Methods for Calculating the Physical Properties of Polymers

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Abstract—The approaches that derive the best predictions of physical properties of polymers from the chemical structure of their repeating unit are the van Krevelen, Bicerano, and Askadskii−Matveev. The potential of these three approaches is analyzed. All of the approaches are computerized and allow online predictions to be made. The PDTools and SYNTHIA programs are briefly overviewed, and the Cascade software (developed at the Nesmeyanov Institute of Organoelement Compounds) is described in detail. All of the approaches and the corresponding computer programs make it possible to estimate over 120 physical properties of polymers, including their volumetric, thermal, mechanical, thermophysical, optical, dielectric, and barrier properties. Particular attention is focused on the solubility and miscibility of polymers and on the properties of copolymers, polymer blends, and nanocomposites. The Cascade software provides the means to carry out computer syntheses of polymers with preset properties, the intervals of which are input by the user, and to calculate the dependences of these properties on temperature, plasticizer and nanoparticle concentrations, and nanoparticle size and shape.

CONTENTS

1. INTRODUCTION

At present, there are three basic approaches to estimating and predicting physical properties of polymers from the chemical structure of their repeating unit.

The van Krevelen approach [1, 2] is based on the group contribution method. Each chemical group contained in the repeating unit of a polymer makes its contribution to a given property of the polymer, and the sum of these contributions characterizes the repeating unit as a whole. This approach is empirical, even though it covers a wide range of polymer properties. The most serious drawback of this approach is that it will be impossible to calculate this property if a polymer contains a chemical group that has a contribution to the given property of zero.

There are computer programs (including PDTools) based on this approach.

The Bicerano approach [3] is based on the so-called connectivity indices, which are the principal descriptors of the topology of the repeating units of polymers. The polymer properties correlate with these connectivity indices.

However, it is necessary to apply simple corrections for particular groups and structures to enhance the accuracy of calculations. Various correlations between properties are established as a result, and these correlations allow the physical properties of polymers to be estimated. This approach is applicable to polymers containing atoms of up to nine elements.

In the **Askadskii–Matveev approach** [4–17], the repeating unit of a polymer or the repeating fragment of a polymer network is considered as a set of anharmonic oscillators describing the thermal motion of atoms in the region of intramolecular and intermolecular forces (including weak dispersion forces, dipole–dipole interactions, and hydrogen and valence bonds). The critical temperature of this set of anharmonic oscillators is correlated either with the glass transition temperature or with the onset temperature of intensive thermal degradation. The introduction of slightly simplifying assumptions into this theory leads to computational schemes that employ a set of atomic constants and a small number of empirical parameters that are independent of the chemical structure of the polymer. In the strict sense, this method cannot be assigned to additivity methods, since many of the calculated properties are not additive with respect to the constituting atoms or groups of the polymer. However, for a small number of properties, such as volumetric properties and cohesion energy, the additivity approach is used as well.

The elements contained in the repeating unit of a polymer or in the repeating fragment of a network are listed below:

H, F, Cl, Br, I, O, S, N, P, As, C, Si, Sn, Pb, B

The Bicerano and van Krevelen methods are limited to the properties of polymers containing only the following nine types of atoms:

C, H, N, O, F, S, Cl, Br

Table 1. Properties of polymers calculated by the three methods considered

No.	Property	Askadskii–Matveev	Bicerano	Van Krevelen
1	Van der Waals volume	x	x	x
2	Molar volume	x	x	x
3	Temperature dependence of molar volume	x	x	x
4	Density	x	x	x
5	Temperature dependence of density	x	x	x
6	Thermal expansion coefficient in the rubbery state	x	x	x
7	Thermal expansion coefficient in the glassy state	x	x	—
8	Glass transition temperature	x	x	x
9	Glass transition temperature as a function of molecular weight	x	—	—
10	Viscous flow transition temperature as a function of molecular weight	x	—	—
11	Solubility parameter	x	x	x
12	Molar cohesion energy	x	x	x
13	Surface energy	x	x	x
14	Temperature dependence of surface tension	x	x	—
15	Molar parachor	—	x	x
16	Molar heat capacity in the rubbery state	x	x	x
17	Temperature dependence of molar heat capacity in the rubbery state	x	x	—
18	Molar heat capacity in the glassy state	x	x	x
19	Temperature dependence of molar heat capacity in the glassy state	x	x	—
20	Thermal conductivity	x	x	—
21	Temperature dependence of thermal conductivity	—	x	—
22	Heat capacity jump at the glass transition temperature	x	x	—
23	Yield strength	—	x	—
24	Bulk modulus in the rubbery state	—	x	—
25	Shear modulus in the rubbery state	—	x	—
26	Elastic modulus in the rubbery state	—	x	—
27	Bulk modulus in the glassy state	—	x	—
28	Elastic modulus of glassy polymers	—	x	—
29	Shear modulus of glassy polymers	—	x	—
30	Poisson's ratio in the glassy state	—	x	—
31	Brittle strength	—	x	—
32	Molecular weight between two cross-linked points	—	x	—
33	Refractive index	x	x	x
34	Temperature dependence of refractive index	x	—	—
35	Molar refraction	x	x	x
36	Dielectric constant	x	x	x
37	Temperature dependence of dielectric constant	x	—	—
38	Dielectric loss factor	x	x	—
39	Dielectric loss factor as a function of frequency	x	—	—
40	Molar polarizability	x	x	—
41	Effective dipole moment	x	x	—
42	Oxygen permeability	x	x	—
43	Nitrogen permeability	x	x	—
44	Carbon dioxide permeability	x	x	—
45	Water permeability	x	—	—
46	Half-weight loss temperature	—	x	—

Table 1. (Contd.)

No.	Property	Askadskii–Matveev	Bicerano	Van Krevelen
47	Onset temperature of intensive thermal degradation	x	—	—
48	Viscosity of melt	—	x	—
49	Activation energy for viscous flow	—	x	—
50	Temperature dependence of zero shear viscosity	—	x	—
51	Molecular weight of the repeating unit	x	—	x
52	Molar volume as a function of the degree of crystallinity	x	—	x
53	Density as a function of the degree of crystallinity	x	—	x
54	Molar volume as a function of the degree of crystallinity	x	—	x
55	Excess molar volume in the glassy state;	x	—	x
56	Increase in molar volume at the melting point	—	—	x
57	Increase in molar volume at the glass transition temperature	—	—	x
58	Melting point	—	—	x
59	Dispersion component of solubility parameter	x	—	x
60	Solubility parameter component due to polar groups	x	—	x
61	Solubility parameter component arising from hydrogen bonding	x	—	x
62	Specific heat capacity in the rubbery state	x	—	x
63	Specific heat capacity in the glassy state	x	—	x
64	Molar enthalpy of melting	—	—	x
65	Difference between the solid- and rubbery-state molar enthalpies	—	—	x
66	Stress-optic coefficient in the glassy state	x	—	—
67	Total intermolecular interaction energy	x	—	—
68	Dispersion interaction energy	x	—	—
69	Dipole–dipole interaction and hydrogen bonding energy	x	—	—
70	Fraction of the dispersion interaction and hydrogen bonding energy in the total intermolecular interaction energy	x	—	—
71	Fraction of the dipole–dipole interaction and hydrogen bonding energy in the total intermolecular interaction energy	x	—	—
72	Polymer/polymer interfacial tension	x	—	—
73	Polymer/solvent interfacial tension	x	—	—
74	Elastic modulus in the rubbery-state plateau region	x	—	—
75	Mechanical segment value (molecular weight or degree of polymerization at which the rubbery state begins to show itself)	x	—	—
76	Activation energy of low-temperature γ-transition	x	—	—
77	Prediction of the solubility of polymers in organic solvents	x	—	—
78	Molecular weight effect on solubility	x	—	—
79	Effect of the degree of orientation on solubility	x	—	—
80	Prediction of polymer–polymer miscibility	x	—	—
81	Softening (glass transition) temperature for polymer–plasticizer blends	x	—	—
82	Temperature dependence of the molecular packing coefficient	x	—	—
83	Identification of chemical groups that are responsible for thermal decomposition	x	—	—

Table 2. Calculated and experimental glass transition temperature data for some polymers
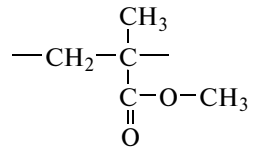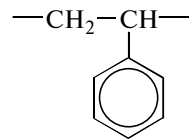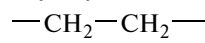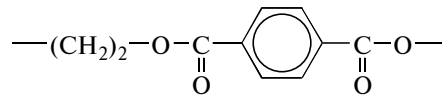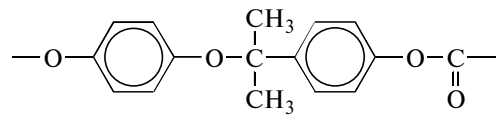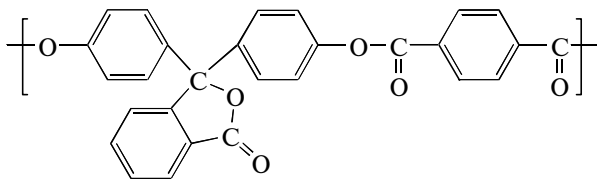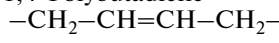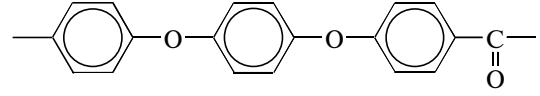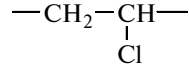
Polymer	Askadskii–Matveev	Bicerano	Van Krevelen	T_g, K experimental value
Poly(methyl methacrylate)	377	355	377	376−379
Polystyrene	376	381	372	365−370
Polyethylene —CH_2—CH_2—	214	192	192	–
Polypropylene	279	230	254	260−267
Polyethylene terephthalate	375	369	361	342−370
Polycarbonate	431	416	411	423
Polyester (polyarylate F-2)	576	558	–	583−593
Polyamide 6	335	334	332	323−348
1,4-Polybutadiene —CH_2—$CH=CH$—CH_2—	171	173	201	166−171
Polyether ether ketone	416	433	426	410−425
Polyvinyl chloride	341	292	353	344

Table 2. (Contd.)

