2]

For a number of polymeric systems[2,39,40] this finding was confirmed experimentally and by computer simulation.[41–44] However, there are data (see, *e.g.*, Ref. 45) which disprove this view.

Thus, it would seem that there are no reasons for casting doubts on the existence of entanglements as structural units and their role in the formation of relaxation properties of polymers. However, a detailed analysis of experimental results shows that such reasons exist.

III. Correlation between viscosity and viscoelasticity

It is usually assumed that the character of the dependence of viscosity on MM, a kink in the curve in the vicinity of certain 'critical' value of M_c[46] and the appearance of a high-elasticity plateau† are determined by the same factor, *viz.*, by the presence of topological nodes or entanglements of polymeric chains.[14] Therefore, it is natural to suggest if not equality, at least a correlation between the parameters M_e and M_c. However, back in 1974, Graessley[17] noticed that such a correlation does not exist and, what is more, the M_c values found from the results of viscosity and compliance measurements are conflicting. Having analysed 70 polymers, Aharoni[49] showed that despite the absence of a correlation between M_c and M_e definite correspondence can be revealed for small groups of similar polymers.[50,51] However, it should be noted that the values of both viscosity at finite concentrations of polymers and their MM exceed critical values and the elasticity moduli in the high-elasticity plateau region

† Based on the concepts of classical theory of network elasticity, the chain length between the network entanglements (M_e) may be calculated from the magnitude of the elasticity modulus in this region.[9,47,48]

depend on the size of the polymeric coil. This circumstance was apparently first brought to light by Fox [52] and this fact was repeatedly confirmed in later studies.[48, 53, 54] It has been shown that the M_c values for many polymers approximately correspond to one size of the macromolecular coil: the characteristic viscosity $[\eta]_c$ corresponding to the M_c value of different polymers amounts to ~ 13 dl g^{-1} (26 polymers were analysed). This conclusion was confirmed by Chee [53] (35 polymers) and He and Porter [54] (37 polymers). The latter study has shown that the mean square radius of the coil of the critical size of a macromolecule $\langle R_e^2 \rangle^{1/2}$ is constant and equal to about 4 nm (the spread of values from 1.3 nm for poly(oxy-2,6-dimethyl-1,4-phenylene) to 5.9 nm for poly(dodecyl methacrylate).

An illustrative example of the invariance of the coil critical size was given in a study of Baird and Ballman.[55] The dependence of viscosities of the rigid-chain poly(*p*-phenylene terephthalate) (the persistence length $A = 130$ nm, $M_c = 1180$) and the flexible-chain nylon-6,6 ($A = 9.4$ nm, $M_c = 5300$) on MM is the same, if not the MM proper but the polymer coil size (characteristic viscosity) is used as the argument. Table 1 contains the values of characteristic

Table 1. Parameters of a macromolecular coil under critical conditions.

Polymer	M_c (see Ref. 49)	$10^4 K_\theta$ /dl g^{-1}	$[\eta]_c$ /dl g^{-1}	ρ /g ml^{-1}	$[\eta]_c\rho$	$\langle R^2 \rangle^{1/2}$ /nm
PE	3500[a]	22.5[a]	–	0.85[a]	–	2.67[e]
PPr	6890	15[b]	0.125	0.85[b]	10.6	2.73
PB	–	–	–	–	–	4.73[e]
PIB	16020	10[b]	0.127	0.86[b]	10.9	3.64
cis-PB	5940	17[b]	0.131	0.92[c]	12.0	2.64
cis-PI	7650	11.9[c]	0.104	0.906[c]	9.4	2.66
PDMS	24500	7.8[d]	0.122	0.970[d]	11.0	4.14
PS	35000	8[b]	0.150	1.06[c]	15.9	4.99
PVA	24540	8.6[d]	0.134	1.108[d]	14.5	4.28
PVC	6250	12.5[b]	0.099	1.38[c]	13.7	2.45
PAA	–	–	–	–	–	4.44[e]
PAM	–	–	–	–	–	2.47[e]
PAN	1330	22.5[b]	0.082	1.154[c]	9.5	1.37
PMMA	31530	6.5[b]	0.115	1.19[c]	13.7	4.42
PBMA	60435	2.95[c]	0.073	1.05[c]	7.7	4.70
PHMA	91900	4.3[c]	0.130	1.007[b]	13.1	6.57
POMA	114000	5.2[b]	0.062	0.971[b]	6.0	7.80
PDDMA	18640[a]	3.5[a]	–	0.98[a]	–	5.89[e]
PEBMA	–	–	–	–	–	3.45[e]
PEO	4410	13[c]	0.086	1.13[b]	9.7	2.08
P-ε-CL	5020	25.3[c]	0.179	0.985[d]	17.6	2.77
PMA	24100	7.2[d]	0.112	1.11	12.4	4.80
1,2-PB	4110	12.5[d]	0.080	0.899	7.2	1.98
PTMO	2530[a]	23.1[a]	–	0.98[a]	–	2.01[e]
PPO	7750	11.6[d]	0.102	1.000	10.2	2.98
P-α-MS	40800	7.4[c]	0.1495	1.04	15.5	5.25
P-*p*-MS	5010[a]	6.9[a]	–	1.04[a]	–	–
P-*m*-MS	–	–	–	–	–	4.48[e]
PTFE	6000[b]	17.8[b]	0.14[b]	–	–	2.69[e]
	3270[a]	21.0[a]	–	1.34[a]	–	–
PEIP	–	–	–	–	–	1.63[e]
PETP	–	–	–	–	–	2.50[e]
PDMP	–	–	–	–	–	1.28[e]
PC	3000[b]	21.4[b]	0.12[b]	–	–	1.88[e]
PDeMS	4000[b]	19.6[b]	0.12[b]	–	–	2.54[e]
PTMA	6000[a]	19.0[a]	–	1.02[a]	–	–
	6000[b]	19.0[b]	0.15[b]	–	–	–
PDeMA	4500[b]	19.8[b]	0.13[b]	–	–	2.53[e]
PDeS	4000[b]	20.2[b]	0.13[b]	–	–	2.57[e]
PHMS	–	–	–	–	–	2.55[e]
PVCz	27100[a]	7.6[a]	–	1.19[a]	–	–
PPS	20 000[a]	6.0[a]	–	1.04[a]	–	–
PVN	14700[a]	6.5[a]	–	1.19[a]	–	–

[a] Data from Ref. 53; [b] data from Ref. 48; [c] data from Ref. 57; [d] data from Ref. 58; [e] data from Ref. 54.

Note. PE, polyethylene; PPr, polypropylene; PB, poly(1-butene); PIB, polyisobutylene; *cis*-PB, poly(*cis*-1,4-butadiene); *cis*-PI, poly(*cis*-1,4-isoprene); PDMS, polydimethylsiloxane; PS, polystyrene; PVA, poly(vinyl acetate); PVC, poly(vinyl chloride); PAA, poly(acrylic acid); PAM, polyacrylamide; PAN, polyacrylonitrile; PMMA, poly(methyl methacrylate); PBMA, poly(n-butyl methacrylate); PHMA, poly(n-hexyl methacrylate); POMA, poly(n-octyl methacrylate); PDDMA, poly(dodecyl methacrylate); PEBMA, poly(2-ethylbutyl methacrylate); PEO, poly(ethylene oxide); P-ε-CL, poly(ε-caprolactam); PMA, poly(methyl acrylate); 1,2-PB, poly(1,2-butadiene); PTMO, poly(tetramethylene oxide); PPO, poly(propylene oxide); P-α-MS, poly(α-methylstyrene); P-*p*-MS, poly(*p*-methylstyrene); P-*m*-MS, poly(*m*-methylstyrene); PTFE, polytetrafluoroethylene; PEIP, poly(ethylene isophthalate); PETP, poly(ethylene terephthalate); PDMP, poly(2,6-dimethyl-1,4-phenylene); PC, poly(bisphenol A carbonate); PDeMS, poly(decamethylene succinate); PTMA, poly(tetramethylene adipate); PDeMA, poly(decamethylene adipate); PDeS, poly(decamethylene sebacate); PHMS, poly(hexamethylene sebacate); PVCz, polyvinylcarbazole; PPS, poly(propylene sulfide); PVN, poly(2-vinyl naphthalate).

viscosity $[\eta]_c$ for different polymers. The coil radius was calculated by the Flory – Fox formula [56]

$$\langle R_c^2 \rangle^{1/2} = \frac{([\eta]_\theta M_c)^{1/3}}{\Phi},$$

where $[\eta]_c$ is the characteristic viscosity of the θ-coil and $\Phi = 2.87 \times 10^{21}$. It is seen that the values of the critical radii of the coils of different polymers are close.

Antonietti *et al.*[59] have shown that macromolecules of polystyrene with different topologies (linear, cyclic and star-like with different numbers of branches and microgel spheres) also exhibit the same dependence of viscosity on MM if the argument is the polymer coil size. An analogous result was also obtained for other types of polymers, *viz.*, rigid-chain,[60] liquid-crystalline,[61] comb-shaped,[62] and branched [63,64] ones. The use of characteristic viscosity allows unification of the data on viscosity of different polymer systems over a wide concentration range.[65]

Such a similarity of the behaviour of macromolecules (including highly cross-linked globules) which differ greatly in their nature and topological type is often interpreted from a purely geometrical viewpoint: entanglements can arise only when the coils overlap, *i.e.*, when the total volume of coils (the product of the coils concentration by the macromolecular coil volume) is larger than the system's volume. The criterion ratios proposed by different authors [49,52–54,66,67] differ in minor details. However, the fact that dense globules [59] and rigid rods [60] obey the same regularity casts doubts on the validity of the topological approach.

The data on the correlation between the elasticity moduli G_e in the high-elasticity plateau region and the molecular characteristics of block polymers have been analysed.[13,49,54,57,68] The value of the effective volume of the network of entanglements ($[\eta]_\theta$)‡ was found to be constant irrespective of the magnitude of M_c, which is determined by the nature (rigidity) of a polymeric chain (Table 2). However, the product $[\eta]_\theta \rho$ is somewhat smaller (~ 8 cm^3 g^{-1}, on the average, for the polymers studied) than that derived from viscosimetric measurements (13 cm^3 g^{-1}). At the first glance, this result does not contradict the simple network model according to which

$$M_c = 2M_e .$$

However, it should be noted that the same regularities are characteristic of both rigid rods [60] and dense highly cross-linked globules [59] as well as latex dispersions,[69] *viz.*, at definite concentrations and/or MM of polymers, the polymeric systems exhibit viscoelastic properties. Evidently, the elastic properties are determined by the network structure resulting from intermolecular interactions which are apparently of an energetic nature.[61,70] The viscoelastic properties of comb-like polymers are presumed to be also determined by intermolecular interactions due to the side groups.

