The effect of modification of polymers on their structure and properties

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With the considerable expansion of use of polymeric materials (in the home, in medicine, and in different sectors of industry), the classification of polymers is now in need of certain refinement and of a shift of focus. This has been dictated chiefly by the appearance of a large number of various composite materials based on polymers that satisfy the requirements of modern technology. Although the synthesis of new monomeric substances is continuing, with the production, on their basis, of new high molecular weight compounds of broad practical application, composite materials consisting of components differing in molecular weight (low molecular weight, oligomeric, and high molecular weight) are used in different areas of technology. Taking this into account, the present-day classification of polymeric systems calls for their division into single-component and multicomponent systems [1]. The traditional classification of polymers [2] specifies their division according to their origin (natural and synthetic) and chemical composition (organic, heteroorganic, and inorganic). Natural polymers include cellulose and its ethers and esters (ethyl cellulose, cellulose acetate, cellulose nitrate). Synthetic polymers include different carbon-chain and heterochain polymers [3]. In carbon-chain polymers, only carbon atoms are contained in the main chains of the principal valencies, while in heterochain polymers the main chains, apart from carbon atoms, contain other atoms (for example, oxygen atoms).

In the structure of the macromolecules, all the polymer systems are customarily divided into linear, branched, and crosslinked systems (these have chemical crosslinks of different density). Comb-shaped, star-shaped, and ladder polymers differ in the spatial disposition of macromolecules and their branches.

Organic polymers are homochain and heterochain. Homochain polymers include hydrocarbons (polyethylene, polypropylene, etc.), halogens (polyvinyl chloride, polytetrafluoroethylene), alcohols and their derivatives (polyvinyl alcohol, polyvinyl ether), aldehydes and ketones (polyacrolein, polymethyl vinyl ketone), and acids and their derivatives (polyacrylamide, polyacrylonitrile). Heterochain polymeric systems include oxygen-containing polymers (polycarbonates, epoxy resins), nitrogen-containing polymers (polyamides, polyurethanes), sulphur-containing polymers (polysulphides), aromatic polymers (polystyrenes, polycrylates), and polymers with conjugated bonds (polyvinylenes, polyphenylenes).

Heteroorganic polymers are subdivided into six types: those with inorganic main chains, those with organic macromolecules, those with organic–inorganic main chains, titanoxane polymers, stanoxane polymers, and chelate polymers.

Inorganic polymers are also homochain (polysilanes, polygermanes) and heterochain (polyborazoles, polysilicic acids). Lamellar (coalinites, zeolinites) and three-dimensional crystalline (asbestos, quartz) inorganic polymers differ in structural features.

According to the present classification, all the polymers indicated are single-component. They are characterised by the presence of long chains of molecules consisting of a large number of successively connected atoms of different types. They are characterised by the presence of intrachain interactions (through valence chemical bonds) and interchain interactions (on account of the presence of weaker physical bonds). Here, the chemical
and physical bonds in the polymers differ considerably in length \( l_b \) (for the former, \( l_b = 1.0-1.5 \, \text{Å} \), and for the latter \( l_b = 3-4 \, \text{Å} \)) and in strength or dissociation energy \( U_0 \) (for the former \( U_0 = 100 \, \text{kcal/mol} \), and for the latter \( U_0 = 10 \, \text{kcal/mol} \)).

In three-dimensionally structured (crosslinked) single-component polymers, chemical and physical bonds act between the chains, which determines the absence in them of viscous flow. Intermolecular interaction in single-component polymeric systems is determined mainly by the presence in the macromolecules of polar atomic groups characterised by different effective dipole moments \( \mathbb{D}_\mathrm{eff} = \mathbb{g} \). Therefore, in non-polar polymers (polyethylene, polybutadiene) the intensity of intermolecular interaction is very low, while in polar polymers (polycrilonitrile, polymethyl methacrylate) it is fairly high.