Polymer	Askadskii–Matveev	Bicerano	Van Krevelen	T_g, K experimental value
Poly(vinyl ethyl ether) $-CH_2-CH-$ $\quad\quad O-CH_3$	245	264	251	239−242
Polydimethylsiloxane $\quad CH_3$ $-Si-O-$ $\quad CH_3$	150	153	148	150
Poly(vinyl alcohol) $-CH_2-CH-$ $\quad\quad OH$	365	333	356	348−358
Polyvinyl acetate $-CH_2-CH-$ $\quad\quad O-C-CH_3$ $\quad\quad\quad\; O$	301	304	302	308

2. PROPERTIES OF POLYMERS CALCULATED BY THE CONSIDERED METHODS

Table 1 lists the polymer properties that are calculated by the above methods. The properties that can be calculated by a given method are marked by the symbol "×"; the properties that cannot be calculated by this method are marked by the symbol "−".

Of the 83 properties considered, 62 can be calculated by the Askadskii−Matveev method, 43 by the Bicerano method, and 32 by the van Krevelen method.

In order to compare the accuracies of calculations, we will select a number of polymer standards, the properties of which have been reliably and investigated multiple times. Comparisons will be made in terms of the glass transition temperature, a very important characteristic of polymers. Table 2 presents the calculated and experimental glas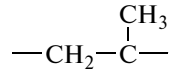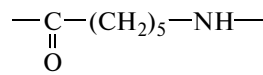s transition temperatures for selected polymers. Clearly, the calculated data in most cases are in good agreement with the experimental data, with the difference not exceeding 3−5%. Note that the van Krevelen method is inapplicable to some polymers and the glass transition temperature calculated by the Bicerano method for polyvinyl chloride differs significantly from its experimental value.

3. MACROMOLECULAR PACKING AND FREE VOLUME IN POLYMERS

Determination of the density of macromolecular packing in polymer materials is of great importance, since many properties of polymers depend on this characteristic. The free volume, which is determined as a result of this analysis, depends on the molar and van der Waals volumes, with the former depending on temperature and on the material preparation method. For this reason, it is initially pertinent to consider the calculation of the van der Waals volume of the repeating unit of the polymer, since this volume is involved in many physical relationships to estimate polymer properties (refractive index, surface energy, interfacial tension, etc.). This quantity is also involved in polymer solubility and miscibility criteria, which are essential in polymer blending. The free volume, which is related to the molecular packing coefficient, provides the means to estimate the density of the polymer material. The latter is involved in a number of physical relationships for calculating the refractive index, dielectric constant, etc.

We will successively consider the estimation of the van der Waals volume from the chemical structure of the repeating unit, an analysis of the molecular packing coefficient for amorphous and crystalline bodies, the temperature effect on this quantity, and the ways of estimating the free volume in amorphous and crystalline materials.

Table 3. Intermolecular radii of some atoms

Atom	R, nm	Atom	R, nm
Carbon, C	0.180	Chlorine, Cl	0.178
Hydrogen, H	0.117	Fluorine, F	0.150
Oxygen, O	0.136	Silicon, Si	0.210
Nitrogen, N	0.157	Sulfur, S	0.221

3.1. General Provisions

Our consideration of the repeating unit volume will be based on ideas developed by Kitaigorodskii [18] in organic crystal chemistry. According to these ideas, each atom is described in terms of a sphere with an intermolecular radius R. The values of these radii are determined from X-ray crystallography data for ideal crystals of organic compounds. It is assumed that the atoms that are not bonded by valence bonds but are involved in intermolecular (nonchemical) interaction—they touch one another at the boundaries of their spheres. According to the same conception, the chemical interaction between two atoms always presses them together; that is, the length of the resulting chemical bond is always smaller than the sum of the two intermolecular radii. Provided that the intermolecular radii R_i for all atoms of the repeating unit of the polymer are known, and so are the lengths of all chemical bonds between these atoms, one can readily calculate the intrinsic (van der Waals) volume of the repeating unit and construct a model of this unit (or a small fragment of a macromolecule) in which the volume of each atom is bounded by a sphere with an intermolecular radius R_i.

Table 3 lists intermolecular radii for some common atoms constituting most polymers.

Table 4 presents the bond lengths for various atomic combinations that are typical of most of the existing polymers.

Knowing these values, one can calculate the repeating unit volume for practically any polymer. Preliminarily, it is necessary to determine the intrinsic volume of each atom in the repeating unit. This calculation is carried out using the formula

$$\Delta V_i = \frac{4}{3}\pi R^3 - \sum_i \frac{1}{3}\pi h_i^2 (3R - h_i), \tag{1}$$

where ΔV_i is the increment of the intrinsic volume of the ith atom, R is the intermolecular (van deer Waals) radius of this atom, and h_i is the height of the spherical segment that is cut off the given atom by a chemically bonded adjacent atom. The h_i value is calculated as

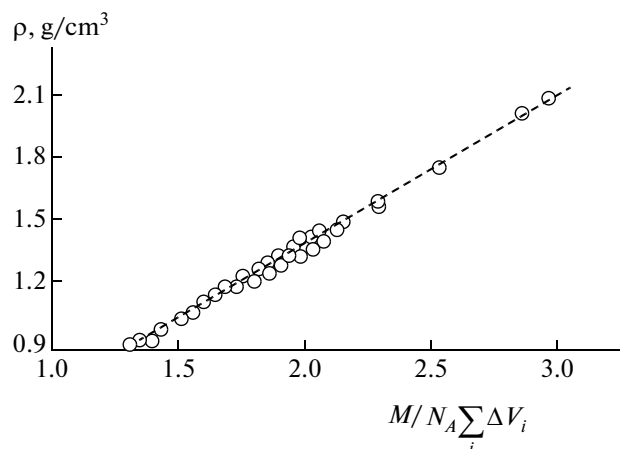$$h_i = R - \frac{R^2 + d_i^2 - R_i^2}{2d_i}, \tag{2}$$

Fig. 1. Density of amorphous and semy-crystalline polymers as a function of the ratio of the molar mass of the repeating unit (M) to its intrinsic molar volume $N_A \sum_i \Delta V_i$.

Table 4. Bond lengths d_i between some atoms

Bond*	d_i, nm	Bond*	d_i, nm
C–C	0.154	C–S	0.176
C–C	0.148	C–Si	0.188
C=C	0.140	C–Si	0.168
C=C	0.134	C–F	0.134
C–H	0.108	C–F	0.131
C–O	0.150	C–Cl	0.177
C–O	0.137	C–Cl	0.164
C–H	0.108	H–O	0.108
C–O	0.150	H–S	0.133
C–O	0.137	H–N	0.108
C–N	0.140	O–S	0.176
C–N	0.137	O–Si	0.164
C=N	0.131	O–F	0.161
C=N	0.127	O=N	0.120
C≡C	0.116	O=S	0.144
C–S	0.156	S–S	0.210

* If a given pair of atoms is linked by an ordinary bond, then the larger bond length value refers to the aliphatic carbon–atom bond and the smaller one refers to the aromatic carbon–atom bond.

where R_i is the intermolecular radius of the valence-bonded adjacent atom and d_i is the length of the chemical bond.

Some increments of the volumes of atoms and atomic groups are listed in Table 5.

Obviously, the volume of each atom of a given kind (carbon, oxygen, nitrogen, etc.) depends on its environment, more specifically on the kinds of atoms that are chemically bonded to it. For example, this is clear from a comparison between the volumes of carbon atom no. 1 (which is chemically bonded to four carbon atoms) and carbon atom no. 2 (which is chemically bonded with three carbon atoms and one hydrogen atom), between the volumes of atom nos. 1 and 17 (the latter is bonded to two carbon atoms and two oxygen atoms), and between the volumes of atom nos. 1 and 23 (the latter is bonded to one oxygen atom by an ordinary bond, to one oxygen atom by a double bond, and to one carbon atom).

Other clear examples can be found in Table 5. The larger the volume of the chemically bonded adjacent atom is, the shorter the chemical bond is and the larger the extent is to which the given atom is pressed in.

3.2. Monolithic Polymer Bodies

After the determination of the volume increments ΔV_i for all atoms constituting the repeating unit of the polymer, the occupied fraction of the total volume of the polymer body is calculated. For polymers, the calculations are conveniently performed in terms of the molar volume of the repeating unit, because polymers are always polydisperse, containing macromolecules of different lengths. The intrinsic molar volume will then be $V_{intr} = N_A \sum_i \Delta V_i$ and the total molar volume will be $V_{tot} = M/\rho$, where ρ is the density of the polymer body and M is the molecular weight of the repeating unit.

Numerous experiments and calculations have demonstrated that $V_{intr} < V_{tot}$ in all cases. Thus, in the first approximation the volume of a polymer body can be divided into the intrinsic volume of the atoms in the solid and the volume of voids, with the latter defined as the difference between V_{tot} and V_{intr}.

The occupied fraction of the volume, or, according to the terminology accepted in organic crystal chemistry, the molecular packing coefficient k, is defined as

$$k = V_{intr}/V_{tot} = \frac{N_A \sum_i \Delta V_i}{M/\rho} \tag{3}$$

Tables 5. Increments of the Van der Waals volumes of atoms

1

C C
1.54 1.54
C
1.54 1.54
C C

5.0

2

C H
1.54 1.08
C
1.54 1.54
C C

9.0

3

C H
1.54 1.08
C
1.08 1.54
H C

13.1

4

C H
1.54 1.08
C
1.08 1.50
H H

17.2

5

H C
1.54 1.54
C
1.34
C

9.0

6

H C
1.08 1.54
C
1.34
C

13.1

14

F
1.64
C
1.40 1.40
C C

10.6

15

Cl
1.64
C
1.40 1.40
C C

9.2

16

C O
1.54 1.50
C
1.54 1.54
C C

8.6

17

C O
1.54 1.50
C
1.50 1.54
O C

10.8

18

C H
1.54 1.08
C
1.08 1.50
H O

16.2

19

O O
1.50 1.50
C
1.28
O

19.0

27

Si H
1.88 1.08
C
1.08 1.54
H C

11.9

28

H
1.08
C

2.0

29

O
1.08
O

4.7

30

C C
1.50 1.50
O

3.4

31

C H
1.50 1.08
O

5.6

32

C C
1.50 1.50
N
1.40
C

2.4

Table 5. (Contd.)