Table 2. Characteristics of the chains of a network of entanglements.

Polymer	M_e	$[\eta]_\theta$ /cm^3 g^{-1}	$[\eta]_\theta \rho$
PE	828[a]	6.47	5.1
PEO	1624[a]	5.24	5.6
PPr	4623[a]	10.20	8.0
PMMA	10013[a]	6.50	7.4
PS	13309[a]	9.23	8.9
PDMS	12293[a]	8.60	7.7
cis - *trans*-PB	2300[b]	9.8	–
cis - *trans*-PI	3900[b]	9.9	–
PEB	5500[b]	9.6	–
PPB	8000[b]	9.8	–
PBB	10800[b]	10.2	–
PIPB	8000[b]	9.8	–
PIBB	1080[b]	10.2	–
cis-PB	3500[b]	10.1	9.3
cis-PI	4500[b]	8.7	7.9
PMB	4400[b]	10.5	–
PP	3600[b]	10.0	–
SKS-25	3450[b]	10.4	–
BPR	2400[b]	10.1	–
EPR	2100[b]	8.9	–
SKF-260	6200[b]	8.7	–
SKF-260 MP	10500[b]	6.15	–
PPO	4500[b]	7.8	7.8
PTMO	2000[b]	10.3	10.1
PIB	8000[b]	10.2	8.8

[a] Data from Ref. 57; [b] data from Ref. 68.

Note. PEB, polyethylbutadiene; PPB, polypropylbutadiene; PBB, polybutylbutadiene; PIPB, polyisopropylbutadiene; PIBB, polyisobutylbutadiene; PMB, polymethylbutadiene; PP, polypiperylene; BPR, butadiene – propylene rubber; EPR, ethylene – propylene rubber; SKS-25, SKF-260 and SKF-260 MP, synthetic rubber brands.

IV. Regularities of viscous flow

It is believed that the viscosities of polymers strongly depend on MM (MM > M_c) and concentration of the polymers (exponents of 3.4 and ~ 5, respectively) and are determined by the formation of interchain topological nodes called entanglements (see, *e.g.*, Refs 9, 10, 12–14, 16–19, 46, 71). The entanglements arise in the concentration region where mutual penetration of polymer coils resulting in a cooperative flow of polymer chains occurs. It is presumed [10,12,13] that in the frame of the reptation model, the translation diffusion of polymer chains during such a flow is restricted by the 'tube', *i.e.*, it becomes substantially anisotropic.

Changes in the size of a macromolecular coil upon concentration of a solution are highly important in the studies of the dependence of the viscosity of a polymer solution on the concentration and MM of this polymer. The dependence of the size of a macromolecular coil on the polymer concentration in the range of semidilute and concentrated solutions was investigated both theoretically [10,13,72,73] and experimentally.[74–76] Flory [77] was the first to notice that the coil changes its dimensions upon transition from dilute to concentrated solutions. In the isolated state (in a dilute solution), the conformation of macromolecules is determined by the competition of two factors, *viz.*, the effect of excluded volume and the energy of interaction of monomeric units with the medium (in an athermal solution where the interaction energy does not play any role and the coil swells owing to the effect of excluded volume), while, according to Flory, the coil should have the θ-dimensions in the bulk.

Edwards *et al.*[13,73] proposed a theory based on the idea of screening of the energy of repulsion of monomeric units of the same chain by the units of the neighbouring chains. With such a screening, the effect of excluded volume is neutralised: as in the case of dilute solutions, the energy of repulsion of monomers of the same chain is compensated by the energy of their attraction owing to the interaction with the monomeric units of the neighbouring chains. In this case, the principal role is played by the entropy factor the nature of which has been clearly explained by de Gennes in a simple example.[10] The entropic nature of this factor is manifested in that the temperature factor influences the size of the θ-coil in a melt to a substantially lesser extent than in a dilute solution.[78]

For the same reason, the concentration dependences of the swelling coefficient shown in Fig. 1 comprise two regions: in the first region, the shape of the curve is substantially dependent on the nature of the solvent and the curve may be monotonic or have

‡ As in this case one deals with the bulk polymers, the macromolecular coil has the θ-dimensions.

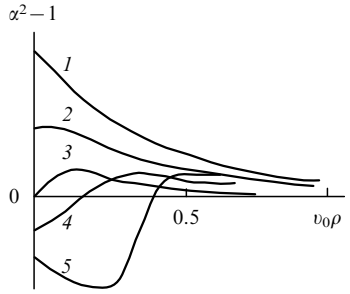


Figure 1. Dependence of the swelling coefficient α on the concentration of polymer segments ρ in a solution at different temperatures (differing solvent quality).[72]
$(1-\theta/T)N$: (*1*) > 0.75, (*2*) 0.75, (*3*) 0; $|1-\theta/T|N$: (*4*) < 0.75, (*5*) > 0.75.
υ_0, segment volume; θ, Flory temperature; N, chain length.

extrema (the region of dilute solutions); in the second region, the shape of the curve is the same for solvents of any type.

Variation of the size of a macromolecular coil as a function of the polymer solution concentration is described by power dependences, for example:[13]

$$\frac{\langle R^2\rangle}{\langle R^2\rangle_\theta} - 1 \propto c^{1/2} \text{ or } R_g = R_g^0\left(\frac{c}{c^*}\right)^{2\nu-1/2(1-3\nu)},$$

where R_g is the hydrodynamic radius of the polymer coil, c^* is the critical concentration (the boundary between dilute and semidilute solutions), ν is the power index in the relation

$$\langle R^2\rangle^{1/2} \propto M^\nu,$$

where M is the molecular mass of a polymer.

Usually, experimental data are also presented in the form of power dependences.[74, 79]

It should be noted that the above dependences can serve as estimates. As is mentioned in the monograph of Doi and Edwards,[13] 'the scaling argumentation gives only a qualitative picture of the dependence on basic parameters'.

The sought dependence of the macromolecular coil size on the polymer concentration may be derived by analysing computer simulation models.[79–81] As a rule, these models take into consideration only the factor of the excluded volume, *i.e.*, the repulsive part of the interaction potential. This means that the computer simulation techniques investigate athermal systems.

The results of such simulations indicate[79, 80–82] that the following simple relation is obeyed over the entire concentration range (Fig. 2 *a*).

$$\frac{V_c}{V_0} = \frac{1}{1+\gamma c}, \qquad (3)$$

where V_c and V_0 are the coil volumes at the concentration c and in an extremely dilute solution, respectively; γ is a coefficient.

The coefficient γ depends on the chain length N (Fig. 3)

$$\gamma = N^a,$$

where the exponent a is equal to 1 for short chains and $a \simeq 0.34$ for long chains. Such a character of the dependence may be explained qualitatively by the relationship between the coil size and the length of the chain contour: the linear dependence in the first case and the exponential dependence with the exponent 1/2 in the second case.

The validity of relation (3) is illustrated in the experiments showing the effect of 'thickening' (increase in concentration) of a polymer solution on the diffusion of macromolecular coils,[83] viscosity[2, 84, 85] and characteristic viscosity of the polymer.[86–90] For corresponding analysis of the experimental results, see Ref. 82.

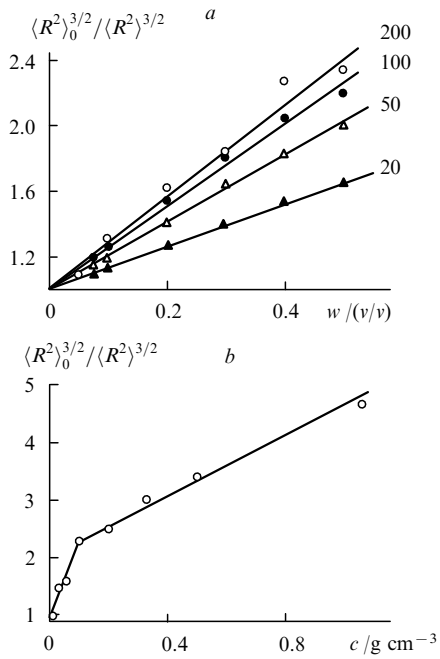


Figure 2. Dependence of the size of a macromolecular coil on the polymer concentration in the coordinates of Eqn (3); (*a*), data from computer simulation,[81] the numerals at the straight lines indicate the chain length; (*b*), system PS – carbon disulfide.[74]

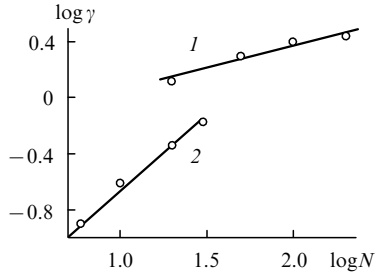


Figure 3. Dependence of the coefficient γ from Eqn (3) on the chain length according to the data reported by de Vos and Bellemans[79] (*1*) and Paul *et al.*[81] (*2*).

By comparing changes in the diffusion coefficients of a rigid sphere (chloroform as the solvent) and a macromolecular PS coil (toluene as the solvent) upon concentration of solutions in the PMMA concentration range from 0% to 5%, Brown and Rymden[83] have concluded that the size of the coil of the PS macromolecule depends on the 'thickener' concentration. As the molecular masses of PS and PMMA are high (ranging from 1.26×10^6 to 15×10^6 for the former and from 1.01×10^5 to 4.45×10^5 for the latter), the solutions in the above-mentioned concentration range are regarded, if not as concentrated, at least as semidilute ones for which the entropy factor is decisive.

In the experiments[86] on measuring the characteristic viscosity of PS (MM = 3.5×10^6) in a mixture of bromoform with PS with MM = 0.46×10^5 or PS with MM = 1.1×10^6 as the 'thickener', the interval of the system's volume 'packing' {parameter $[\eta]c$} is overlapped almost 10 times which is undoubtedly indicative of the transition to the region of concentrated solutions.

The results of the studies on the variation of the coil size as a function of concentration of polymers obtained by the neutron scattering method (Fig. 2 *b*)[74] are not described by relation (3). Possibly, in this system the break in the straight line corresponds to the critical concentration of transition from a dilute solution to semidilute one, *i.e.*, the energy factor plays the decisive role in the initial stage. Daud *et al.*[74] used carbon disulfide which is a good

solvent. There are no accurate data on the characteristic viscosity of PS in this solvent, although it may be assessed using the Mark – Kuhn equation

$$[\eta] = KM^a ;$$

if it is assumed that $K = 1 \times 10^{-4}$ dl g^{-1} and $a = 0.72$,[58] then $[\eta] = 0.44$ dl g^{-1}, while the critical concentration is ~ 0.02 g ml^{-1}. Of course, these values are lower than the value of characteristic viscosity corresponding to the inflection point on the graph, though they are close in their orders of magnitude.