An intermediate position in relation to single-component and multicomponent polymeric systems is occupied by copolymers in whose macromolecules different monomers (butadiene and styrene, ethylene and propylene) are successively connected. The properties of such copolymers (butadiene-styrene, ethylene-propylene) are normally intermediate in comparison with the properties of the corresponding single-component polymers polybutadiene, polystyrene, and polyethylene, polypropylene). Multicomponent polymeric systems are normally classified according to the types of component: polymers with polymers, polymers with low molecular weight (or oligomeric) substances, and polymer + polymer + low molecular weight (oligomeric) substances. The first include block copolymers and mechanical mixtures of polymers. The second include plasticised and filled polymeric systems containing inert or chemically active low molecular weight substances, which have been termed composite materials. They have now been studied to the greatest degree. The third are the most complex and most promising for practical use in different areas of modern technology. The laws governing the relationship between their composition and properties can be established only after a detailed study of polymeric systems of the first and second types.

From the above it follows that it is presently most urgent to study the laws governing the behaviour of multicomponent polymeric systems of the first type, i.e. block copolymers and mechanical mixtures of polymers.

On the basis of the examined classification of polymeric systems, we selected materials for investigation that are of both scientific and practical interest. From the single-component polymeric systems we chose amorphous polystyrene (PS) and polymethyl methacrylate (PMMA). Their similarity consists in the presence of bulky side groups (phenyl and methyl ether groups respectively) and in the absence of crystallisability, and their difference consists in the degree of polarity (the effective dipole moment of PS \( \mathbb{D}_\mathrm{eff} = 0.3 \, \text{debye} \), while for PMMA \( \mathbb{D}_\mathrm{eff} = 1.33 \, \text{debye} \) which determines the intensity of intermolecular interaction. The latter determines the substantial difference in their dielectric losses at a fixed frequency (\( 10^2 \, \text{Hz} \)) in the temperature range of unfreezing of segmental mobility (in PS \( \delta_m = 3 \times 10^{-4} \), and in PMMA \( \delta_m = 3 \times 10^{-2} \)) and the different degree of dependence of dielectric permittivity on frequency at a fixed temperature of 298 K (in non-polar PS at frequencies of \( 10^3 \) and \( 10^6 \, \text{Hz} \), \( \varepsilon_r = 2.56 \), and in polar PMMA at these frequencies \( \varepsilon_r \) is equal to 2.84 and 2.63 respectively).

Of the crystalline single-component polymeric systems, low-density polyethylene (LDPE) and polypropylene (PP) were chosen. Their similarity consists in their both being non-polar polymers (they are characterised by a low intensity of intermolecular interaction) and having crystalline formations. Their difference consists in their composition and structure of the macromolecules (in LDPE the units of the linear chains consist of methylene groups \( CH_2 \), while for PP, besides the \( CH_2 \) groups, there are methine groups \( CH \) and methal groups \( CH_3 \), the latter playing the role of side chains), and in the degree of crystallinity (for LDPE, the X-ray degree of crystallinity is 39%, and for PP it is 55%).

The multicomponent polymeric systems chosen for investigation were mechanical mixtures consisting of amorphous and crystalline components (LDPE + sodium-catalysed butadiene rubber SKB, and polypropylene 1111 + methylstyreene rubber) and block copolymer BSP PBPA consisting of flexible-chain amorphous polybutadiene blocks of PB and rigid-chain crystalline blocks of PA. Their similarity consists in the fact that they have two components each, one of which is amorphous and the other crystalline, and their difference consists in features of their chemical composition and molecular structure, and in values of the degree of crystallinity. Interest in investigating these multicomponent systems by methods of relaxation spectrometry is determined by the presence of conditions of molecular mobility within different components and at their boundaries [4].

For any polymeric materials there are two problems of both scientific and practical importance. The first problem is knowing all the features of the given polymer: its chemical composition, molecular structure, supermolecular structure, and the characteristic temperature ranges in which most properties of the polymer undergo sharp changes (glass transition temperature, melting temperature, temperature of transition to the viscous flow state, temperature of polymeric transformation). The second problem consists in knowing the behaviour of the polymer under certain conditions of its storage and service, which is necessary for establishing its guaranteed service lives.

The diagnostics of the polymers is called upon to solve the first problem, and prediction of their properties to solve the second. The diagnostics of polymers
consists in establishing a clear relationship between the chemical composition, the molecular structure, the supermolecular structure, and their different physical properties. Prediction consists in scientifically sound forecasting of the degree of variability of the properties of the polymers during their storage and service under conditions close to real conditions.