7

17.1

20

17.1

33

5.0

8

12.7

21

6.5

34

9.2

12.9

9

8.4

22

14.7

35

19.5

10

11.6

23

17.4

36

20.3

11

10.2
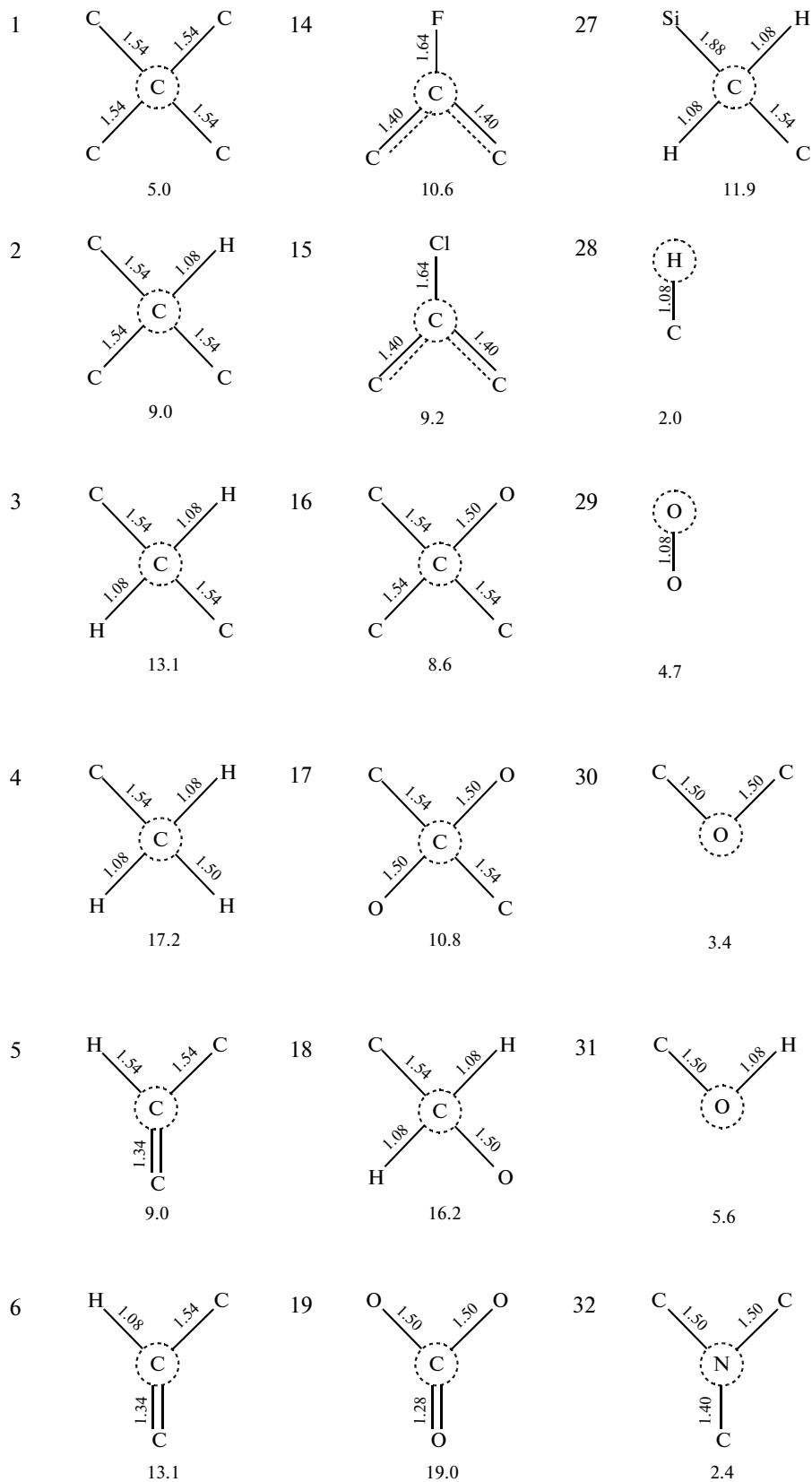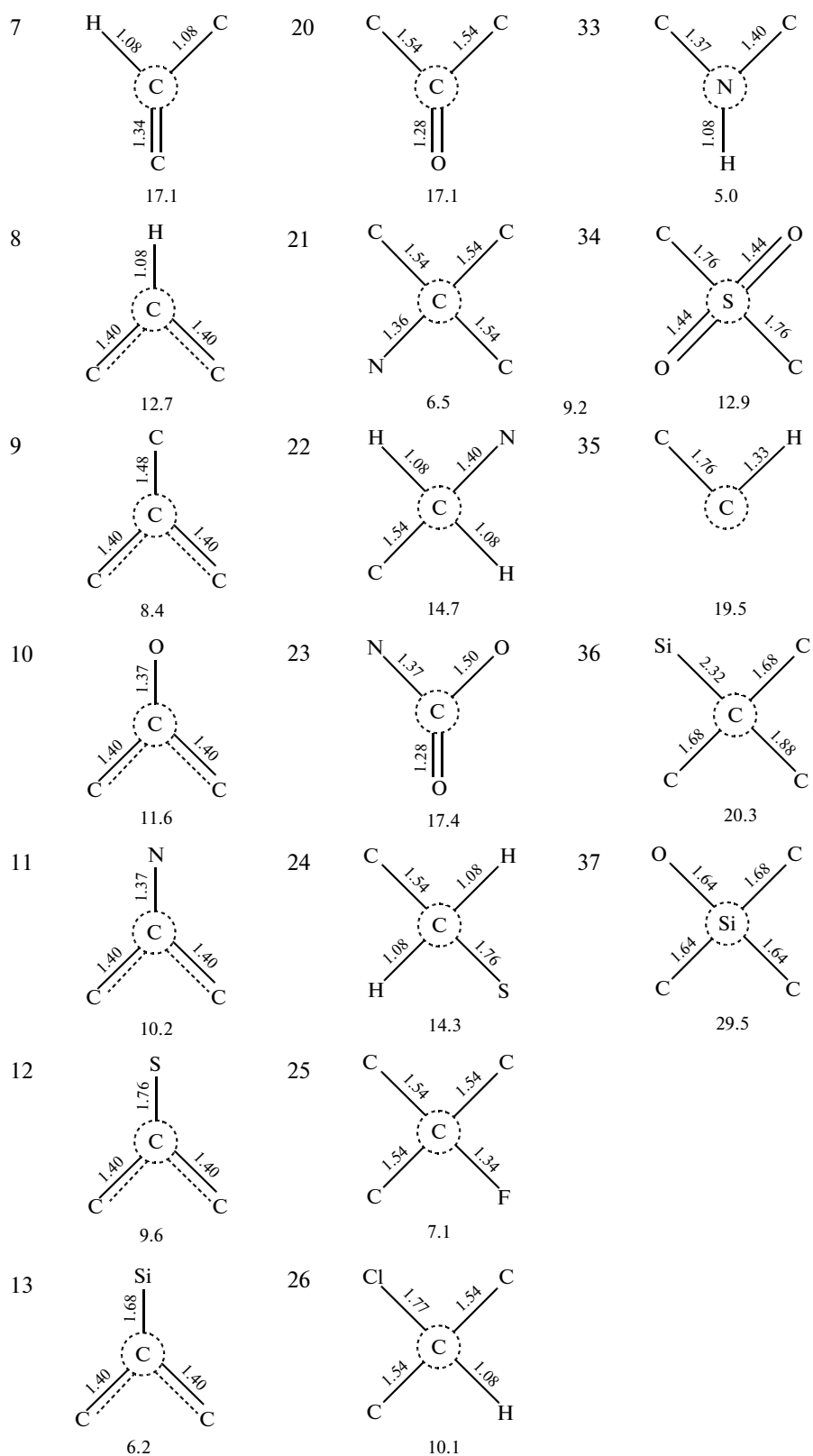
24

14.3

37

29.5

12

9.6

25

7.1

13

6.2

26

10.1

The value of k for a given polymer depends on temperature, because ρ is a temperature-dependent quantity. The calculations carried out for a large number of amorphous polymer monoliths in the glassy state demonstrated that, in the first approximation, k is constant and depends only slightly on the chemical structure of the polymer. Passing from chemically simple polymers to polymers with a very complex chemical structure does not cause any significant change in the occupied volume fraction (i.e., k). Table 6 presents chemical structures and molecular packing coefficient data for some glassy and semy-crystalline polymers.

The k values for these polymers are actually equal in the first approximation. In order to clearly illustrate this experimental fact, we will plot the density ρ of some polymers versus the $M/N_A \sum_i \Delta V_i$ ratio (Fig. 1).

All of the experimentally determined ρ values fall on the same straight line, which represents the linear dependence of the density on the ratio of the mass of atoms to their volume. According to Eq. (3), the slope of this line gives the molecular packing coefficient k, which is a universal constant in the case of amorphous monolithic systems in the first approximation. The polymer density ρ can, therefore, be calculated via the equation

$$\rho = \frac{kM}{N_A \sum_i \Delta V_i}, \tag{4}$$

which follows immediately from Eq. (3) with $k = \text{const}$.

In the case of amorphous monolithic polymers, the average molecular packing coefficient at room temperature is $k_{av} = 0.681$. Variation of the chemical structure of the polymer cannot exert a significant effect on the occupied volume fraction in an amorphous polymer body, and the value of density itself depends practically only on the ratio of the mass and volume of the repeating unit.

The coefficient k as a function of temperature is calculated via formulas following from relationship (3):

$$k(T) = \frac{N_A \sum_i \Delta V_i}{M \nu_g \left[1 + \alpha_G \left(T - T_g \right) \right]}, \quad T < T_g \tag{5}$$

$$k(T) = \frac{N_A \sum_i \Delta V_i}{M \nu_g \left[1 + \alpha_L \left(T - T_g \right) \right]}, \quad T > T_g \tag{6}$$

where ν_g is the specific volume of the polymer at the glass transition temperature T_g, and α_G and α_L are the volumetric thermal expansion coefficients of the polymer below and above the glass transition temperature, respectively.

Calculations demonstrated that, in a closer approximation, the molecular packing coefficient is the same for each polymer at its glass transition temperature. All of this is true for only amorphous polymer materials. For crystalline polymers, as distinct from amorphous polymers, the molecular packing coefficient varies widely. By way of example, we present crystallographic densities and molecular packing coefficients for a number of crystalline polymers (Table 7).

The molecular packing coefficients of crystalline polymers vary in a wide range, depending on the chemical structure and unit cell type.