It is also possible that a definite role in the above discrepancy is played by some additional factors, *e.g.*, the sample prehistory.[91]

Thus, the analysis of experimental data and results of computer simulation make it possible to conclude that formula (3) may be used for the description of the concentration dependence of the coil size in the range of semidilute and concentrated solutions of polymers.

It is noteworthy that relation (3) is a consequence of the dependence established for dilute solutions [84, 85]

$$V_c = V_0 (1 - \gamma[\eta]c + ...) . \quad (4)$$

For low concentrations of polymers

$$V_c - V_0 = -kV_0^2 c , \quad (5)$$

since

$$[\eta] \propto V_0 .$$

If the latter expression is assumed to hold for finite values of concentration c, then Eqn (5) may be presented in form of the differential equation

$$dV = -kV^2 dc, \quad (6)$$

from which Eqn (3) is derived by integration. It is seen that the coefficient

$$\gamma = kV_0$$

is a function of MM.

The fact that the principal quantity in Eqn (3) is the product $[\eta]c$ means that the scaling relations are virtually fulfilled,[10, 13] *i.e.*, the macromolecular coil size depends on the dimensionless parameter c/c^*.

Equation (6) is valid over the entire range of concentrations for both dilute and concentrated solutions of polymers (the differing k values, see Fig. 2*b*). This means that a polymeric solution of any concentration acts as a continuous medium for a macromolecular coil and that there is no difference in principle between the solvent and the polymer solution: the difference is purely quantitative due to different energetic interaction of the polymer chain with the medium and viscosity, which is confirmed by diffusion experiments.[83]

This may also mean that macromolecular coils behave independently during the flow of a polymeric solution and/or a melt *viz.*, interactions of the entanglement type do not affect the viscosity. In other words, Eqn (3) holds over the entire range of polymer concentrations (up to its melt).

This hypothesis formed the basis for the analysis of the viscosity dependence on the concentration and MM of a polymer.[2, 92–95] It turned out that over a certain concentration interval depending on the glass transition temperature of a system, all polymers obey the following law:

$$\ln \eta_{rel} = K^{-1} \ln[1 + K[\eta]_c (c - c^*)] , \quad (7)$$

where $\eta_{rel} = \eta/\eta_c$, η_c is the viscosity of a polymer solution at the critical point, $[\eta]_c$ is the characteristic viscosity of a polymer at the critical point, $K = 0.125$ for all the polymers studied.

As an example, Fig. 4 shows the data on the viscosity of polydimethylsiloxane solutions in siloxane pentamer.[96] The curves plotted in the coordinates of Eqn (7) are straightened over the entire range of concentrations and MM, the straight line slope {the product $K[\eta]_c$} being dependent on MM in conformity with

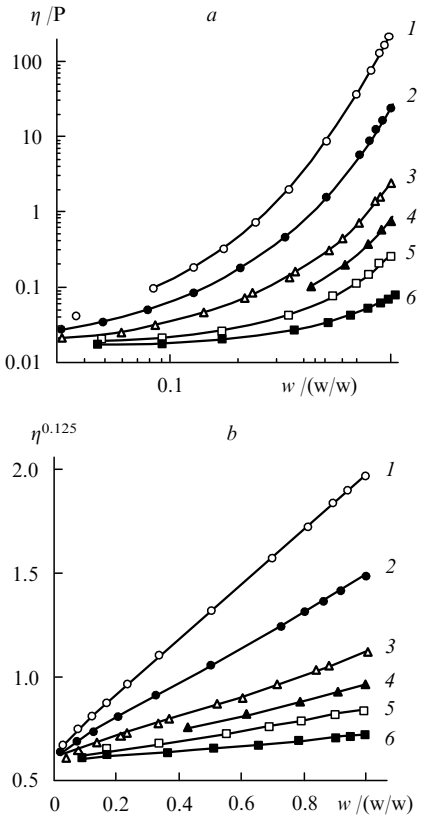


Figure 4. Dependence of the viscosity of polymethylsiloxane on its MM and concentration in the siloxane oligomer with the chain length equal to 5 plotted in the logarithmic coordinates (*a*) and the coordinates of Eqn (7) (*b*);[96] $10^3 M_w$: (*1*) 490; (*2*) 152; (*3*) 88; (*4*) 36; (*5*) 11.2; (*6*) 2.9.

the Mark – Kuhn equation. In this case, the exponent a is equal to 0.54, which is somewhat larger than under θ-conditions but smaller than in an athermal solution. Analogous conclusions have been drawn from other studies.[89, 94] The corresponding data are listed in Table 3.

According to the data reported by Kataoka and Ueda,[96] the M_c of the bulk polymer is 27 000 (30 000, according to Ref. 48). However, there is no kink in the dependence of viscosity on MM plotted in the coordinates of Eqn (7) (Fig. 5*a*). Naturally, such a kink will certainly be absent at lower polymer concentrations.

The results obtained may be suggested to be due to that the polysiloxane fractions had a broad molecular-mass distribution ($\overline{M}_w/\overline{M}_n \approx 2$). However, the data on the viscosity of PS [59] with a rather narrow molecular-mass distribution ($\overline{M}_w/\overline{M}_n \geqslant 1.1$) and of polybutadienes [102] also with a narrow molecular-mass distribution over a very wide MM range (from 10^3 to 10^7) point to the preservation of the above regularity (Fig. 5*b*). The linear law

Table 3. Parameters of the Mark – Kuhn equation for the critical point.[94]

Polymer	$10^4 K$ /dl g^{-1}	a	Ref. [c]
PDMS	5.8	0.54	96
PIB [a]	9.7	0.50	97
PIB [b]	–	0.53	98
PVA	2.95	0.56	99
PVC	3.2	0.66	100
P-α-MS	–	0.4	101

[a] Solvent, xylene. [b] Solvent, carbon tetrachloride. [c] The references comprise the studies the results of which were used to calculate parameters of the Mark – Kuhn equation.

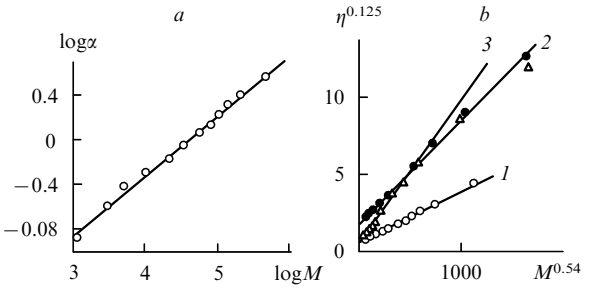


Figure 5. Dependence of Eqn (7) parameters on MM of polydimethylsiloxane [96] (*a*) and bulk polydimethylsiloxane [96] (*1*), PE [59] (*2*) and polybutadiene [102] (*3*) (*b*); α is the slope of the straight lines in Fig. 4 *b*.

holds up to MM of the order of 10^6. Deviation from the linearity observed for samples with larger MM may be due to their higher polydispersity. It should be noted that an analogous deviation from linearity is observed in double logarithmic coordinates.

The conclusion about the independence of macromolecular coils in concentrated solutions was confirmed by the data on the relationship between the solution viscosity and the longest relaxation time (τ) determined from the critical gradient rate in the longitudinal flow of solution between two coaxial capillaries.[87] It was shown that the following relation holds over a wide range of polymer concentrations

$$\tau = A\frac{M[\eta]\eta_0}{RT},$$

where A is a coefficient and η_0 is the solvent viscosity. In this equation which is valid for dilute solutions,[56] the role of the solvent viscosity is played by the solution viscosity.

The above results make it possible to conclude that the critical conditions under which a kink in the plot of the viscosity dependence on MM and concentration of a polymer is observed, are not associated with the transition of the individual flow of coils into a cooperative one. This artefact is determined by the representation of the sum of two magnitudes in logarithmic coordinates [see Eqn (7)].

Apparently, the reptative character of the displacement of chains in the flow of polymer solutions is manifested at the MM and concentrations of polymers which are appreciably larger than the critical ones. Thus it was suggested that [13] the true reptation manifests itself in the range of MM of about 800 M_e, *i.e.*, the values of the order of tens of millions.

V. Diffusion of macromolecules

Various aspects of the translational diffusion of polymers have been reviewed by Green.[20] In experiments, the criterion of transition from the R-dynamics to the reptation dynamics was the dependence of the diffusion coefficient on the molecular mass of the chain, which is linear in the R-model and quadratic in the reptation model. Various methods (ranging from radioactive labelling NMR spectroscopy) and different polymers (PS, PE, PDMS, *etc.*) were used for deriving quantitative data. Having analysed the available experimental results concerning the diffusion of polymers in bulk and in mixtures, Green [20] concluded that the diffusion coefficient depends on the mixture composition, the dependence being often non-monotonic.

In many cases, the validity of the dependence characteristic of the reptation mechanism was revealed.

$$D \propto M^{-a},$$

where $a = 2$. It should however be emphasised that in the graphs plotted from the results of Green's study [20] all the points fall onto the same straight line for both MM > M_c and MM < M_c. At the same time, this author points to numerous data which show that the exponent a for the polymers with MM substantially higher than M_c is markedly smaller than 2 (*e.g.*, for PDMS [103]). In the case of polyisoprene,[20] this exponent is, on the contrary, close to 3, while in the 60% solution of PS in dibutyl phthalate [104] $a = 2.6\pm0.2$. Comparative investigation of the dependences of viscosity and diffusion of hydrogenated polybutadiene has been carried out by Pearson *et al.*,[105] who have shown that at the MM much higher than M_e (MM > $9M_e$) the following relation is respected

$$(D\eta)_{rep} = (D\eta)_R\left(\frac{M}{M_e}\right),$$

where the subscripts 'rep' and 'R' denote the reptation and Rouse models, respectively.

Similar results were obtained for PS and hydrogenated polyisoprene. It was proposed to describe diffusion in the general form using the expression

$$D\eta = (D\eta)_{rep} + (D\eta)_R = (D\eta)_R\left[1 + \left(\frac{M}{M^*}\right)^d\right],$$

where $M^* = (9.5\pm1.1)M_e$ and $d = 1.5\pm0.1$.