Diagnostics and prediction of the properties of polymers are carried out most effectively using relaxation spectrometry data. Different methods of relaxation spectrometry make it possible to fix the macroscopic appearance in integral form (for example, from the sharp increase or reduction in any physical quantity, and also from the inflection points of certain dependences) or differential form (for example, from the maxima of mechanical or dielectric losses, and also from the minima on the temperature dependences of the spin–lattice relaxation time and the maxima on the temperature dependences of the intensity of radiothermal luminescence (RTL)). Comparative analysis of the quantitative characteristics for polymers of different classes showed that the use of differential dependences is more effective since for the maxima it is possible to use a larger number of parameters (four) by comparison with the integral dependences, for which one or two parameters are typical. In earlier studies [5, 6], on the basis of an analysis of numerous experimental data, the physical meaning of each of the four parameters was established. The temperature of the appearance of a maximum (or minimum) characterises the intensity of intermolecular interaction of the polymers. The height of the maximum characterises the effective size of the kinetic unit (relaxer) taking part in thermal motion. The breadth of the maximum characterises the degree of structural inhomogeneity of the polymer (different conditions of mobility of relaxers of different form in parts of the volume of the polymer that differ in molecular ordering or density) or the differences in the surroundings of the kinetic units (for example, segments) taking part in thermal motion. Finally, the area bounded by the maximum and by the temperature (or frequency) axis characterises the number of relaxers taking part in the process.

It is known that thermal motion in different substances (including polymers) exists even close to zero on the Kelvin scale. Depending on the type (composition, structure) of polymer and on the value of the temperatures, vibratory, rotational, or translational mobility can be achieved with correspondingly increasing kinetic energy. At extremely low temperatures, because of the low kinetic energy, \( E_v = kT \), and vibratory mobility of small atomic groups of low mass can appear. With increase in temperature, on account of increase in \( E_v \), either vibratory mobility of the more massive groups (side groups, end groups, or in the main chains) may “unfreeze”, or rotational mobility may appear. Further increase in temperature leads to the appearance of translational mobility of relaxers of even greater mass. Maximum mechanical (or dielectric) losses of greater height and appearing at higher temperature correspond to each such involvement in thermal motion of larger relaxers. All these relaxation maxima appear against a general background (level) of internal friction (Figure 1). This background (1) increases with increasing temperature, since there is an increase in the total molecular weight of the relaxers involved in motion, each type of relaxer having its corresponding maximum (2, 3, and 4 or \( \gamma, \beta, \) and \( \alpha \) respectively). The background value of internal friction depends on many quantities [7], and its nature has not been entirely studied:

\[
\tan \delta_b = f(T, \nu, \gamma_{str}, \alpha, n, D, \ldots)
\]

where \( T \) is the temperature, \( \nu \) is the linear frequency, \( \gamma_{str} \) is the characteristic structural parameter of the polymer (the density, crosslink density, degree of crystallinity), \( \alpha \) is the strength of the force field (for example, the mechanical stress), \( n \) is the concentration of additive modifying the polymer (filler, plasticiser), and \( D \) is the radiation dose (for example, with high-speed high-energy electrons).

The value of \( \tan \delta_b \) depends on other parameters, for example, on the crosslink density, and on the temperature and time of heating of the polymers during their heat treatment.

To the appearance of each maximum there corresponds a certain region of relaxation that is connected with the corresponding kinetic units. It is characterised by its activation energy \( U \), the most probable relaxation time \( \tau_{m_p} \), and the relaxation time distribution function \( P(\ln \tau/\tau_{m_p}) \). An interesting method for graphic representation of multiple relaxation processes of polymers was proposed by Hedvig [8]. For each relaxation maximum he compared an equivalent triangle of the same area (Figure 2). The base of this triangle \( b = (\ln T) = T_2 - T_1 \) characterised the width of the region of relaxation, and the height \( h = \tan \delta_b \) was proportional to the activation energy \( U \), which depended on the value

![Figure 1. Schematic of temperature dependence of background of change in molecular mobility and relaxation maxima of polymeric systems](image-url)
of the temperature $T_m$ and was assessed using the ratio $U = cT_m$ (where constant $C = 64$ kcal/mol K).