3.3. Free Volume of Polymers

There are three basic definitions of the free volume (apart from various modifications):

(1) The free volume is the difference between the true molar volume V_M of the body and its van der Waals molar volume,

$$\Delta V = V_M - N_A \sum_i \Delta V_i = M/\rho - N_A \sum_i \Delta V_i \tag{7}$$

The ΔV value is often called the empty volume. Obviously, the empty volume depends on temperature, since the molar volume $V_M = M/\rho$ is temperature-dependent.

The temperature dependences of the empty volume for the glassy and rubbery states appear as follows:

$$\Delta V(T) = N_A \sum_i \Delta V_i \left\{ \frac{\left[1 + \alpha_G \left(T - T_g \right) \right]}{k_g} \right\}; \quad (T < T_g) \tag{8}$$

$$\Delta V(T) = N_A \sum_i \Delta V_i \left\{ \frac{[1 + \alpha_L (T - T_g)]}{\kappa_g} - 1 \right\}; \quad (T > T_g) \tag{9}$$

Here, T_g is the glass transition (or softening point) of the polymer.

(2) The free volume is the difference between the volume of the body at absolute zero and the volume of the same body at a given temperature; in other words, the free volume is the excess volume resulting from the thermal expansion of the body.

(3) The free volume is the difference between the volume of the polymer body at a given temperature and the volume of the ideal crystal built from a polymer of the same chemical structure. This molar free volume is described by the following relationship:

$$\Delta V = \frac{N_A \sum_i \Delta V_i}{k_{am}} - \frac{N_A \sum_i \Delta V_i}{k_{cr}} = N_A \sum_i \Delta V_i \left(\frac{1}{k_{am}} - \frac{1}{k_{cr}} \right), \tag{10}$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit of the polymer, and k_{am} and k_{cr} are the molecular packing coefficients for the amorphous polymer and ideal crystal, respectively.

The method of estimating the k_{am} value at a given temperature was described above. For ideal crystals, k_{cr} can be taken from monographs [4−8]. For polymers whose ideal crystals have not been investigated, k_{cr} can be taken to be 0.74 (for rough calculations).

The specific free (empty) volume Δv is described by the following relationship:

$$\Delta v = \frac{N_A \sum_i \Delta V_i}{M k_{am}} - \frac{N_A \sum_i \Delta V_i}{M k_{cr}} = \frac{N_A \sum_i \Delta V_i}{M} \left(\frac{1}{k_{am}} - \frac{1}{k_{cr}} \right) \tag{11}$$

The fractional free volume (FFV) of polymers is commonly calculated using Bondi's empirical formula [19]:

$$FFV = (v - 1.3 v_w)/v, \tag{12}$$

where v is the specific volume of the polymer and v_w is the specific van der Waals volume.

Another formula is written as

$$FFV = (V - 1.3 V_w)/V, \tag{13}$$

where V is the molar volume and V_w is molar van der Waals volume.

The coefficient 1.3 is an empirical parameter. The physical meaning of this parameter is as follows [20]. From formula (11),

$$1.3 V_w = \frac{N_A \sum_i \Delta V_i}{k_{cr}} \tag{14}$$

Therefore, $1.3 = 1/k_{cr}$. This means that, according to Bondi, the molecular packing coefficient of all ideal crystals is $k_{cr} = 0.769$. In fact, k_{cr} depends on the chemical structure of the polymer and on the crystallographic type of its unit cell (see, e.g., [4−8]). In rough calculations, it is accepted that $k_{cr} = 0.74$. The formula for FFV will then appear as

$$FFV = (1 - k/k_{cr}), \tag{15}$$

where k is the molecular packing coefficient of the polymer at a given temperature. In precise calculations, experimental k_{cr} data should be used and is derived from experimental density data [4−8].

The above analysis demonstrates that the molecular packing coefficient for amorphous and for amorphous−crystalline polymers (with a degree of crystallinity no higher than 50−60%) has a constant value of 0.68 in the first approximation. For ideal crystals, this parameter depends on the chemical structure of the polymer and on the crystal lattice type. All of the physical parameters appearing the above relationships were calculated using the computer program Cascade.

Having performed a detailed analysis of the calculation of the van der Waals volume, density, and free volume of polymers, we will briefly consider the physical characteristics reported in our monographs [4−8] and, in greater detail, the properties for which computational methods have been suggested in recent years.

4. THERMAL PROPERTIES

4.1. Glass Transition Temperature of Linear Polymers

A number of relationships have been suggested for calculating the glass transition temperature T_g of linear polymers. We will consider the following expression [4−8]:

$$\frac{1}{T_g} = 4.55R\left\langle\frac{1}{zD_0}\right\rangle,\tag{16}$$

where $\left\langle\dfrac{1}{zD_0}\right\rangle = \dfrac{\sum\limits_i \dfrac{1}{z_iD_{0i}}\Delta V_i}{\sum\limits_i \Delta V_i}$, z_i is the coordination number of the ith atom, D_{0i} is the energy of the bonding

between the ith atom and the adjacent atoms, ΔV_i is the van der Waals volume of the ith atom, and R is the gas constant.

The numerical values of $1/(z_iD_{0i})$, which are characteristic of each atom and each type of intermolecular interaction, were determined by least-squares processing of experimental data. The bond energies resulting from the statistical processing of experimental data are equal to the corresponding intermolecular interaction energies. The presence of polar groups leading to strong intermolecular interaction in the polymer is taken into account by introducing appropriate increments.

For practical calculations, formula (16) can be rewritten as

$$T_g = \frac{\sum\limits_i \Delta V_i}{\sum\limits_i a_i\Delta V_i + \sum\limits_j b_j}\tag{17}$$

Here, a_i is the set of atomic constants that are related to the energy of weak dispersion interaction and characterize the averaged contribution from each atom to this interaction, and b_j is the set of increments that are related to the strong specific intermolecular interactions (dipole−dipole interaction, hydrogen bonding, etc.). The values of a_i and b_j are presented in our monographs [4−6].

For copolymers, the glass transition temperature is calculated using the relationship

$$T_g = \frac{\sum\limits_{k=1}^{k=n} \alpha_k\left(\sum\limits_i \Delta V_i\right)_k}{\sum\limits_{k=1}^{k=n} \alpha_k\left(\sum\limits_i a_i\Delta V_i + \sum\limits_j b_j\right)_k + 0.03\sum\limits_{k=1}^{k=n} \alpha_k\left(1 - \alpha_k\right)}\tag{18}$$

where α_k, $\left(\sum\limits_i \Delta V_i\right)_k$, and $\left(\sum\limits_i a_i\Delta V_i + \sum\limits_j b_j\right)_k$ are, respectively, the mole fraction, van der Waals volume, and set of atomic constants and increments for the kth component.

In order to calculate the glass transition temperature of a copolymer via formula (18), it is unnecessary to know the experimental glass transition temperatures of the constituent homopolymers. Formula (18) can be represented as

$$T_g = \frac{\sum\limits_{k=1}^{k=n} \alpha_k\left(\sum\limits_i \Delta V_i\right)_k}{\sum\limits_{k=1}^{k=n} \alpha_k\dfrac{\left(\sum\limits_i \Delta V_i\right)_k}{T_{g,k}} + 0.03\sum\limits_{k=1}^{k=n} \alpha_k\left(1 - \alpha_k\right)},\tag{19}$$

where $T_{g,k}$ is the glass transition temperature of the kth component.

In calculations via formula (19), it is possible to use both calculated and experimental $T_{g,k}$ data.

Since the glass transition temperature is among the most important charcteristics of polymers, we will dwell on the van Krevelen and Bicerano methods of calculating it.

According to van Krevelen [1, 2], T_g is calculated via the relationship

$$T_g = 10^3 \left(\frac{\sum_i Y_{g,i}}{M} \right), \tag{20}$$

where $Y_{g,i}$ is the molar contribution to the glass transition temperature from the ith group and M is the molecular weight of the repeating unit.

The group contributions $Y_{g,i}$ can be found in monographs [1, 2]. For hydrocarbon polymers with side groups,

$$Y_g \approx 0.2M_9 = Y_{g,9} \quad \text{for} \quad N = 9$$
$$Y_g = Y_{g0} + (N/9)(Y_{g9} - Y_{g0}) \quad \text{for} \quad N < 9$$
$$Y_g = Y_{g9} + 7.5(N - 9) \quad \text{for} \quad N > 9$$

Here, N is the number of methyl groups in the side chain. The values of Y_{g0} and Y_{g9} can be taken from monographs [1, 2].

In the Bicerano method, T_g is calculated using the following correlation [3]:
$$T_g = 351.0 + 5.63\delta + 31.68(N_{Tg}/N) - 23.94x_{13};$$

Here, δ is the Hildebrand solubility parameter and $N_{Tg} = 15x_1 - 4x_2 + 23x_3 + 12x_4 - 8x_5 - 4x_6 - 8x_7 + 5x_8 + 11x_9 + 8x_{10} - 11x_{11}4x_{12}$; and N is the number of hydrogen atoms per repeating unit; the x_i values are related to characteristic features of the chemical structure: the presence of aromatic and aliphatic rings, the positions of substituent groups (*ortho*, *meta*, and *para*), hydrogen bonding, the presence of double bonds, etc.

The Bicerano method has no limitations imposed on the chemical structure of the polymer, while the van Krevelen method is limited to polymers containing atomic groups with available group contributions.

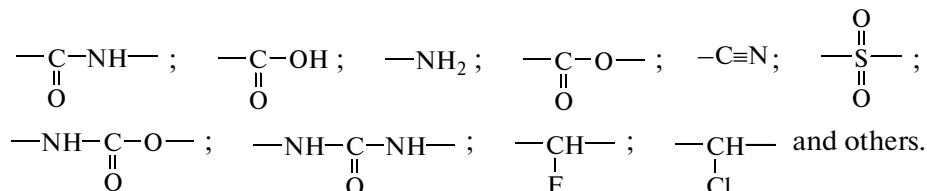### 4.2. Onset Temperature of Intensive Thermal Degradation

Experimentally, this characteristic (T_d) is determined as the intersection point of the tangents to two branches of the thermogravimetric curve. It is calculated via the following relationship [4−8]:

$$T_d = \frac{\sum_i \Delta V_i}{\sum_i K_i \Delta V_i}, \tag{21}$$

where K_i stands for the atomic constants related to the parameters of the Morse potential; $K_i = \dfrac{63}{2} \dfrac{R}{(ad_0E)_i}$

where a and d_0 are the parameters of the Morse potential and E is the chemical bond energy.