In order to describe the dependence of diffusion coefficient on MM and concentration of a polymer, more complex expressions are used, in particular the 'stretched' exponent:[106, 107]

$$D \propto \exp(-kM^b),$$

where $b = 1$ for low MM and $b < 1$ for high MM. Such a character of the dependence is related [108] to the Kohlrausch–Williams–Watts law.[109] This expression is empirical but this does not prevent its use because the power dependences fit experimental results poorly. Indeed, the results reported by Pahl *et al.*[110] indicate that the dependence of the diffusion coefficient of PDMS (with MM ranging from 118 000 to 716 000) on MM is an exponential function rather than a power one. These investigators revealed a trend towards the transition of the translational diffusion to the reptation regime; however, the reptation regime was not achieved because of the time limit ($\sim$ 1 s, with the use of NMR in a gradient field).[110]

Experimental studies of diffusion were carried out in dilute and semidilute solutions of polymers using different methods, in particular NMR spectroscopy in a gradient field,[22, 29, 111, 112] dynamic light scattering [113] and neutron spin echo.[23, 114]

The dependence of dynamic (including also diffusive) characteristics of macromolecules on the solution concentration is determined by the characteristic parameter ξ, *viz.*, the correlational length of the excluded volume.[10, 13] The dependence of this parameter on concentration, for example, for a semidilute solution is as follows:

$$\xi \propto c^{-\nu/(3\nu-1)} \propto c^{-3/4}.$$

With the consideration of this formula, the diffusion coefficient of a polymeric chain in the range of concentrations corresponding to semidilute solutions is expressed as

$$D \propto N^{-2}c^{-1.75}.$$

As noted above, experimental results are more likely to indicate an exponential function.[106, 107, 115] Thus depending on the nature of the solvent and the polymer, the value of power ν in the 'stretched' exponent varied from 0.42 to 2.21.[115] In addition, ν depends on MM

$$\nu \propto M^{-0.25}$$

as results from the analysis of more than 40 systems show.

The validity of specific models is confirmed by the results of computer simulation of the dynamics of polymers[116, 117] using molecular dynamics [30, 32] and Monte Carlo methods.[118–124]

Despite its somewhat artificial character, the Monte Carlo method is often used in studies of physical properties of polymers,[31] and it was this method that provided basic information on the dynamics of macromolecules. As the investigation of dense

(bulk) systems by computer simulation techniques is a rather complex problem, the concentration factor was found to play a substantial role: basic results were obtained for the systems in which the polymer concentrations did not exceed 50%.

With the Monte Carlo method, the main attention is paid to the investigation of the dependence of the chain diffusion coefficient on the concentration and MM.[118] In this context, the following trends have been brought to light:

(i) as the concentration increases, the power index a in the dependence of maximum relaxation time τ on MM

$$\tau \propto N^a$$

varies from 2 to 3, which corresponds to the change in the conditions of chain displacement, *i.e.*, from the R-regime to the reptation regime;

(ii) at low concentrations, the temporal dependence of the displacement of the macromolecule mass-centre obeys the relation

$$g_m \propto t^{0.54};$$

(iii) as the concentration increases, the power index approaches 0.50, which is related to the above-discussed compression of the polymer coil to the θ-dimensions;

(iv) the squared shear of the inner monomeric chain depends over some time interval on the current time (t)

$$g_m \propto t^{0.3},$$

which is interpreted as manifestation of the reptation mechanism in which the power index should be equal to 0.25.

It should be noted that the extension of the results obtained to the range of polymer concentrations close to 100% leads to a paradoxical conclusion that the dependences of diffusion coefficient and maximum relaxation time on MM become stronger than those predicted by the reptation model: the power indexes increase to 2.4 and 3.6, respectively.[120] Furthermore, restriction of the lateral shift of the segregated chain was revealed solely in the case on 'frozen' environments. If in a mobile system, all chains are equally mobile, the 'tube' effect, expressed in the anisotropy of the differentiated chain motion, is not manifested.

On the other hand, the analysis of the dependences of the diffusion coefficient D and maximum relaxation time τ reported by Paul *et al.*[81, 119] shows that the relationship between τ and D^{-1} is linear over the entire range of concentrations studied for all lengths of chains and for all lengths of chains except for 20 (*i.e.*, 50, 80, 100, 200), a single dependence has been established (Fig. 6 *a*)

$$\frac{\tau}{N^2} = \frac{2.6 + 0.027}{D\langle R^2\rangle^{1/2}}.$$

This formula expresses essentially the Stokes law in which the minimum time of R-relaxation τ/N^2 plays the role of viscosity, whereas the concentration is implicitly accounted for in the values of τ and $\langle R^2\rangle$. Here, the minimum relaxation time§ should not depend on the concentration and MM of a polymer due to the effect of hydrodynamic screening.[13] However, as one can see from the data shown in Fig. 6 *b*, such a dependence does exist: the minimum relaxation time is functionally related to the length of the polymeric chain and its solution concentration. It should be emphasised that the dependences observed are linear in the corresponding coordinates and that they have no kinks, which could suggest the transition from the R-mode of relaxation to the reptation regime. Consequently, as in the case of maximum viscosity, cooperativity is not manifested in slow processes of macromolecular diffusion.

VI. Stress relaxation

In the curves of the stress relaxation of linear polymers with a narrow molecular-mass distribution, one can differentiate several zones corresponding to different states of the system:[125] glassy, transient, highly elastic (plateau of high elasticity) and terminal states (see, *e.g.*, Fig. 7 *a*). It is seen that MM has no effect on the shape of relaxation curves in the glassy and transient states, this effect being manifested only at the end of the high-elasticity plateau, *viz.*, in the terminal zone. This fact is well known. The high-elasticity modulus exhibits rather small variation in the plateau region. A drastic drop of this modulus (by 90% and

§ This magnitude corresponds to the friction coefficient of a bead of the R-chain. According to the R-model, the polymeric chain is a system of beads (friction elements) connected by elastic elements.

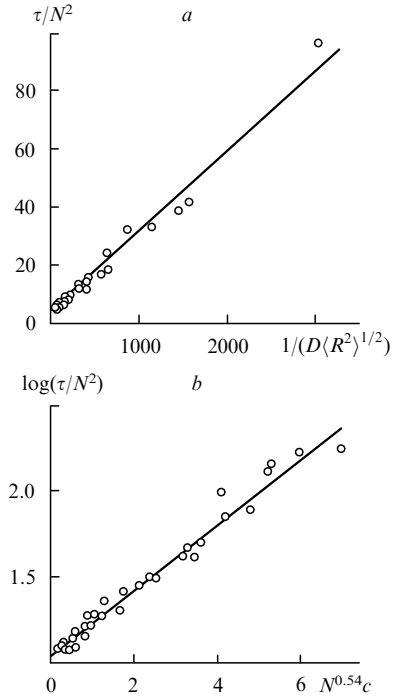


Figure 6. Dependence of the minimum time of R-relaxation τ/N^2 on the macromolecule size:[81, 119] (*a*) in the Stokes equation coordinates; (*b*) concentration dependence.

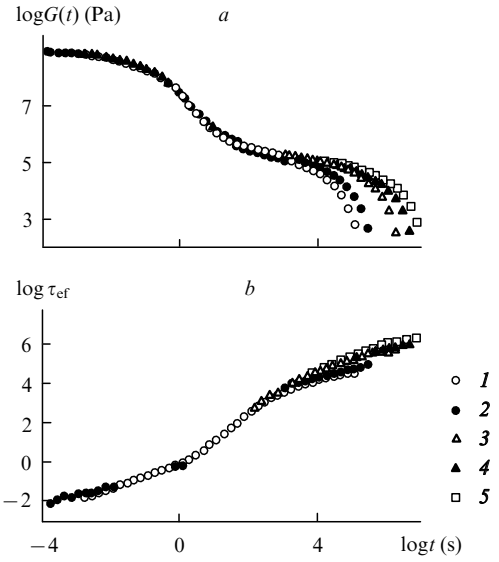


Figure 7. Curves of relaxation of the stress of PS with a narrow molecular-mass distribution;[126] (*a*) elasticity modulus; (*b*) effective time of relaxation; $10^{-3}M$: (*1*) 80; (*2*) 125; (*3*) 193; (*4*) 239; (*5*) 267.

more) occurs in the terminal zone, and the kinetics of its decrease strictly obeys the exponential law.

All the zones corresponding to the above-listed ranges are clearly seen in the curves of the dependence of effective relaxation time τ_{ef} on the current time (Fig. 7 *b*) [126]

$$\tau_{ef} = -\left(\frac{d\ln G(t)}{dt}\right)^{-1} . \quad (8)$$

The relaxation time is approximately proportional to the square root of the time in the region of the transient state, this dependence is almost linear (the power index is slightly larger than 1) in the high-viscosity region, then it weakens in the region where MM begins to have its effect and, finally, the relaxation time becomes invariant with time, *i.e.*, $\tau_{ef} = \tau_{max}$.

The data reported by other investigators [127–129] confirm the above-noted regularities of changes in the stress relaxation. The maximum time of relaxation is MM-dependent (Fig. 8)

$$\tau_{max} \propto M^4 .$$

However, this law cannot always be revealed. Indeed, as is seen from the data shown, on the one hand, if the MM interval is not too large, the regularity may be distorted. On the other hand, relaxation measurements of polymers in a wide MM range are usually performed at strongly differing temperatures, and the use of the temperature–time superposition principle reduces them to a certain selected temperature. Minor inaccuracies in such normalisation may lead to some errors (Fig. 8). The analysis of the whole body of available data provides evidence that it is the above-mentioned law that is observed.

Let us emphasise that the data shown in Figs 7 and 8 refer to polymers with a narrow molecular-mass distribution; therefore, the peculiarities of the stress relaxation noted above are characterised namely by the dependence on the chain length.

It is presumed that the relaxation of relatively short chains is well described by the R-model, while the relaxation of fairly long chains is fitted by the Doi–Edwards (DE) model. Herewith, the R-relaxation occurs in a small segment of the transient zone, which adjoins the high-elasticity plateau and is characterised by the exponential dependence of relaxation on the current time with the exponent 1/2.[13] However, a thorough analysis [130] of the shape of the relaxation curves corresponding to the R- and DE-models has shown (Figs 9 and 10) that one can differentiate three segments (in the logarithmic coordinates) in the dependence of the elasticity modulus relaxation on time

$$\frac{G(t)}{G(0)} = \frac{1}{n}\sum_{p=1}^{n} \exp\left(-\frac{p^2 t}{\tau_{max}}\right) , \quad (9)$$

where

$$G(0) = \frac{6n}{\pi^2 \tau_{max}} \left(\int_0^\infty G(t)dt\right)^{-1} \quad (10)$$

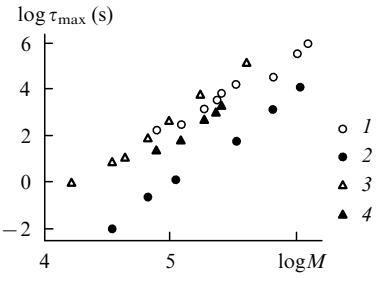


Figure 8. Dependence of the maximum relaxation time on MM of PE according to the data of Akovali [127] (*1*), McGrory and Tuminello [128] (*2*), Lin [129] (*3*) and Aklonis and Tobolsky [126] (*4*). Normalised temperature/°C: (*1* and *4*) 129; (*2*) 160; (*3*) 127.5.