The area of the triangle (as with the area bounded by the maximum) characterised the number of relaxers taking part in the given process of sharp change in molecular mobility. For all the regions of relaxation appearing in various polymers, Hedvig obtained graphic diagrams making it possible to compare values of the characteristic temperatures ($T_g$ and $T_{melt}$) for amorphous and partially crystalline polymers (Figure 3).

Most polymers, in wide temperature and frequency ranges, are characterised by the appearance of two types of relaxation process: local and segmental. The former are connected with change in the mobility of different atomic groups, and the latter are connected with change in the mobility of different segments (parts of macromolecules containing several tens of units). On the temperature dependences of factors of mechanical (or dielectric) losses, at a fixed frequency $v_1$, two regions of relaxation normally appear (local A and segmental B) in the form of maxima with different parameters (Figure 4). A similar dependence taken at a higher frequency $v_2$ is characterised by an uneven shift in these regions towards higher temperatures. With the same difference $\Delta v = v_2 - v_1$, the value $\Delta v_1 > \Delta v_2$, which is due to the considerable smaller size and mass of the atomic groups by comparison with segments (to this there corresponds the absence of activation energies of local and segmental processes: $U_s > U_l$).

In earlier studies [7, 9], double correlation diagrams were introduced (Figure 5), and methods of using them for analysis of data from the relaxation spectrometry of polymers were developed. On the basis of experimental data of the type presented in Figure 4, with account taken of the relationships...
In the viscous flow state III the nature of coexistence of local and segmental processes changes form and curves 1, 2, and 3 initially converge and then merge entirely into a single line. Here, the activation energy of the segmental process decreases and becomes constant and equal to the activation energy of the local process, which is characterised by the smallest size and mass. This is due to the fact that, in the viscous flow state, at increased temperatures, on account of intense thermal flow, there is a considerable increase in the flexibility of the polymer chains and a sharp reduction in the effective size of the segments, which become commensurate with the size of the atomic groups.

2. Since many polymers are used as constructional materials (i.e. are used in the solid glassy state), it is important to know under which temperature and frequency conditions they begin to soften (segmental mobility arises). This does not always occur at the temperature of structural glass transition of polymers, and at extremely high frequencies it may occur at \( T > T_g \). Taking this into account, use is made of the extrapolation of the curvilinear dependence describing segmental mobility and the frequency value \( v = 1 \text{ Hz} \).

To this there correspond the ordinates of the double correlation diagram \( \lg v_m = 0 \) and \( \lg \tau_{m,p} = 0 \). Drawing between these points a line parallel to the lower and upper abcissa axes, finding on it the point of intersection with a segment that is a continuation of the geometric point relating to the segmental process, and drawing through this point a line that is parallel to the ordinate axes, we will find the softening point (glass transition temperature) being predicted. It is the upper boundary of the temperature range in which it is possible reliably to predict the efficiency of polymers as solid constructional materials. This is particularly important when special modification of polymers is being carried out in order to expand the temperature range of their efficiency.

3. Among those used to study the molecular mobility of polymers, there are reliable, and simpler than most frequency methods, so-called “static” (non-frequency) methods. They include, for example, methods of dilatometry and radiothermoluminescence which make it possible to determine the corresponding temperatures of relaxation transitions. In this case, to establish the nature and characteristics of the process of change in the molecular mobility (its assignment or identification), it is necessary to know the values of the most probable relaxation time \( \tau_{m,p} \) and effective frequency \( v_{m,\text{eff}} \). On the double correlation diagram (Figure 4), dropping from the point corresponding to the found temperature of transition \( T_{m1} \) or \( T_{m2} \) a perpendicular line onto the rectilinear and curvilinear segments and drawing through the points of their intersection lines parallel to the absissa axes, at their intersection with the ordinate axes we will find the quantities \( \tau_{m,p} \) and \( v_{m,\text{eff}} \) of interest to us.

\[ v = v_0 \exp(-U / \kappa T) \]  
\[ \tau_{m,p} = \tau_0 \exp(U / \kappa T) \]

in the coordinates \( \lg v_m = -1/T, \) K and \( \lg \tau_{m,p} = -T, \) °C, geometric points are obtained in the form of rectilinear \((1, 2)\) and curvilinear \((3)\) segments relating respectively to local and segmental processes. Using the double correlation diagrams given in Figures 5 and 6, it is possible to solve the following problems:

1. Determination of the ranges of physical states of polymers and the values of the temperatures and frequencies at which the polymers pass from one state into another. From the data in Figure 3 it can be seen that, in the glassy state I, only local mobility appears on account of low values of the kinetic energy \( E_1 = \kappa T \). To the local processes there correspond geometric points in the form of rectilinear segments, which indicates the constancy of their activation energy and the validity for them of Arrenius equations of types (2) and (3). The dependences 1 and 2 given in Figure 5 correspond to local processes 2 and 3 depicted in Figure 1, and consequently \( U_2 > U_1 \), i.e., the smaller the slope of the rectilinear segment, the smaller are the size and mass of the corresponding atomic groups. No segmental processes appear in the glassy state I. In the rubbery (high-elastic) state II, the coexistence of local \((1, 2)\) and segmental \((3)\) processes occurs, but the nature of their occurrence differs considerably. The segmental processes are characterised by a higher value of the activation energy \( U_3 > U_2 > U_1 \). Furthermore, the curvilinear nature of dependence 3 indicates the inconstancy of the activation energy of the segmental process. It also depends on temperature \( T \) and on the strength of the force field \( \sigma \), i.e.

\[ U_3 = U_{\text{seg}}, \text{ const, } v_3 = f(T, \sigma) \]
To predict the changes in the properties of the polymers during their storage, during their service under conditions close to real conditions, and with different types of modification, it is expedient to use the method of plotting and analysing Debye spectrograms [5, 7]. This is particularly effective when temperature or frequency dependences of the mechanical or dielectric losses are available, obtained with different modifying parameters (plasticiser or filler concentrations, radiation dose, temperature and time of heating) of specimens subjected to heat treatment. In plotting Debye spectrograms from such differential curves (Figure 7) during double normalizing (with respect to the abscissa and ordinate axes) there is the possibility of a switch from the above-mentioned four parameters of maxima to one parameter, which simplifies considerably and defines concretely the prediction procedure. In the capacity of this parameter it is expedient to choose the half-width of the maxima, providing on the Debye spectrograms a graphic picture of the effect of the corresponding modifying parameter $P_m$. From the schematic picture presented in Figure 8(a) it can be seen that, as modifying parameters of the temperature $P_m = T$ (1) and the concentration of the low molecular weight plasticiser $P_m = n_{pl}$ (3), the degree of structural inhomogeneity decreases (the conditions of mobility of parameters of the same type become equal in various parts of the volume of specimens). At the same time, when the frequency $v$ (2) or the concentration of active filler $n_{af}$ (4) is chosen as $P_m$, the degree of structural inhomogeneity increases. Plotting, from experimental data based on Debye spectrograms, the dependences $[] = f(P_m)$ for the case where, for example, $P_m = v$ (region II in Figure 8(b), corresponding to a change in $P_m$ from $P_1$ to $P_2$), and assuming constancy of the nature of the dependences $[] = f(P_m)$ with $P_m < P_1$ and $P_m > P_2$, we obtain Figure 8(b) the possibility of predicting the change in [] (and, consequently, other properties) in regions I and III respectively without carrying out additional experiments.

At present it is known that there are chemical, physicochemical, and physical methods of modifying polymers [10, 11]. When different chemical methods of modification of polymers are used, new atomic groups are added to them, and consequently there is a change in the chemical composition of the materials, which, again, requires determination of all their characteristics [12].

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**Figure 7.** Characteristic bell-like diagrams (Debye spectrograms) intended for comparative quantitative assessment of degree of structural inhomogeneity of polymers according to Debye’s theory (1) and experimental data (2a – polyvinylcarbazole; 3a – polyvinyl acetate; 2b – polymethacrylate; 3b – polyvinyl chloride)

**Figure 8.** Schematic representation of dependences of degree of structural inhomogeneity [] on parameters of various types of modification of polymers $P_m$ (a) and method of prediction of [] from experimental values in range of variation in $P_m$ from $P_1$ to $P_2$ (b)
In the case of physicochemical modification of polymers there is a change in their molecular structure, which also leads to necessary reassessment of the entire complex of quantities corresponding to the substantially updated material [13]. And only with the physical modification of polymeric systems, when both their chemical composition and their molecular structure remain unchanged, and only the supermolecular structure of materials changes, are we actually dealing with the same polymer in which only the properties largely determining its molecular ordering, i.e. supermolecular organisation, have changed [14].