If some atoms are components of polar groups involved in specific intermolecular interactions, their contribution to thermal stability will differ from the contribution from the same atoms involved in ordinary van der Waals interactions. Examples of polar groups are given below:

$$-\underset{\overset{\|}{O}}{C}-NH- \; ; \quad -\underset{\overset{\|}{O}}{C}-OH \; ; \quad -NH_2 \; ; \quad -\underset{\overset{\|}{O}}{C}-O- \; ; \quad -C\equiv N; \quad -\underset{\overset{\|}{O}}{\overset{\|}{S}}- \; ;$$

$$-NH-\underset{\overset{\|}{O}}{C}-O- \; ; \quad -NH-\underset{\overset{\|}{O}}{C}-NH- \; ; \quad -\underset{\overset{|}{F}}{CH}- \; ; \quad -\underset{\overset{|}{Cl}}{CH}- \quad \text{and others.}$$

In the calculation of T_d via Eq. (21), the specific interaction is taken into account in the following way. If the atom is not in a polar group, then its contribution is designated K_i and is multiplied by the corresponding van der Waals volume. If the atom is a component of a polar group, then its contribution is designated K_i^h or K_i^d (h = hydrogen bond, d = dip[ole−dipole interaction) and only K_i^h or K_i^d is multiplied by the corresponding van der Waals volume; that is, the contribution from this atom to the van der Waals (dispersion) interaction, a much weaker one, is neglected. The parameters K_i, K_i^d, and K_i^h were reported in our earlier works [4−6]. Since T_d depends on the heating rate and on the medium in which degradation takes place, all of these data [4−6] refer to heating of the sample in an inert medium at a rate of 5 deg/min.

An analysis of the chemical structure effect on thermal degradation in terms of relationship (21) can be carried out both for the entire repeating unit of the polymer and for its fragments, which may be the

weakest ones. It is also possible to analyze the effect of terminal groups on the thermal stability of the polymer. All of these calculations can be carried out using the Cascade software.

4.3. Glass Transition Temperature of Network Polymers

It was suggested [4–6] that the dependence of the glass transition temperature T_g be quantitatively described in terms of Eq. (22). This equation was set up by analyzing the system of anharmonic oscillators constituting the repeating fragment of the polymer network and taking into account the energy of intermolecular interaction in the linear fragments between network cross-linked points and the energy of the chemical bonds in the cross-linked points:

$$T_g = \frac{\sum_i \Delta V_i}{\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_\varLambda + \left(\sum_i K_i \Delta V_i\right)_y}, \tag{22}$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the repeating fragment of the polymer network,

$\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_\varLambda$ is the set of constants for the linear chains linking network cross-linked points, and

$\left(\sum_i K_i \Delta V_i\right)_y$ is the set of constants for the network cross-linked points. The physical meaning of the parameters a_i, b_i, and K_i is the same as in Eqs. (17) and (21).

A network node is defined as a group of atoms that includes the atom at which branching takes place and the chemically bonded adjacent atoms together with their nearest substituents [4–6].

In the limiting case of a very sparse network, the value of $\left(\sum_i K_i \Delta V_i\right)_y$ is negligibly small and Eq. (22) reduces to relationship (17), which is valid for linear polymers. In the opposite limiting case, when the network is so dense that it consists only of cross-linked points, $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_\varLambda$ becomes zero and Eq. (22) turns into relationship (21). The loosening of this dense network can result only from its thermal degradation. Equation (22) provides the means both to accurately estimate the glass transition temperature of network polymers and to analyze the structure of polymer networks.

4.4. Volumetric Thermal Expansion Coefficient

In quantitative analysis of the chemical structure effect on the volumetric thermal expansion coefficient of polymers in the glassy state, α_G, it is necessary to take into account that α_G is not an absolute constant of a polymer body and varies even within the glassy state on passing from one temperature range to another. In low-temperature transitions, α_G increases with an increasing temperature. The relationship for the thermal expansion coefficient present below is valid only near the glass transition temperature T_g. The following relationship was suggested [4–6] for calculating α_G from the chemical structure of the repeating unit of the polymer:

$$\alpha_G = \frac{\sum_i \alpha_i \Delta V_i + \sum_j \beta_j}{\sum_i \Delta V_i}, \tag{23}$$

where $\alpha_i = a_i(k_0/k_g - 1)$; $\beta_j = b_j(k_0/k_g - 1)$; k_0 and k_g are the molecular packing coefficients near absolute zero and at the glass transition temperature, respectively ($k_0 = 0.731$ and $k_g = 0.667$). Here, $\alpha_i = 3R\beta_j/(\gamma_i^2 r_{0,i})$, β_i is the anharmonicity coefficient, $\beta_j = \frac{1}{2}\frac{\partial^3 \varphi}{\partial r^3}\bigg|_{r_{0i}}$; φ is the potential of the interaction of

the ith atom with the adjacent atoms (Lennard-Jones potential); γ_i s the harmonic force constant,

$$\gamma_i = \left.\frac{\partial^2 \varphi}{\partial r^2}\right|_{r_{0i}} \; ; r_{0i} \text{ is the distance between the } i\text{th atom and the adjacent atoms.}$$

The numerical values of α_i and β_j can be found in our monographs [4–6].

The volumetric thermal expansion coefficient for polymers in the rubbery state, α_L, can be approximately determined from the familiar relationship

$$(\alpha_L - \alpha_G)T_g = 0.115 \tag{24}$$

For this purpose, it is necessary to initially calculate the T_g and α_G values via Eqs. (17) and (23), respectively.

4.5. Intermolecular Interaction Energy

With the above approach to calculating the glass transition temperature [6], it is possible to calculate the total intermolecular interaction energy and its components associated with dipole−dipole interaction and different types of hydrogen bonds. The total intermolecular interaction energy $\langle D \rangle$ is described by the relationship

$$\langle D \rangle = \frac{R\sum_i \Delta V_i}{0.455\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)} m, \tag{25}$$

where m is the number of atoms in the repeating unit of the polymer.

Substituting Eq. (17) into formula (25), we obtain

$$\langle D \rangle = \frac{RT_g}{0.455} m \tag{26}$$

and, for copolymers,

$$\langle D \rangle = \frac{RT_{g,\text{cop}}}{0.455} \sum_{k=1}^{k=n} \alpha_k m_k, \tag{27}$$

where $T_{g,cop}$ is the glass transition temperature of the copolymer and m_k is the number of atoms in the repeating unit of the kth polymer.

The dispersion interaction energy $\langle D \rangle_d$ is determined from the following expression:

$$\langle D \rangle_d = \frac{R\sum_i \Delta V_i}{0.455\left(\sum_i a_i \Delta V_i\right)} m \tag{28}$$

For statistical copolymers,

$$\langle D \rangle_d = \frac{R\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \Delta V_i\right)_k}{0.455\sum_{k=1}^{k=n} \alpha_k \left(\sum_i a_i \Delta V_i\right)_k} \sum_{k=1}^{k=n} \alpha_k m_k \tag{29}$$

The dipole−dipole interaction and hydrogen bonding energy is calculated as

$$\langle D \rangle_{dd+h} = \langle D \rangle - \langle D \rangle_d = \frac{mR\sum_i \Delta V_i}{0.455}\left[\frac{1}{\sum_i a_i \Delta V_i + \sum_j b_j} - \frac{1}{\sum_i a_i \Delta V_i}\right] \tag{30}$$

The ratio of the dispersion interaction energy to the total intermolecular interaction energy is

$$\frac{\langle D \rangle_{\mathrm{d}}}{D} = 1 + \frac{\sum_j b_j}{\sum_i a_i \Delta V_i} \qquad (31)$$

The ratio of the dipole–dipole interaction and hydrogen bonding energy to the total intermolecular interaction energy is calculated via the relationship

$$\frac{\langle D \rangle_{\mathrm{dd+h}}}{D} = 1 - \frac{\langle D \rangle_{\mathrm{d}}}{D} = 1 - \frac{\sum_i a_i \Delta V_i + \sum_j b_j}{\sum_i a_i \Delta V_i} = -\frac{\sum_j b_j}{\sum_i a_i \Delta V_i} \qquad (32)$$

Thus, with the approach briefly described above, it is possible both to calculate the glass transition temperature of polymers and copolymers and to estimate other important physical characteristics of polymers, such as total intermolecular interaction energy and its components, that are due to dispersion and dip[ole–dipole interactions and hydrogen bonding.

4.6. Melting Point

The equation for the ratio of the glass transition temperature T_g to the melting point T_m [4–6] was derived from experimental data according to which the molecular packing coefficient of a crystalline polymer at its melting point is approximately equal to the molecular packing coefficient of an amorphous polymer at the glass transition temperature; that is, the melting of a crystalline polymer and the transition of an amorphous polymer from the glassy state to the rubbery state occur once approximately the same vale of free volume (more precisely, empty volume) is reached. The relationship for T_g/T_m is written as follows [6]:

$$\frac{T_g}{T_m} = \left[\frac{\sum_i \Delta V_i}{\sum_i (\delta_i \Delta V_i) + \sum_j \gamma_i} - A \right]^{-1}, \qquad (33)$$

Here, $\delta_i = (k_0 - k_g)/k_i$; k_i is the partial packing coefficient for the ith atom, the constants γ_j account for the contribution from strong intermolecular interactions, and $A = 10.418$. The other designations are the same as in relationship (23). The values of δ_i and γ_j are presented in our works [4–6].

4.7. Flow Point of Amorphous Polymers

The flow point is determined from the following relationship [4–7]:

$$\frac{T_g}{T_f} = 1 + \frac{1}{26} \ln \frac{0.5}{\left(\frac{M}{M_s}\right)^{1.5} \left\{ \left[\left(12.4 \frac{M}{M_s} \right)^{0.5} - 1 \right]^3 + \frac{1}{3} \right\}}, \qquad (34)$$

where T_g is the glass transition temperature, T_f is the flow point, M_s is the molecular weight of the mechanical segment, and M is the molecular weight of the polymer.