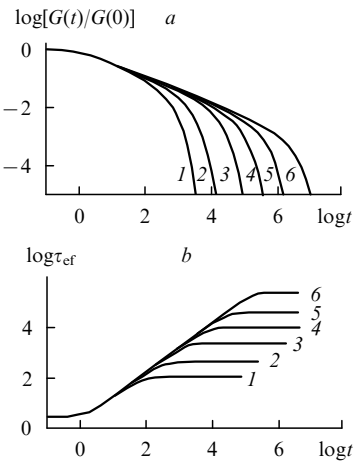


Figure 9. Curves of the stress relaxation (*a*) and the temporal dependence of the effective time of R-relaxation (*b*) according to Eqns (8)–(10). The chain length: (*1*) 11; (*2*) 21; (*3*) 51; (*4*) 101; (*5*) 201; (*6*) 501.

where τ_{max} is the maximum relaxation time and n is the R-chain length.

These are

(i) the linear segment for the interval of relative relaxation $\sim 0.9 < G(t)/G(0) < 1$ and $t/\tau_0 \leqslant 1$ (τ_0 is the minimum time of R-relaxation);

(ii) the segment of the power dependence with the power index 1/2 for the interval $0.1 < G(t)/G(0) < 0.9$ (depending on the chain length, the left limit may be smaller)

$$\frac{G(t)}{G(0)} \propto \left(\frac{t}{\tau_0}\right)^{-1/2} ,$$

this relaxation interval corresponds to the time t of variation of the relaxation time from its minimum to maximum value;

(iii) the segment of the exponential decay of the relaxation modulus

$$\frac{G(t)}{G(0)} \cong \frac{1}{n} e^{-t/\tau} .$$

This segment of the curve corresponds to the region in which the elasticity modulus amounts to fractions of a percent of the initial value, while the time t is longer than the maximum relaxation time: $t/\tau_{max} > 1$.

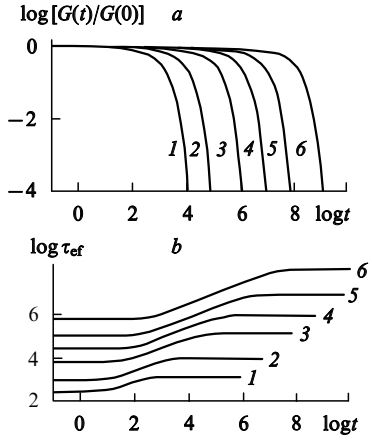


Figure 10. Curves of the stress relaxation (*a*) and the temporal dependence of the effective time of DE-relaxation (*b*) according to Eqns (8), (11) and (12). The chain length: (*1*) 11; (*2*) 21; (*3*) 51; (*4*) 101; (*5*) 201; (*6*) 501.

Characteristically, regardless of the time, each of the relaxation curve segments refers to a strictly definite range of values of the relaxation degree $G(t)/G(0)$. Thus the criterion of R-relaxation may be the observance of the power law with the power index equal to 1/2 in the region of the degree of relaxation 0.8 – 0.1. The interval corresponding to this relaxation is the longer the higher is the MM of a polymer, which is also inherent in the R-model.

It is also typical that the dependence of the effective time of R-relaxation on time τ_{ef} proves to be proportional to time, namely, in the wide range (where the elasticity modulus decreases proportionally to the square root of the time) (see Fig. 9 *b*). According to the R-model,

$$\tau_{max} \propto M^2.$$

According to the DE-model, temporal changes in the relaxation modulus obeying the relations

$$\frac{G(t)}{G(0)} = \frac{8}{\pi^2} \sum_{p=1,3...}^{n} p^{-2} \exp\left(-\frac{p^2 t}{\tau}\right), \tag{11}$$

$$G(0) = \frac{12}{\pi^2 \tau} \left(\int_0^\infty G(t) \mathrm{d}t \right)^{-1}, \tag{12}$$

are characterised by substantially farther extension of the region of high-elasticity plateau than in the R-model (Fig. 10). In this case, the drop of the modulus in the plateau region is insignificant (see Fig. 10 *a*). The plateau passes smoothly to the exponential decay; the transition interval is rather narrow, while its position in the time scale depends on MM.

The temporal dependence of the effective time of DE-relaxation has its characteristic features, too (Fig. 10 *b*). In the R-model, the minimum value of τ_{ef} is independent of MM and its maximum value is proportional to the square of MM, whereas in the DE-model the minimum and maximum values of τ_{ef} are proportional to the square and the cube of MM, respectively.

The temporal dependence of the effective relaxation time in the transient range obeys the law

$$\tau_{ef} \propto t^{1/2}.$$

Comparison of the features of the relaxation curves corresponding to the models considered with experimental results shows that none of these models fit the experimental results. According to the experimental data, the elasticity modulus decreases by $\sim 30\%$ in the region of high-elasticity plateau, whereas the models studied suggest a substantially smaller drop, particularly in the case of the DE-model.

The experimental curves of relaxation comprise no segment corresponding to the exponential dependence with the power index 1/2, which contradicts the R-model. A segment of the exponential dependence of τ_{ef} on t, which may be ascribed to the DE-relaxation, can be found only in individual curves in the transient range (transition from the plateau to the exponential drop) (see, *e.g.*, curve *5* in Fig. 7 *b*). Though, such a segment is virtually absent on the curves describing the relaxation of PS over a wider MM interval. However, one cannot assume that the high-elasticity plateau corresponds totally to the R-relaxation for the following reasons. Firstly, the dependence of τ_{ef} on t is non-linear: in the logarithmic coordinates, $\tan\alpha > 1$ (~ 1.3) in the maximum dependence region. Secondly, as noted above, in the R-relaxation the segment corresponding to the transient state covers a considerable interval of the relaxation degree which is the longer the larger is the MM. In the experimental curves, this segment is little dependent on the chain length and covers the range of $\sim 90\%$ relaxation, which, of course, is substantially more than follows from the DE-model. Finally, the dependence of the maximum relaxation time on MM is a function with the exponent 4 and is not a quadratic function as in the case of R-relaxation, nor is it a cubic function as in the case of reptation model.

The frequency (ω is the frequency of impact) dependence of the relaxation of the real and imaginary parts of the elasticity modulus for narrow PS fractions is shown in Fig. 11.[131] The corresponding dependences for the R- and DE-models are presented in Figs 12 and 13. It is seen that the relaxation curves cannot be described by any of the models discussed. Thus the curve reflecting the frequency dependence of the relaxation of the real part of the elasticity modulus has virtually no segment of exponential dependence with the exponent 1/2 characteristic of the R-model. However, in contrast to the curves typical of the DE-model, the experimental curves exhibit a substantial decay (by almost one order of magnitude) of the elasticity modulus in the region of the high-elasticity plateau.

The decrease in the imaginary part of the elasticity modulus in the high-frequency region occurs much more slowly than those predicted by the R- and DE-models: the power index in the dependence of elasticity modulus relaxation is equal to 1 for the

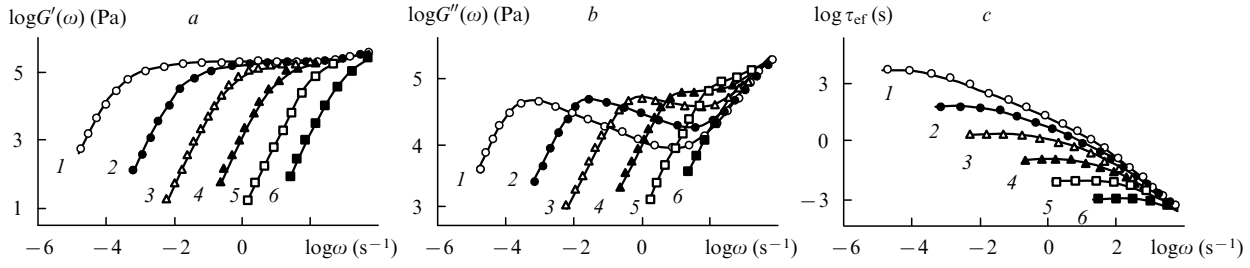


Figure 11. Frequency dependences of the real (*a*) and imaginary (*b*) parts of the elasticity modulus and of the effective time of PS relaxation (*c*).[131] $10^{-3}M$: (*1*) 3000; (*2*) 770; (*3*) 275; (*4*) 128; (*5*) 70; (*6*) 39.

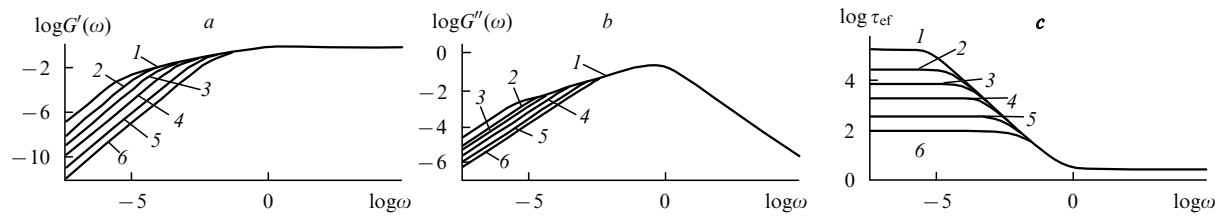


Figure 12. Frequency dependences of the real (*a*) and imaginary (*b*) parts of the elasticity modulus and of the effective relaxation time (*c*) in terms of the R-model equations. The chain length: (*1*) 501; (*2*) 201; (*3*) 101; (*4*) 51; (*5*) 21; (*6*) 11.

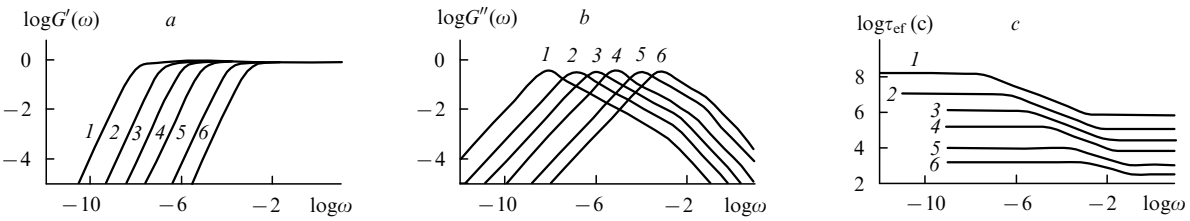


Figure 13. Frequency dependences of the real (*a*) and imaginary (*b*) parts of the elasticity modulus and of the effective relaxation time (*c*) in terms of the DE-model equations. The chain length: (*1*) 501; (*2*) 201; (*3*) 101; (*4*) 51; (*5* 21; (*6*) 11.