The physical modification of polymers can be carried out either under the action on them of different force fields (mechanical, electrical, magnetic) or as a result of heat effects [15]. A promising method for synthesising and simultaneously modifying polymers by impact effects with shear [16] must be pointed out. It has been established that, at room temperatures, the process of producing high-density polymers is realised. However, this method has yet to be used to produce articles of specimens of definite geometric shape and has therefore not been used in practice. An effective method for physical modification of polymers is their mechanical working [17]. Here there is a reduction in the free volume of the polymers, stable physical bonds are formed, and old chemical bonds can be broken and new ones created.

Interesting investigations into the effect of isostatic compression on polymers are being carried out at the Institute of High Pressures of the Russian Academy of Sciences. Specimens of solid polymers were preheated to a temperature 20-40 K above \( T_g \) (or \( T_{mol} \)) and then rapidly subjected to a pressure of 10-15 kbar and held under these conditions for 1 h. Then, the specimens of modified polymers were gradually cooled to room temperature. Further tests on them showed that the elastic modulus of these polymers increased by 10-15%. To give the polymers better service properties, their moulding with the application of vibration is also carried out [11, 18]. In this case there is a reduction in the number and volume of microcavities, and also a reduction in the internal mechanical damage. However, it remains unclear at which amplitudes, frequencies, and temperatures the maximum effect of vibrations is achieved. Investigation of the effect of ultrasound on polymers showed [18] that it leads to the development of processes accompanied with the breaking of chemical bonds. The effect of ultrasound on the strength properties of polymers has been studied little to date and has not yielded definite results. Fruitful investigations of the effect on the properties of polymers of electric [19] and magnetic [20] fields showed that an important role in this case is played by processes of orientation of macromolecules. Taking this into account, it is promising to conduct investigations into the effect on the structure formation and properties of polymers of the simultaneous action of electric and mechanical and magnetic and mechanical fields [21]. Change in their thermomechanical prehistory has a considerable effect on the properties of polymers of various classes. This is connected with change in the structural morphology of the supermolecular formations of the polymers, which most affects their deformation and strength mechanical properties, which depend also on the nature of the relaxation processes of molecular mobility that occur in them [22, 23].

In connection with the above, an extremely effective method of physical modification of polymers is their heat treatment in different media [24, 25]. Heat treatment is one of the widely used methods for changing the structure and properties of polymers by the action on them of temperature fields, which is governed by change in the molecular ordering under the influence of thermal motion. It is important, during prolonged high-temperature heating of polymers as a result of intense thermal motion, for complete breakdown of the molecular structure of the polymers to occur. This determines the need to select a heating temperature \( T_{heat} > T_g \) for amorphous polymers and \( T_{heat} > T_{mol} \) for crystalline polymers. For partially crystalline polymers with a low degree of crystallinity (30-60%) it is possible to use the ratio \( T_g < T_{heat} < T_{mol} \). The criterion for selecting the heating time \( t_{heat} \) is the absence of thermo-degradative effects while ensuring breakdown of the structural formations. After completion of heating of the specimens, they can be subjected to quenching (with rapid cooling) or annealing (with slow cooling). In the case of quenching, amorphisation of the polymers occurs, which leads to an increase in their deformability and to a certain reduction in strength. In the case of annealing, there is an increase in the structural ordering and an increase in the density of the polymers, which leads to an increase in their strength and to a certain reduction in deformability. During the annealing of crystallising polymers, processes of structure formation (on the molecular and supermolecular levels) are realised. This is shown by a change in the molecular weight of polymers, a change in the degree of their structural inhomogeneity, and in the realisation of crystallisation processes (most often this is either recrystallisation or secondary crystallisation). The extent of these processes depends on many factors: on the type of polymer and its mechanical prehistory, on the values of \( T_{heat} \) and \( t_{heat} \), and also on the heating and cooling schedules (continuous or stepped change in temperature). In the case of stepped (cascade) heating and cooling schedules, a great extent of structural changes of the polymers is achieved by comparison with continuous heating and cooling schedules. Taking into account the differences in the heat treatment conditions of polymers in different media (for example, the absence of oxidative processes during the heating of specimens in inert gas), it is necessary to introduce the parameter of the medium \( \xi_{med} \). Finally, for complete characterisation of the process of heat treatment of polymers in an arbitrary medium, it
is expedient to take into account the values of the initial temperature \( T_{\text{init}} \) and final temperature \( T_{\text{fin}} \) to which cooling of the heated specimen occurs.