5. OPTICAL AND OPTOMECHANICAL PROPERTIES

5.1. Refractive Index

The following modified Lorentz–Lorenz equation was obtained for calculating the refractive index n [4–6]:

$$\frac{n^2 - 1}{n^2 + 2} \frac{N_A \sum_i \Delta V_i}{k_{av}} = \sum_i R_i, \qquad (35)$$

where R_i are molecular refractions, the values of which for various atoms and bonds are presented in our monographs [4–6]. The other designations are the same as in relationship (3).
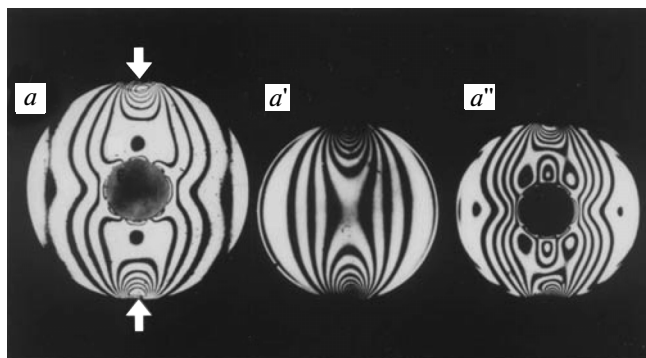
Fig. 2. Stress distribution in a disc compressed by a concentrated force along the disc diameter: (*a*) disc with a low-modulus insert in its center, (*a'*) disc made from a monolithic polymer, and (*a''*) disc with a hole in its center.

5.2. Optomechanical Properties

Optomechanical properties are important, because polymer materials have found wide application in the optical polarization method of stress determination. This method is based on the birefringence phenomenon, which was discovered by D. Brewster. It occurs in transparent, optically isotropic materials upon their deformation and is due to the anisotropy of the refractive index in two mutually perpendicular directions. By way of example, we show the stress distribution in a disc that is compressed by a concentrated force along its diameter (Fig. 2).

In the case of glassy polymers, changes in the interatomic distances and bond angles in the polymer chain are the primary consequence of the applied load. These changes determine the instantaneous elastic strain. The latter is related to the mobility of the atoms constituting the macromolecule units inside the statistical segment of the macrochain. In the deformation of polymers in the glassy state, the appearance of birefringence and its magnitude are mainly determined by the displacement of the atomic electron shells and electron clouds that form chemical bonds and by the distortion of bond angles, which leads to polarizability anisotropy of the repeating unit of the macromolecules. In glassy polymers, birefringence can also be due to the elastic orientation of optically anisotropic molecules or their parts (e.g., mobile pendant methyl groups in polyacrylates and fluoride groups in polymethacrylic esters) near their equilibrium state. An elastic component of birefringence appears here, and it reaches its maximum immediately after the application of a load. In the case of ideal elastic bodies, the total birefringence would be determined by the elastic strain, since the elastically strained polymer would be in the equilibrium state under these conditions. Note, however, that the behavior of real polymer bodies differs from elastic behavior. The strain and birefringence of real polymers vary with time, even in the glassy state.

For optically sensitive polymers in the glassy state, the experimentally established Wertheim law is valid up to certain load levels. This law relates the optical path difference δ at any point of a polymer model in the plane stress state to the difference between the principal normal stresses σ_1 and σ_2 acting at the same point in the planar model and to the model thickness d:

$$\delta = C_\sigma(\sigma_1 - \sigma_2)d \tag{36}$$

or

$$\Delta n = n_1 - n_2 = C_\sigma(\sigma_1 - \sigma_2)d, \tag{37}$$

where C_σ is the relative stress-optical coefficient, Δn is birefringence, and n_1 and n_2 are the refractive indices along and across the optical axis.

The C_σ value is determined from the following relationship [21]:

$$C_\sigma = \frac{15.6T_g}{n_0 E} \frac{\sum_i C_i \Delta V_i}{\sum_i \Delta V_i} + P^* \tag{38}$$

$$C_i = \frac{\partial \varepsilon}{\partial T},$$

where ε is the dielectric constant, T is temperature, n_0 is the refractive index, E is elastic modulus, T_g is the glass transition temperature, C_i stands for atomic constants, and P^* is a parameter.

6. DIELECTRIC PROPERTIES

6.1. Dielectric Constant

The dielectric constant of polymers and their organic solvents was calculated in an earlier work [35]. The dielectric constant ε characterizes the polarization of dielectrics under the action of an electric field. The relationship between the polarization vector (P) and the electric field vector in a vacuum (E) and in a dielectric is given by

$$D = E + 4\pi P = \varepsilon E \tag{39}$$

where D is the electric displacement vector.

The theory leads to the following expression for the dielectric constant of nonpolar dielectrics:

$$\varepsilon = 1 + \frac{\sum_i n_i \alpha_i}{1 - \sum_i n_i \alpha_i \beta_i}, \tag{40}$$

where n_i is the concentration of atoms, ions, or molecules of the ith sort, α_i is the polarizability of these structural elements, and β_i is the factor accounting for dipole–dipole interaction.

The Clausius–Mossotti formula is convenient in practice:

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = P, \tag{41}$$

where P is molecular polarization, ρ is density, and M is molecular weight.

In the case of polymers, the calculation is performed for the repeating unit of a given polymer.

Since the density of a polymer can be calculated via formula (3), the substitution of this formula into formula (41) yields the following expression, which is convenient for dielectric constant calculations:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{k_{av} P}{N_A \sum_i \Delta V_i}, \tag{42}$$

where k_{av} is the average molecular packing coefficient ($k_{av} = 0.681$ for monoliths and 0.695 for films), $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit, and N_A is the Avogadro number.

The molar polarizability P is an additive quantity and is the sum of atomic polarizabilities and polarizability increments associated with the presence of different types of chemical bonds (double, triple) and with other molecular structural features. Here, we have the same situation as in the case of molar refraction.

For nonpolar dielectrics, the dielectric constant is solely due to deformation polarization and, according to the Maxwell equation, is nearly equal to the squared refractive index at high frequencies ($\varepsilon \approx n^2$). For such polymers (polyethylene, polytetrafluoroethylene, polybutadiene, etc.), the molar refraction R practically coincides with the molar polarization P. A more complicated situation is observed for polar dielectrics. Under the action of an electric field, their permanent dipoles undergo orientation. These dipoles are due to the presence of polar groups, such as
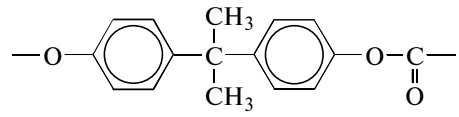
$-OH, -C(O)-, -C(O)-O-, -Cl, -NH-C(O)-, -NH-C(O)-O-, -C \equiv N$, and others
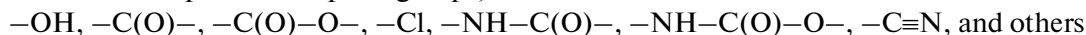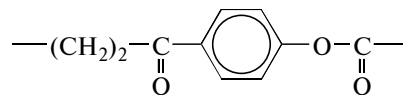
in the polymer. As a consequence, the P value for these polymers is larger than R. Table 8 lists the corrections ΔR_i that must be applied to refraction for calculating the polarizability of a molecule.

In other words, for the polar groups specified in Table 8, polarizability is calculated as $P_i = R_i + \Delta R_i$, where R_i is the molar refraction for a given group and ΔR_i is the dipole orientation correction. The values of this correction were calculated by an analysis of refractive indices and dielectric constants for a large number of polar polymers. Table 9 lists calculated and experimental dielectric constant data for representatives of different classes of polymers. The calculated and experimental data are in quite satisfactory agreement.

6.2. Dielectric Loss Tangent

We previously suggested a computational scheme for estimating the dielectric loss tangent $\tan \tan \delta$ for linear and network polymers [36]. This scheme is applicable to both polar and nonpolar dielectrics in a wide frequency range, from 10^2 to 10^6 Hz. To carry out these calculations, it is necessary to know only the

Table 6. Molecular packing coefficients for some polymers

Polymer	M_0	ρ, g/cm³	$\sum\limits_i \Delta V_i$, nm³	k
Polyethylene $-CH_2-CH_2-$	28.1	0.942 (at 50% crystallinity)	0.0341	0.688
Polypropylene CH_3 $\mid$ $-CH_2-CH-$	42.1	0.954 (at 50% crystallinity)	0.0512	0.699
Polyvinyl chloride $-CH_2-CH-$ $\mid$ Cl	62.5	1.44	0.0489	0.678
Polyamide 6 $-C-(CH_2)_5-NH-$ $\parallel$ O	113	1.10	0.116	0.680
Polycarbonate	254	1.20	0.239	0.680
Polystyrene $-CH_2-CH-$	104	1.07	0.110	0.682
Poly(methyl methacrylate) CH_3 $\mid$ $-CH_2-C-$ $\mid$ $C-O-CH_3$ $\parallel$ O	100	1.17	0.0964	0.679
Polyisoprene $-CH_2-CH=C-CH_2-$ $\mid$ CH_3	68.1	0.946 (at 40% crystallinity)	0.0813	0.680
Polyethylene terephthalate $-(CH_2)_2-C$ ... $O-C-$	192	1.31	0.116	0.682

chemical structure of the repeating unit of the linear polymer or that of the repeating fragment of the polymer network. According to Debye's theory, the molar polarization $P(\omega)$ is expressed as follows:

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{M}{\rho} = P(\omega) = \frac{4\pi N_A}{3}\left[\alpha_0 + \frac{\mu^2}{3kT}\frac{1}{1+i\omega\tau}\right], \tag{43}$$

where ε is the dielectric constant, M is the molecular weight of the substance (in our case, molecular weight of the repeating unit or that of the repeating fragment of the polymer network), ω is the angular frequency ($\omega = 2\pi f$, where f is frequency in Hz), N_A is the Avogadro number, μ is the intrinsic dipole moment of the molecule, k is the Boltzmann constant, T is absolute temperature, τ is the relaxation time, and $i = \sqrt{-1}$.