R-model and to 1/2 for the DE-model, whereas according to experimental data, it makes up 0.2–0.3, the latter dependence being the more clear-cut the larger is the MM of polymers. The position of the maximum on the curves reflecting the frequency dependence of the imaginary part of the elasticity modulus depends on MM, though it is not cubic, as follows from the DE-model, but has the exponent 4, *i.e.*, it is analogous to the maximum relaxation time dependence.

Variation of the effective time of relaxation

$$\tau_{ef} = \frac{G'(\omega)}{\omega G''(\omega)} \tag{13}$$

also points to an appreciable distinction from the R- and DE-models, on the one hand, and to a discrepancy between the predictions based on these models and the experimental results, on the other: as in the case of the temporal dependence, on the curve reflecting the frequency dependence of the effective relaxation time one can differentiate two segments with constant values of minimal and maximal times and a transition region where τ_{ef} is proportional to the frequency (R-model) or to the square root of the frequency (DE-model). According to the experimental data, this dependence is expressed by the relation

$$\tau_{ef} \propto \omega^{a},$$

where $0.5 < a < 1$.

Hence, the analysis of experimental data shows that the regularities of relaxation of such narrow fractions of linear polymers cannot be described even qualitatively by either the R-model or the DE-model.

The quantitative description of the relaxation of polymers based on the models considered faces serious difficulties; therefore, numerous semi-empirical and empirical approaches which recommend the use of exponential laws or dependences of the 'stretched' exponent type have appeared. For example, it is proposed [125, 132, 133] to express the elasticity modulus relaxation with sums [see, *e.g.*, Eqns (9) and (11)] by analogy with the R-model, though with a different spectrum of relaxation times and a small number of the sum members. The physical meaning of such presentation is unclear.

There are equations of the type [134]

$$G(t) \approx t^{a} e^{-\beta t},$$

which can be used for deriving the dependences of the elasticity modulus relaxation on the frequency of measurements of the type of the Havriliak–Negami dependence [135]

$$G(\omega) \approx [1 + (\omega\tau)^2]^{-\alpha},$$

as well as the Kohlrausch–Williams–Watts equation

$$G(t) = a_1 \exp(-k_1 t^{\beta_1}) + a_2 \exp(-k_2 t^{\beta_2}).$$

Equations of this type often give a satisfactory description of the regularities of relaxation processes over a certain time or frequency interval. Attempts are being made to provide them with a theoretical base (*e.g.*, some studies [122, 136, 137] were devoted to the development of coupling theory). It should however be noted that no substantial progress concerning the region of highly elastic state has been achieved.

VII. Relaxation of chain orientation

The adequacy of a specific model is judged from the results of experimental studies on the orientation of non-cross-linked polymer chains in a concentrated solution, melt or a network polymer.[10, 13] According to current theoretical concepts, the orientation of chains in a non-cross-linked polymer is possible if the chain length exceeds the magnitude of M_e, *i.e.*, if in a given time interval the polymer chain is a network with its nodes formed by entanglements. However, many experimental studies [138–145] have shown that oligomeric and short chains with the MM much lower than M_e can also be oriented in a polymeric matrix composed of the chains the MM of which is substantially larger than M_e or which form a network polymer. In this case, the motive force of the orientation is the so-called nematic interaction, *i.e.*, the manifestation of intermolecular forces of non-topological character.[140, 141] The nature of this interaction remains the subject of discussions (see, *e.g.*, Refs 142, 143). It was speculated that the important role is played by the free volume [9] or configurational entropy in the implementation orientation.[146–148]

It has been proposed [142, 143, 149] that the coefficient ε determined by the relation

$$\langle \mathbf{u}_i \times \mathbf{u}_j \rangle_{\text{probe}} = \varepsilon \langle \mathbf{u}_i \times \mathbf{u}_j \rangle_{\text{matrix}}, \tag{14}$$

be used as the measure of nematic interaction where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the components of the vector of orientation of monomeric chains.

The value of ε depends on the concentration and MM of short chains: as the concentration of long chains increases, the relaxation of the orientation of short chains is decelerated.[140] For example, the value of coefficient ε reaches 0.9 for short polybutadiene chains (MM $\leqslant$ 1000) and decreases to 0.4 as the chain length increases (see Ref. 142). Approximately the same value of ε is characteristic of the nematic interaction in polybutadiene, ethylene–propylene [140, 150] and polystyrene [151] block copolymers, as well as of the orientation of short molecules in the polydimethylstyrene [152] and polyisoprene [153, 154] matrices. The value of ε equal to 1 was found for the polydimethylsiloxane matrix–oligomer system (see Refs 155, 156). Most studies have not revealed any temperature dependence of ε, though the opposite data are also available (see, *e.g.*, Refs 157–159).

Sotta [160] studied the phenomenon of a free segment orientation in a polymer network by the Monte Carlo method and found that $\varepsilon = 0.397$. The only factor whose action can explain the occurrence of orientation is the effect of excluded volume.

The theoretical approach to the estimation of ε magnitude developed by Merrill *et al.*[161] consists in a modification of the DE-model and bears a semi-empirical character. This approach proposes the use of the notion of 'nematic interaction' of the end unit of a test chain with the matrix, though its physical meaning is not explained.

Upon introduction of groups capable of strong intermolecular interaction, *e.g.*, formation of hydrogen bonds, into polymeric chains, the coefficient ε increases substantially and becomes temperature-dependent.[149] This points to an important role

played in this phenomenon by the intermolecular interaction of energetic origin. However, an attempt at theoretical consideration of this factor [162] did not go beyond the frame of empirical increment to the diffusion coefficient which takes into account the lifetime of the arising hydrogen bond.

It should be noted that the temperature dependence of the equilibrium constant of the reaction of hydrogen bond formation in macromolecular systems (polybutadienes with the MM ranging from 26 000 to 48 500) is markedly weaker than that in low-molecular systems (squalene):[163] as the temperature is increased from 20 to 100 °C, the equilibrium constant is changed 4-fold in the polymer and more than 10-fold in squalene. In contrast with the low-molecular model, the entropy of hydrogen bond formation decreases with temperature (provided the enthalpy remains constant, 28.6 kJ mol^{-1}). It may be presumed that weak intermolecular bonds (of the van der Waals type) will exhibit a still weaker temperature dependence. The effect of groups capable of forming hydrogen bonds that have been specially introduced in the polymeric chains on the relaxation properties of polymers is significant:[163–169] the region of high-elasticity plateau is widened by several orders of magnitude with regard to frequency, the maximum of the $G''(\omega)$ is shifted to the low-frequency region also by a few orders; in addition, a shoulder appears on the low-frequency branch.[163, 164, 167] Such changes occur upon addition of as little as 1%–4% of phenylurazole groups modifying polybutadiene. The observed effect of hydrogen bonds proves to be significantly stronger than the reptative deceleration of the relaxation of polymeric chains.[165]

VIII. The network of physical bonds as a dynamic factor

The effect of fluctuating physical entanglements on the dynamics of a macromolecule was studied by the Monte Carlo method [170] using a classical chain model on the Verdier–Stockmayer cubic lattice with two types of kinetic units.[116, 117] The chain length was varied from 5 to 1000 monomeric units within the observation time intervals which made it possible to follow the motion of the chain as of an integral system. The behaviour of the chain was typical of the R-model, *i.e.*, the displacement of a random monomeric unit $g_m(t)$ obeyed the law expressed by relations (1).

If the chain was fixed on the lattice by a virtual network of physical bonds, the number of bonds and their lifetimes being set randomly, the dynamic behaviour of the chain had the features characteristic of the reptation diffusion, *i.e.*, at certain lifetimes and concentrations of nodes, at the distance equal to the medium-length chain scale a regime appeared determined by the relation (Fig. 14)

$$g_m(t) \propto t^{\alpha},$$

where α was 0.25 (the value characteristic of the reptation regime) or even smaller. The motion of the chain mass-centre is characterised by the same dependence [see also relation (2)].

Consequently, the long-living fluctuating physical nodes can provide a polymer system with dynamic properties the manifestation of which is usually related to the availability of a network of topological nodes.

However, it is unclear whether the appearance of such type of fluctuating long-lived nodes in polymeric systems is possible above the glass transition temperature.

IX. On the nature of a physical network nodes

It is known that polymeric systems are characterised by rather strong intermolecular interactions of energetic origin above the glass transition temperature.[1] This is manifested, for instance, as the ll-transition in their melts.[171] This transition temperature is related to the glass transition temperature by the simple expression

$$T_{ll} \approx (1.2 \pm 0.05) T_g.$$

In other words, supramolecular structural units are preserved up to the temperatures 20–60 °C higher than the glass transition temperature: in the opinion of Bershtein and Egorov,[171] the liquid–liquid transition temperature T_{ll} represents the upper temperature limit of the cooperative segmental motion.

Bartenev and Barteneva [172] developed concepts of the λ-transition, *viz.*, the relaxation process characteristic of the highly elastic and liquid state of polymers. They argue that the λ-relaxation is determined by the existence, at temperatures above the glass transition temperature, of microvolume physical entanglements which have linear sizes ranging from 10 to 100 nm and