Purposeful investigation of the effect of heat treatment on the structure and physical properties of polymers of various classes enabled one of the present authors to formulate the fundamental “fork” rule and its corollary [5, 9, 25, 26]. This rule states: “The characteristics of the structures and all physical properties of polymers in the initial state always occupy an intermediate position in relation to the corresponding values of quenched and annealed specimens”. This rule can be illustrated graphically in the following way. Let the structure or a certain physical property of the initial polymer (“init”) correspond to a certain central position of the vector \( B_{\text{init}} \) (Figure 9). An entirely quenched specimen (“quench”) possessing the most disordered structure will be characterised by the vector \( A_{\text{quench}} \). The structure and properties corresponding to the maximum molecular ordering of the annealed specimen (“anneal”) will be characterised by the vector \( C_{\text{anneal}} \). Whatever the quenching schedule, the vectors \( 1, 2 \) characterising the structure and properties of the polymer will be found in the left half of the diagram, occupying a position between vectors \( A_{\text{quench}} \) and \( B_{\text{init}} \). Similarly, whatever the annealing schedule, the vectors \( 3, 4 \) characterising the structure and properties will occupy a position between vectors \( B_{\text{init}} \) and \( C_{\text{anneal}} \) in the right-hand part of the diagram. In this case, neither vectors 1 and 2 nor vectors 3 and 4 can transfer via vector \( B_{\text{init}} \). This rule, which is fulfilled for all polymer systems investigated, has an important corollary: “For all polymers in the initial state (before heat treatment) there exists a particular molecular ordering in the form of the corresponding supermolecular formations”.

To describe the processes of heat treatment, a multiparametric equation of the form

\[
F(\gamma_{\text{str}}, \xi_{\text{med}}, T_{\text{init}}, \omega^+, T_{\text{heat}}, t_{\text{heat}}, \omega^-, T_{\text{fin}}) = 0 \tag{5}
\]

was proposed. Here, \( \gamma_{\text{str}} \) is a parameter characterising the structural organisation of the polymer (the degree of crystallinity, the density, the crosslink density), \( \xi_{\text{med}} \) is a factor corresponding to a certain medium in which heat treatment is carried out (liquid, air, inert gas, vacuum), \( T_{\text{init}} \) is the initial temperature from which heating of the specimens is carried out, \( \omega^+ \) is the heating rate of the specimens in continuous or stepped (cascade) schedules, \( T_{\text{heat}} \) is the heating temperature of the specimens in the heating chamber, \( t_{\text{heat}} \) is the heating time of the polymers in the corresponding medium, \( \omega^- \) is the cooling rate of the specimens in continuous or cascade schedules, and \( T_{\text{fin}} \) is the temperature to which the specimens are cooled after their annealing.

To this equation there corresponds the following scheme of heat treatment presented in temperature–time \((T-t)\) coordinates (Figure 10). The heating time of the polymers \( t_{\text{heat}} \) is the difference \( t_2 - t_1 = t_{\text{heat}} \). The remaining quantities are interpreted in the caption to this figure.

The given equation makes it possible to establish the functional relationship between the structural and physical characteristics of the polymers subjected to quenching or annealing, and the parameters of the heat treatment schedule. Consequently, physical modification of the polymers by their heat treatment is a fairly effective method of purposeful control of their structure and properties with the aim of achieving compliance with certain service requirements.

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Figure 9. Schematic diagram of heat treatment of polymers (AB – quenching schedule; BC – annealing schedule; 1, 2 – processes with different quenching schedules; 3, 4 – processes with different annealing schedules; AD – limiting quenching schedule; DC – limiting annealing schedule; BD – initial state of polymer before its heat treatment)

Figure 10. Schematic of process of heat treatment of polymers in quenching and annealing schedules with continuous and stepped heating rates \( \omega^+ \) and cooling rates \( \omega^- \) (here, \( t^*_h \) and \( t^*_c \) are holding times of specimens at fixed temperatures during heating and cooling)
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