Table 7. Molecular packing coefficients k for some crystalline polymers

Polymer	Crystal system	Chemical formula	ρ, g/cm^3	K
Polyethylene	Orthorhombic	$-CH_2-CH_2-$	1.000	0.736
	Pseudomono-clinic		1.014	0.746
			0.965	0.710
	Triclinic		1.013	0.745
Polypropylene isotactic	Monoclinic	$-CH_2-CH-$ CH_3	0.936	0.693
syndiotactic	Monoclinic		0.910	0.674
1,4-*cis*-Polyisoprene	Monoclinic	$-CH_2-C=CH-CH_2-$ CH_3	1.00	0.725
Polyamide 6	Monoclinic	$-NH-C-(CH_2)_5-$ $\overset{\|}{O}$	1.23	0.758
Polyformaldehyde	Hexagonal	$-CH_2-O-$	1.506	0.808

Table 8. ΔR_i data for polarizability calculations

Group	ΔR_i, cm^3/mol	Group	ΔR_i, cm^3/mol
$-O-$	3.557	$-C-NH-$ $\overset{\|}{O}$	21.000
$-C-$ $\overset{\|}{O}$	5.371	$-F$	0.845
$-O-C-$ $\overset{\|}{O}$	8.728	$-Cl$	3.900
$-O-C-O-$ $\overset{\|}{O}$	17.085	$-CF_2-$	1.352
$-OH$	3.500	$-NO_2$	10.300
$-C\equiv N$	5.464	$-N=C-$	8.148

The $\tan\delta$ value can be derived from Eq. (43):

$$\tan\delta = \frac{(\varepsilon_1 - \varepsilon_0)x}{\varepsilon_1 + \varepsilon_0 x^2}, \tag{44}$$

where ε_0 and ε_1 are determined from the following conditions:

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\frac{M}{\rho} = \frac{4\pi N_A}{3}\alpha_0. \quad \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\frac{M}{\rho} = \frac{4\pi N_A}{3}\left[\alpha_0 + \frac{\mu^2}{3kT}\right] \tag{45}$$

$$x = \frac{\varepsilon_1 + 2}{\varepsilon_0 + 2}\omega\tau \tag{46}$$

According paragraph 6.1, expressions (45) can be rewritten as

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\frac{M}{\rho} = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}\frac{\sum\limits_i \Delta V_i}{k} = \sum\limits_i R_i = R \tag{47}$$

Table 9. Calculated and experimental dielectric constant data for some polymers

Polymer	Chemical structure of the repeating unit	ε_{calc}	ε_{exp}
Plytetrafluoroethylene	$-CF_2-CF_2-$	1.98	2.00; 1.96; 2.01; 2.10
Poly(4-methyl-1-pentene)	$-CH_2-CH-$ $\quad\quad CH_2$ $\quad\quad CH-CH_3$ $\quad\quad CH_3$	2.27	2.13
Polypropylene	$-CH_2-CH-$ $\quad\quad CH_3$	2.27	2.15; 2.20
Polyisobutylene	$\quad\quad CH_3$ $-CH_2-C-$ $\quad\quad CH_3$	2.23	2.23
Poly-1-butene	$-CH_2-CH-$ $\quad\quad CH_2$ $\quad\quad CH_3$	2.25	2.27
Polyethylene	$-CH_2-CH_2-$	2.23	2.20; 2.30
Poly($\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-$p$-xylylene)	$-CF_2$-p-$C_6H_4-CF_2-$	2.40	2.35
Polyisoprene	$-CH_2-CH=C-CH_2-$ $\quad\quad\quad\quad CH_3$	2.28	2.37
Poly(1,4-butadiene)	$-CH_2-CH=CH-CH_2-$	2.27	2.51
Polystyrene	$-CH_2-CH-$ $\quad\quad C_6H_5$	2.57	2.50; 2.55; 2.60
Poly(α-methylstyrene)	$\quad\quad CH_3$ $-CH_2-C-$ $\quad\quad C_6H_5$	2.54	2.57
Poly(cyclohexyl methacrylate)	$\quad\quad CH_3$ $-CH_2-C-\quad H_2C-CH_2$ $\quad\quad C-O-HC\quad\quad CH_2$ $\quad\quad \|\!\|\quad\quad H_2C-CH_2$ $\quad\quad O$	2.70	2.58
Poly(chlorotrifluoroethylene)	$-CF-CF_2-$ $\quad Cl$	2.70	2.60; 2.80
Poly-xylylene	$-CH_2$-p-$C_6H_4-CH_2-$	2.58	2.65
Poly(isobutyl methacrylate)	$\quad\quad CH_3$ $-CH_2-C-$ $\quad\quad C-O-CH_2-CH-CH_3$ $\quad\quad \|\!\|\quad\quad\quad\quad CH_3$ $\quad\quad O$	2.71	2.70

Table 9. (Contd.)

Polymer	Chemical structure of the repeating unit	ε_{calc}	ε_{exp}
Polydimethylsiloxane	$-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{Si}}-O-$	2.75	2.75
Polyvinylidene chloride	$-CH_2-CCl_2-$	2.87	2.90; 2.92; 2.85
Polyvinyl chloride	$-CH_2-CHCl-$	3.14	3.15; 3.05; 2.95
Poly(methyl methacrylate)	$-CH_2-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle C-O-CH_3}{\vert}}{C}}-$ $\underset{\displaystyle O}{\overset{\displaystyle \Vert}{}}$	2.94	2.94; 3.15; 3.10
Polyoxymethylene	$-CH_2-O-$	2.96	2.95; 2.85

$$\frac{\varepsilon_1-1}{\varepsilon_1+2}\frac{M}{\rho}=\frac{\varepsilon_1-1}{\varepsilon_1+2}\frac{\sum_i \Delta V_i}{k}=\sum_i R_i+\sum_i \Delta R_i=P \tag{48}$$

It follows from expressions (47) and (48) that

$$\varepsilon_0=\frac{1+2\dfrac{\rho}{M}R}{1-\dfrac{\rho}{M}R} \tag{49}$$

$$\varepsilon_1=\frac{1+2\dfrac{\rho}{M}P}{1-\dfrac{\rho}{M}P} \tag{50}$$

By substituting expressions (49) and (50) into (44), we obtain

$$\tan\delta=\frac{\left(\dfrac{1+2\dfrac{\rho}{M}P}{1-\dfrac{\rho}{M}P}-\dfrac{1+2\dfrac{\rho}{M}R}{1-\dfrac{\rho}{M}R}\right)x}{\dfrac{1+2\dfrac{\rho}{M}P}{1-\dfrac{\rho}{M}P}+\dfrac{1+2\dfrac{\rho}{M}R}{1-\dfrac{\rho}{M}R}x^2} \tag{51}$$

From relationships (51) and (46),

$$\tan\delta=\frac{Ax}{B+Cx^2}, \tag{52}$$

where $A=\dfrac{1+2\dfrac{\rho}{M}P}{1-\dfrac{\rho}{M}P}-\dfrac{1+2\dfrac{\rho}{M}R}{1-\dfrac{\rho}{M}R}$, $B=\dfrac{1+2\dfrac{\rho}{M}P}{1-\dfrac{\rho}{M}P}$, $C=\dfrac{1+2\dfrac{\rho}{M}R}{1-\dfrac{\rho}{M}R}$, $D=\dfrac{\varepsilon_1+2}{\varepsilon_0+2}$, $x=D\omega\tau$.

Then,

$$\tan\delta=\frac{AD(\omega\tau)}{B+CD^2(\omega\tau)^2} \tag{53}$$

Expression (53) can be put into the following form:

$$\tan\delta = \frac{A}{\sqrt{BC}}\frac{\omega/\omega_{max}}{1+(\omega/\omega_{max})^2}, \tag{54}$$

where ω_{max} is the frequency at the $(\tan\delta)_{max}$ point, with $\omega_{max} = (\sqrt{B/C})/(\tau D)$.

The relaxation time τ is determined from the relationship

$$\tau = \tau_0 e^{\frac{U}{RT}}, \tag{55}$$

where τ_0 is the preexponential factor, U is the activation energy of the dielectric relaxation process, R is the universal gas constant, and T is absolute temperature.

Debye's expression (54), in which A, B, C, and D are constants, does not quite precisely describe the observed dependences of $\tan\delta$ on frequency. (The calculated curve is "narrower" than the experimental curve.) This drawback of expression (54) can be eliminated by considering A, B, and C as frequency-dependent effective parameters. In this case, expression (54) can be rewritten as

$$\tan\delta = \frac{A(\omega)}{\sqrt{B(\omega)C(\omega)}}\frac{\omega/\omega_{max}}{1+(\omega/\omega_{max})^2} \tag{56}$$

If $\omega/\omega_{max} \ll 1$, then, since $\omega_{max}\tau = 1$, we obtain

$$\tan\delta = \frac{A(\omega)}{\sqrt{B(\omega)C(\omega)}}\omega\tau \tag{57}$$

If $\omega/\omega_{max} \gg 1$, then, since $\omega_{max}\tau = 1$, we obtain

$$\tan\delta = \frac{A(\omega)}{\sqrt{B(\omega)C(\omega)}}\frac{1}{\omega\tau} \tag{58}$$

It is necessary to substitute the τ values determined via formula (55) into Eqs. (57) and (58). The activation energy U appearing in formula (55) is the sum of energy components of separate atoms and atomic groups. In order to determine these components, it is convenient to represent Eq. (58) as

$$\tan\delta = \frac{e^{100\frac{\sum_i d_i}{M}}}{10^5} \tag{59}$$

or

$$\ln\tan\delta = 100\frac{\sum_i d_i}{M} - 11.513, \tag{60}$$

where d_i stands for atomic and group constants related to the intermolecular interaction energy and M is the molecular weight of the repeating unit of the linear polymer or that of the repeating fragment of the polymer network.

To calibrate the method (determine the d_i values), we used experimental $\tan\delta$ data measured at different frequencies for so-called polymer standards for which $\tan\delta$ values had been reliably determined.

The polymer standards were polyethylene, polypropylene, poly(methyl methacrylate), polycarbonate, polyethylene terephthalate, and many others. To solve the problem, we composed an overdetermined system of equations based on Eq. (60), and this system was solved by the least squares method. As a result, we obtained a set of d_i values for each atom and for the specific intermolecular interaction arising from the presence of separate polar groups, rings, and the like in the repeating unit. The results of these calculations are presented in Table 10 and 11.

Formula (59) is valid for polar dielectrics with an effective dipole moment that is nonzero. In an earlier work [36], we considered the possibility of performing calculations for nonpolar dielectrics using the same formula containing other parameters.

7. SOLUBILITY AND MISCIBILITY OF POLYMERS

7.1. Cohesive Energy Density (Solubility Parameter)

The following relationship was suggested [4–7] for calculating the solubility parameter δ from the chemical structure of a molecule of a liquid or from that of the repeating unit of a polymer:

$$\delta^2 = \frac{kE^0}{N_A \sum_i \Delta V_i} = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \tag{61}$$

The quantity $\sum_i \Delta E_i^* = kE^0$ (k is the molecular packing coefficient, and E^0 is the internal energy of evaporation of the liquid) is the cohesion energy of a liquid reduced by a factor that indicates how many times the van der Waals volume of the molecule is smaller than the molar volume, with ΔE_i^* designating the contribution from each atom and intermolecular interaction type to the total cohesion energy $\sum_i \Delta E_i^*$.