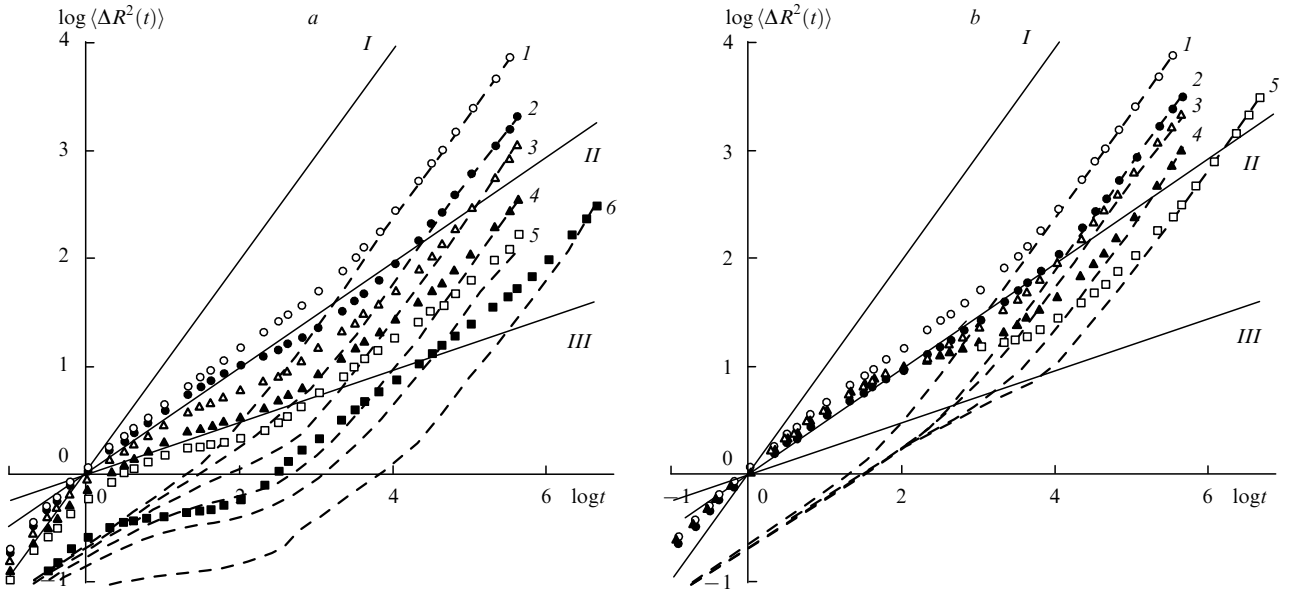


Figure 14. Dependence of displacements of a random monomeric unit and of the chain mass-centre (dashed lines) on time [170] for chains with the unit number $N = 100$ for different quantities of fixed monomeric units (p_f) with a lifetime (τ_l) of 6×10^3 (*a*) and 5% of fixed monomeric units (*b*) with different lifetimes; (*a*): $p_f = 0\%$ (*1*), 5% (*2*), 10% (*3*), 20% (*4*), 30% (*5*) and 60% (*6*); (*b*): $\tau_l = 0$ (*1*), 3×10^3 (*2*), 6×10^3 (*3*), 3×10^4 (*4*), 10^5 (*5*). For comparison, the Roman numerals *I*–*III* designate the lines with the slopes corresponding to t, $t^{1/2}$, $t^{1/4}$.

represent long-lived ($\sim 10^4 - 10^5$ s) fluctuations of the local orientation of segments.

Numerous data point to the formation of structural (including microphase) long-lived fluctuations. Thus the application of the techniques of static and dynamic light scattering has shown that [173] that large-scale density fluctuations occur in poly(methyl-*p*-toluylsiloxane ($T_g = -17$ °C) up to 90 °C. Poly(methyl methacrylate) was found to preserve its 'memory' about the glass structure ($T_g = 65$ °C) [174] up to 132 °C (^{13}C NMR). The use of EPR and NMR revealed [175] structural heterogeneities in a number of linear and network polyurethanes at temperatures 30–70 °C higher than the glass transition temperatures. The characteristic sizes of heterogeneities are ~ 10 nm, while their lifetimes are longer than 100 ms. The use of double-quantum NMR spectroscopy [176] revealed an anomalously high degree of orientation of monomeric units in the PB melt. It should be emphasised that the stability of heterogeneities (associates) is strongly dependent on the MM of polymers.[176, 177] Naturally, the trend towards the increase in the concentration of long-lived associates in polymeric systems is enhanced as the temperature is decreased and the solvent concentration is increased.[178]

Simulation of properties of polymer solutions by the Monte Carlo method has shown [179] that there is a trend towards formation of dynamically fluctuating local domain structures with a parallel arrangement of segments if a polymeric chain is locally rigid. Mutual attraction of monomeric units enhances this effect.

Analogous results were obtained in a study of polymeric liquids of the n-alkane type by the method of molecular-dynamic simulation.[180] In this case, use was made of the Lennard–Jones potential with the energy of attractive interaction of non-bound monomeric units equal to 500 J mol^{-1}. The extent of ordering decreases with the increase in temperature, although its total collapse is observed at a temperature approximately twice as high as T_g.

Experimental studies [181, 182] indicate that associates of reactive oligomers substantially influence the kinetics of their polymerisation and the rate of relaxation processes in oligomer–polymer systems.[181]

We considered several clear examples of the existence of long-lived structures in polymeric melts, and numerous other examples can be found in recent reviews.[1, 182, 183]

The role of intermolecular bonds in the manifestation of relaxation properties of polymers is great. It has been shown [163, 165] that even a small number of hydrogen bonds formed in a polymeric chain lead to an appreciable extension of the high-elasticity plateau. The presence of functional groups capable of association substantially influences the rheological properties of polymer systems.[184, 185]

A characteristic property of polymers is their ability to fix multicentre entanglements.[186, 187] Relevant computations [187] indicate that the lifetime of a complex formed by several bonds, with the energy of each bond reaching a value of the order of kT, increases exponentially as a function of the number of bonds, the exponent growing substantially as the energy increases (Fig. 15). In this case, the lifetime of the complex exceeds by many orders of magnitude the lifetime of a single bond. For example, the lifetime of a complex formed by three bonds ($10RT$) at 27 °C is 1 s, whereas the lifetime of each bond is $\sim 10^{-9}$ s.[189] Such is the effect of connectivity! Even in the absence of energetically strong physical bonds, the monomeric units localised within the same volume element can remain in contact for a long time (which is at least twice as long as the time of release from the 'tube').[32, 190] In this situation, the number of such 'contacting' units is fairly large: it can amount to a half of the total number of units.[190] These results were obtained by the methods of molecular dynamics applied to systems in which only the impermeability of chains and the effect of excluded volume were taken into consideration. Ben-Naim *et al.*[190] believe that such long-lived contacts are formed due to the presence of entanglements, *viz.*, topological

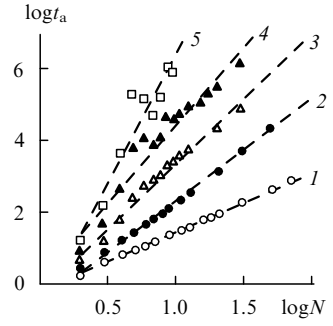


Figure 15. Dependence of the lifetime of associates t_a on the chain length N at different values of the bond energy;[188] E/kT: (*1*) 0; (*2*) 0.5; (*3*) 1.0; (*4*) 1.5; (*5*) 2.0.

nodes. However, in our opinion, in this case the nature of the nodes is not significant: the presence of some long-lived nodes leads to the appearance of others in long chains, and it is their ensemble that determines the dynamics of chains in concentrated systems.

X. Theoretical approaches other than the reptation model

Most theoretical approaches proposed for the description of dynamic properties of polymeric systems take into consideration the existence of a network of topological nodes.[10, 13, 17–20, 117] For this reason, there is no need to discuss them here. Instead, let us dwell briefly upon some new ideas.

1. The coupling theory

A series of reports (see the bibliography in Ref. 137) discuss various aspects of the coupling theory, the fundamentals of which were formulated by Ngai and Plazek.[191] A modification of the R-model is used for describing the dynamics of low-molecular polymeric systems with the MM of a test chain exceeding certain critical MM which corresponds to the chain length between entanglements. The relaxation times τ_p of all modes increase proportionally to the magnitude $(t/t_c)^{n_p}$, where n_p is the coupling parameter, t_c is the time of transition of the test chain from the R-motion to a decelerated motion due to its interaction with the surrounding macromolecules. As a result, a simple exponent describing relaxation at short time intervals ($t < t_c$) is transformed into the 'stretched' exponent

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right],$$

where τ^* is the effective relaxation time

$$\tau^* = \left(\frac{\tau_0}{t_c^n}\right)^{1/(1-n)}.$$

The latter relation takes into account the cooperative motion of the 'test' chain and the surrounding chains with a relaxation time characterising the motion of the non-interacting chain (τ_0).

The coupling parameter n varies from 0 to 1; it is dependent on the character of intermolecular interaction, and in many cases $n = 0.4$.

The proposed approach made it possible to describe to a good approximation a broad spectrum of dynamic experiments (see, *e.g.*, Ref. 137).

To our mind, the coupling theory is of a semi-empirical character, though its authors argue that this theory is based on fundamental ideas of classical mechanics with a chaotic structure determined by the non-harmonic (non-linear) nature of the interaction between molecules.[137] The authors do not provide any clear-cut physical justification of the relations used and confine themselves solely to claiming that any cooperative process

(be it segmental motion or motion of a polymeric chain) is described by the 'stretched' exponent.

2. The model of lateral diffusion

Some studies [192–196] consider diffusion of contacts of a given chain with surrounding chains instead of the diffusive motion of the chain along the 'tube'. Since the diffusion occurs over the chain contour, the friction coefficient determined by the presence of contacts is time-dependent. Taking into account this fact and also the lifetimes of contacts measured by Herman [192, 193] the following expression for the relaxation modulus was proposed:

$$G(t) = G_N\left[\sum_{j=1,3,\ldots}\frac{8}{\pi^2 j^2}\exp\left(-\frac{j^2 A t^{2/3}}{N^2}\right)\right]^2,$$

where A and N are constants.

This model describes well the dependence of self-diffusion coefficient on MM in melts of PE, PEO and PDMS.[195] A characteristic feature of the model is the isotropic character of the motion of macromolecules in space, despite the fact that the coefficients of lateral and longitudinal (along the chain) diffusion differ, though not as substantially as predicted by the reptation model, which prohibits the lateral displacement of the chain.

The physical meaning of the approach proposed consists in that the friction elements (beads) of the R-model interact with the medium in a more complex manner; in such interactions, the friction coefficient depends on time and the composition of the system (concentration and MM of the matrix).

3. The monomolecular model

A generalised linear form of the equation of macromolecule dynamics in the monomolecular approximation has been proposed (see the bibliography in Refs 197, 198)

$$m\frac{\mathrm{d}^2 r_i^{\mathrm{a}}}{\mathrm{d}t^2} = \int_0^\infty \beta(s)(\dot{r}_i^{\mathrm{a}} - v_{ij}r_j^{\mathrm{a}})_{t-s}\mathrm{d}s - \int_0^\infty \varphi(s)(\dot{r}_i^{\mathrm{a}} - \omega_{ij}r_j^{\mathrm{a}})_{t-s}\mathrm{d}s -$$

$$-2\mu T A_{\alpha\gamma} r_i^{\gamma} + \phi_i^{\mathrm{a}}(t)\,, \qquad (15)$$

where m is the mass of a Brownian particle which is associated with a segment of the macromolecule; r_{ij}^{a} is the coordinate of the point in which the particle having the number i, j and belonging to the macromolecule 'a' is located; $\beta(s)$ and $\varphi(s)$ are the memory functions; v_{ij} and ω_{ij} are the symmetrised and antisymmetrised components of the velocity gradient; μ and A are the coefficient and the matrix characterising the equilibrium form of the macromolecular coil; $t-s$ is the time interval; T is temperature and ϕ is the random force.

This approach allowed consideration of various hypotheses relative to the form of the memory functions $\beta(s)$ and $\varphi(s)$ and comparison of computational and experimental results. In particular, in a simple case of the single relaxation time τ:

$$\beta(s) = 2\xi\delta(s) + \frac{\xi}{\tau}B\mathrm{e}^{-s/\tau}\,,$$

where ξ is the liquid viscosity and $\delta(s)$ is the delta-function. In this expression, the relaxation time of the environment proves to be the characteristic relaxation time of the macromolecular coil. The increase in the parameter B, which is the measure in the increase of the particle friction coefficient due to the fact that during slow motions the probe chain pulls the tail from the surrounding macromolecules, obeys the exponential law:[197]

$$B \propto M^b,$$

where $b > 2$.

The first term in the right hand part of Eqn (15) reflects the strength of the interchain interaction, while the second term expresses the strength of the internal resistance associated with changes in the macromolecular coil shape and determined by the presence of surrounding molecules bound to the chain under consideration.

Equation (15) describes essentially the motion of an isolated macromolecule in a continuous medium possessing viscoelastic properties. Thus, the approach proposed takes into consideration the effect of the environment, *i.e.*, the theory does not go beyond the semi-empirical framework.

4. The mode-coupling theory

Over the last decade, following the publication of Schweizer's paper,[199] many studies have been reported which develop the model of local interaction of monomeric units of polymeric chains.

The theory of polymer mode-coupling makes an attempt to describe the chain motion at the microlevel under the action of fluctuating intermolecular forces.[200]

Microscopic description of the dynamics of a single polymeric chain in a condensed medium is performed using a non-Markovian generalisation of the Langevin equation with consideration of the fluctuating force of the intermolecular interaction. The central point of this theory is the conclusion about the memory function, which takes into account the local four-particle (two particles belonging to the probe chain and two others, to the neighbouring chains) contact; in this case, the effect of excluded volume, *i.e.*, the repulsion energy, is regarded as essential. The cell (contact) in which the above-mentioned interaction occurs behaves as an entanglement. These long-lived contacts are presumed to be distributed along the probe chain and their concentration to be proportional to the square root of the chain length (see the theory of local diffusion). It is also assumed that the existence of these contacts ensures high cooperativity of the motion of all segments of the probe chain, contrary to what is predicted by the simple R-model.

Thus, according to the mode-coupling theory, the relaxation of a polymeric system results from the highly cooperative but isotropic motion of the probe chain and the surrounding chains. It is still unclear whether this picture is realistic or the provided averagings overestimate the 'cellular' effect.[201]

Schweizer *et al.*[202, 203] have thoroughly reviewed and generalised the theoretical studies and the results of their comparison with the experimental data. It was shown that the conclusions drawn from the theory of polymer mode-coupling and the reptation theory are qualitatively analogous. The mode-coupling theory makes it possible to reveal the sensitivity of diffusion constants to various factors, such as fluctuation of concentrations, degree of polymerisation, composition of a mixture, temperature, concentration of a solution and proximity to the interface.[201]

A disadvantage of this theory consists in a definite arbitrariness of the choice of the memory function mode (*cf.* the monomolecular model). Furthermore, a detailed analysis has shown [204] that the renormalised procedure does not result in the convergence of results and, consequently, is physically incorrect.

5. The physical network model: relaxation of stress

A new approach has been proposed recently for considering the extent and character of the intermolecular interaction in polymeric systems within the frame of the physical network model.[130]

Sufficiently long chains of networks with both covalent nodes and entanglements, as well as suspended 'tails' were found to exhibit some features of the R-relaxation (see, *e.g.*, Refs 205–207). It is therefore natural to represent a macromolecule as if it contained k R-subchains of length m connected by physical nodes. In this case, relaxation may be described in the frame of the R-model taking into account that the relaxation of the rigidity of the 'springs' connecting the nodes follows the R-mechanism, whereas the nodes themselves are characterised by a friction coefficient, which is determined by the interchain interaction and hence depends on the concentration and MM of a polymer.

The initial system of differential equations which describes the relaxation of the R-chain is expressed as [71]

$$\eta \frac{dy_i}{dt} = G(2y_i - y_{i+1} - y_{i-1}) , \quad (16)$$

where y_i is the coordinate of the ith bead and G is the elasticity modulus of the spring connecting the friction nodes.

Solution of this system provides an expression for the temporal dependence of the elasticity modulus relaxation [see Eqn (9)].

The physical network model assumes that G is time-dependent. Introduction of the time function φ into Eqn (16):

$$\varphi(t) = \int_0^t G(\xi)d\xi ,$$

and its solution yield the equation analogous to that for the R-model, though the expression of time in it is more complex:

$$G(t) = \frac{1}{k}\sum_{p=1}^{k} \exp\left(-p^2 \varphi \frac{t}{\tau}\right) ,$$

where

$$\varphi(t) = gt + \frac{\psi}{m}\sum_{q=1}^{m} q^{-2}\left[1 - \exp\left(-q^2 \frac{t}{\psi}\right)\right] , \quad (17)$$

g is the elasticity modulus of the R-springs, $\psi = \psi_0 m^2$ is the maximum time of R-subchain relaxation and ψ_0 is the minimum relaxation time.

Evidently, the total chain length is

$$n = mk ,$$

where k is proportional to the chain length. According to the R-model, the relaxation time τ is proportional to the squared chain length and to the friction coefficient. But the latter parameter *per se* should depend on n. This dependence is rather complex and its determination is a separate problem, though it may be presumed that the second power is a fairly reasonable magnitude. Thus, in conformity with the experimental results, we derive the general dependence $\tau \propto n^4$.

The relaxation curves calculated from Eqn (17) are qualitatively similar to the experimental curves.[130] Thus changes in the relaxation of elasticity modulus in the region of high-elasticity plateau are rather significant, and the dependence $G(t) \propto t^{-a}$, where $a \simeq 0.25$, is observed to hold over a certain interval. The segment of the exponential dependence with the exponent 1/2 is absent if the number of nodes k is not too large. At longer times, the exponential decay is determined by the relaxation time which is proportional to the chain length raised to the fourth power (more precisely, to k^4); extrapolation of the curve to the ordinate axis gives a segment whose magnitude is dependent on the total length of the chain and the number of physical nodes:

$$\ln G(0) = -\ln k - \frac{\psi_0 n}{\tau_0 k^5} b - \frac{g}{\tau_0 k^4} t ,$$

where $b = \sum_{p=1}^{m} p^{-2} \approx 1.6$ for sufficiently large m; at $m \to \infty$,

$b = \pi^2/6 = 1.645$.

A detailed analysis of experimental results (including studies of diffusion of macromolecules, rheology of solutions and melts, frequency dependence of relaxation modulus, *etc*.) with consideration of physical bonds is a matter for the future, but even now one can discern good prospects for this approach for studying the dynamics of polymeric systems. For example, Walkenhorst [208] showed that the process of physical network rearrangement is responsible for the long-term relaxation.

The concept of the network of physical nodes was used by Soloviev *et al.*[209–211] for the description of the relaxation properties of elastomers. In these studies, analysis of the deformation curves differentiated two types of processes differing in their relaxation times: fast diffusive displacements of 'free' segments which are not involved in the formation of intermolecular nodes of the physical network and a slow diffusive process of rearrangement of the network itself. Using basic postulates of non-equilibrium thermodynamics and considering the destruction of physical nodes as a reversible chemical reaction, these authors derived a system of equations which describe viscoelastic properties of elastomers over a wide range of deformation rates. Investigation of the stretching of copolymers of acrylamide with nonyl acrylate at the rates ranging from 1 to 0.01 s^{-1} and in the temperature range 20–120 °C has demonstrated that experimental data correlate with theoretical predictions. The approach of Soloviev *et al.* represents, in its essence, the development of Bartenev's idea [172] about the occurrence of a fast (α-process) a slow (λ-process) stages of the relaxation of elastomers.

Wientjes *et al.*[212] made an attempt to employ the physical network model for describing rheological properties of polymers.

XI. Conclusion

This review has analysed the available experimental data on the dynamics of polymers with consideration of the network of physical bonds. It has been found that these data are at variance with the reptation model and that this model is insufficient for understanding the relaxation behaviour of polymers. The authors of this theory agree that the classical variant of the reptation theory yields results which are inconsistent in many respects with the experimental data.[13] The attempts to refine the reptation model through consideration of the 'tube' relaxation and the disappearance of restricting entanglements [13, 18] have resulted in a certain enhancement of the dependence of maximum relaxation time and viscosity on MM. These and analogous amendments 'facilitate' the relaxation process and decrease the relaxation times compared to those given by the simple non-modified theory. At the same time, the review demonstrates that the theoretical relaxation times are underestimated compared to those obtained experimentally, whereas the reptative behaviour is characteristic of the chains with the MM substantially larger than M_e.

The existence of a network of physical bonds confirmed experimentally is indisputable. However, its role in determining a broad spectrum of dynamic phenomena has not yet been elucidated. Unfortunately, the physical network model has not been developed to the extent reached, *e.g.*, by the reptation model. The investigators have still to clarify whether the intermolecular interactions play a role in the formation of relaxation properties of polymeric systems or these interactions merely make some contribution to the network of entanglements.[213, 214]

The existence of the network of physical bonds is taken into account explicitly or implicitly in the consideration of dynamic properties of polymers. It underlies many approaches: for instance, some aspects of the problem of physical nodes and their effect on relaxation processes in polymers were discussed by Bartenev and Barteneva.[172] As a matter of fact, the theory of polymer mode coupling also uses the physical network model (the network nodes are assumed to be areas with high local packing). The results reported by Sotta [160] point to an important role played by the network: orientation of a 'free' segment is brought about under the action of the oriented matrix without introduction of some energetic factors due only to the excluded volume effect.

Apparently, the fact that the temperature position of the beginning of the high-elasticity plateau (T_g) corresponds not to MM but rather to M_e, which is much smaller in order of magnitude than the corresponding size of the kinetic segment,[215] should be interpreted from the same viewpoint. This may imply that an important, if not decisive, significance in the physical network formation belongs to the high-density fluctuations, which seem to play the role of nuclei of the glassy state [216] or of the regions of local order in terms of the cluster model of the structure of amorphous polymers.[217]

Only the existence of long-lived nodes of the network, and not their nature, is important for the manifestation of 'reptative'

properties; therefore, the physical network model may be used for describing dynamic properties of a large number of systems ranging from physical gels to polymers with intermolecular interactions of the dispersive type.

It should be mentioned in conclusion that about three decades ago a vivid discussion was underway on whether or not such a structural formation as topological entanglements exists in polymeric systems. The discussion was initiated by the appearance of the 'packet' model of the structure of polymers [218] which was the antithesis of the 'felt' structure of Flory.[77] This discussion resulted in the triumph of the idea of entanglements not only in the structural respect; it also laid the foundation for the subsequent models of the dynamics of macromolecules. Now, the time has come for a new discussion on whether the entanglements do play the role ascribed to them in the dynamics of polymers or this role is at least overestimated.

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