Tabulated ΔE_i^* data for various atoms and specific intermolecular interaction types are presented in our monographs [4–7].

7.2. Surface Tension

The surface tension γ_1 of organic liquids is calculated by the following relationship [4–7, 22]:

$$\gamma_1 = A_j \frac{\sum_i \Delta E_i^*}{\left(\sum_i \Delta V_i \right)^{2/3}} \tag{62}$$

where $\sum_i \Delta E_i^* -$ are the effective cohesion energy values that are used in the calculation of the solubility parameter, ΔV_i is the van der Waals volume of the ith atom, and A_j values differ from on group to another in organic compounds.

For hydrocarbons, perfluorinated compounds, halogen-containing compounds, esters, aldehydes, ketones, and nitro compounds (group I), $A_j = 0.0287$; for alcohols and acids (group II), $A_j = 0.0181$; for nitriles (group III), $A_j = 0.0229$. The quantity ΔE_i^* is expressed in joules; ΔV_i is in cubic angstroms; so, with the coefficients specified above, A_j, γ_1 is expressed in dyn/cm or mN/m units.

Relationship (62) provides the means to estimate the contribution from separate polar groups and specific intermolecular interactions to surface tension. For example, it is usually of interest to determine the contribution from hydrogen bonding to the surface tension of organic liquids. To estimate this contribution, relationship is transformed to

$$\gamma_1 = \frac{A_j}{(\Delta V_i)^{2/3}} \left(\sum_i \Delta E_h^* + \sum_i \Delta E_{id}^* \right), \tag{63}$$

where $\sum_i \Delta E_h^*$ is the contribution from hydrogen bonding to the cohesion energy and $\sum_i \Delta E_{id}^* = \sum_i \Delta E_i^* - \sum_i \Delta E_h^*$ is the contribution from dispersion interaction to the cohesion energy.

From relationship (63), we will then obtain

$$\gamma_1 = \gamma_h + \gamma_d \tag{64}$$

(γ_h and γ_d are the contributions from hydrogen bonding and weak dispersion interaction to surface tension), with

$$\gamma_h = \frac{A_j}{\left(\sum_i \Delta V_i \right)^{2/3}} \sum_i \Delta E_h^* \tag{65}$$

Table 10. Numerical d_i data for particular atoms

Atom	Frequency f, Hz				
	10^2	10^3	10^4	10^5	10^6
Carbon C	−0.77650	−0.58255	−0.31407	−1.95941	−1.31583
Oxygen O	1.57926	1.80674	2.22513	2.53358	3.24946
Hydrogen H	0.87953	0.80332	0.59074	1.32710	0.90637
Nitrogen N	3.42258	4.43276	3.56456	4.34022	3.23995
Fluorine F	1.52747	1.24679	1.97541	2.52043	2.08883
Sulfur S	0.10039	3.24939	−0.27859	0.90188	−1.50601
Chlorine Cl	4.06076	4.75600	3.68090	4.71854	4.14816

Table 11. d_i data for atomic groups and selected structural features of a given structure

Group	Frequency f, Hz				
	10^2	10^3	10^4	10^5	10^6
Aromatic ring	3.34519	1.90102	1.97409	8.72933	7.43053
Aliphatic ring	−0.34436	−1.32105	−0.54683	1.71924	1.04865
C3N group	1.22433	−0.29105	0.25041	2.05772	2.29044
Double bond	0.68904	0.02221	0.20939	2.54530	2.86422
H-bond	−3.07179	−3.42018	−1.64552	−2.32473	0.53993
Double bond with oxygen, >C=O	2.78958	2.23972	2.31170	4.38634	3.40370
Ether bond	1.57926	1.80674	2.22513	2.53358	3.24946
Cl, *meta*-substitution	6.94391	6.96755	5.76474	6.30723	4.43655
Cl, *para*-substitution	2.30991	2.17155	1.90274	3.13923	3.67237
Naphthalene ring	0.90462	2.22796	0.38782	−0.56766	−1.12806
Correction for a hydrogen atom in aliphatic hydrocarbons	−0.267	−0.337	−0.219	−0.157	−0.087
Correction for a hydrogen atom in aromatic hydrocarbons	−0.150	0	−0.047	−0.069	−0.266

$$\gamma_d = \frac{A_j}{\left(\sum_i \Delta V_i\right)^{2/3}} \sum_i \Delta E_d^* \tag{66}$$

The fraction of surface tension that is due to hydrogen bonding is

$$\frac{\gamma_h}{\gamma_1} = \frac{\sum_i \Delta E_h^*}{\sum_i \Delta E_h^* + \sum_i \Delta E_{id}^*} \tag{67}$$

The surface tension γ_1 can be related to the solubility parameter δ by the following relationship [6]:

$$\delta = C_j \left(\frac{\gamma_1}{V^{1/3}}\right)^{1/2} \tag{68}$$

or

$$\gamma_1 = \frac{\delta^2 V^{1/3}}{C_j^2}, \tag{69}$$

Table 12. Physical parameters of two miscible polymers

Polymer	M	Van der Waals volume, Å^3	Glass transition temperature $T_{g,\,calc}/T_{g,\,exp}$	Molar volume, cm^3/mol	Solubility parameter, (J/cm^3)$^{0.5}$	Surface energy, mN/m
PEO	44.1	43.7	204/212	40.7	18.9	29.8
PMMA	100	96.4	377/377	85.3	19.1	30.6

Table 13. Physical parameters of two miscible polymers

Polymer	M	Van der Waals volume, Å^3	$T_{g,\,calc}/T_{g,\,exp}$	Molar volume, cm^3/mol	Solubility parameter, (J/cm^3)$^{0.5}$	Surface energy, mN/m
PS	104	110	376/376	98.1	18.7	40.4
PC	310	305	469/465–470	270	18.8	30.3

Table 14. Physical characteristics of polymer 1 at different temperatures

Temperature, K	Molar volume, cm^3/mol	Solubility parameter δ, (J/cm^3)$^{0.5}$	Surface tension, mN/m	μ_1	$1.374\beta_1$	$1.374\beta_1 - \mu_1$
				polymer 1 is introduced into polymer 2		
293	256	22.0	41.75	1.19	1.27	0.08
303	256.5	21.97	41.6	1.19	1.27	0.08
323	258	21.9	41.37	1.19	1.27	0.08
343	262	21.7	40.62	1.17	1.27	0.10
363	266	21.53	39.99	1.16	1.28	0.12
383	270	21.36	39.36	1.16	1.28	0.12

where $C_1 = 7.67$ (group I), $C_2 = 9.58$ (group II), $C_3 = 8.56$ (group III), V is the molar volume of the liquid (in relationships (68) and (69), V is expressed in cm^3/mol, γ_1 in dyn/cm (or mN/m), and δ in (J/cm^3)$^{1/2}$).

If it is necessary to express the surface tension of a liquid in terms of the solubility parameter δ and van der Waals volume $\left(\sum_i \Delta V_i\right)$ of the molecule of the liquid, then we will obtain from Eqs. (62) and (61)

$$\gamma_1 = A_j \delta^2 N_A \left(\sum_i \Delta V_i\right)^{1/3} \tag{70}$$

or

$$\delta^2 = \frac{\gamma_1}{A_j N_A \left(\sum_i \Delta V_i\right)^{1/3}} \tag{71}$$

The following relationship was obtained for the surface tension of a polymer, γ_p [6]:

$$\gamma_p = C_j \frac{\sum_i \Delta E_i^*}{\left(\sum_i \Delta V_i\right)^{2/3} m^{1/3}}, \tag{72}$$

Table 15. Physical characteristics of polymer 2 at different temperatures

Temperature, K	Molar volume, cm³/mol	Solubility parameter δ, (J/cm³)^0.5	Surface tension, mN/m	μ_2	$1.374\beta_2$	$1.374\beta_2 - \mu_2$
				polymer 2 is introduced into polymer 1		
293	220	20.2	36.12	0.84	1.28	0.44
303	220.4	20.18	36.05	0.84	1.28	0.44
323	221.5	20.1	35.76	0.84	1.28	0.44
343	222.5	20.04	35.55	0.85	1.28	0.43
363	223.6	19.98	35.34	0.86	1.29	0.43
383	225.7	19.86	34.92	0.86	1.29	0.43

where m is the number of atoms in the repeating unit of the polymer. The other designations are the same as in relationship (61). The calculation is performed for the repeating unit of the polymer.

For group I nonpolar polymers (perfluorinated hydrocarbon polymers, polyethers), $C_{1,n} = 0.1277$; for group I polar polymers (polyesters, polyamides, polymers containing a nitro group, etc.), $C_{1,p} = 0.0751$; for polymers containing alcohol and acid groups (all of them are polar), $C_2 = 0.0476$; for polymers containing nitrile groups (all of them are also as well), $C_3 = 0.0600$. Here, ΔE_i^* is expressed in joules; $\left(\sum_i \Delta V_i\right)$ is in Å³; and γ_p is in dyn/cm (mN/m).

The surface tension of polymers can be expressed in terms of their solubility parameter δ:

$$\gamma_p = C_j N_A \delta^2 \left(\frac{\sum_i \Delta V_i}{m}\right)^{1/3} \tag{73}$$

(in the above units, with $N_A = 0.6023$).

Accordingly,

$$\delta^2 = \frac{\gamma_n}{C_j N_A} \left(\frac{m}{\sum_i \Delta V_i}\right)^{1/3} \tag{74}$$

Table 16. Physical characteristics of polystyrene at different molecular weights

No.	M	V, cm³/mol	δ, (J/cm³)^0.5	γ, mN/m	Low-molecular-weight PS is introduced into PPO		PPO is introduced into low-molecular-weight PS	
					μ_1^*	$1.374\beta_1$	μ_2^*	$1.374\beta_2$
1	314	314	20.1	47.1	1.21	1.26	0.83	1.26
2	418	205.5	19.4	43.7	1.12	1.29	0.89	1.26
3	522	169.4	19.2	42.6	1.10	1.27	0.91	1.25
4	626	151.3	19.05	42.1	1.08	1.27	0.92	1.25
5	730	140.5	19.0	41.7	1.08	1.26	0.93	1.25
6	834	133.2	18.9	41.5	1.07	1.26	0.94	1.25
7	938	128.1	18.9	41.4	1.07	1.26	0.94	1.25
10	1250	118.8	18.8	41.1	1.06	1.26	0.95	1.25
15	1770	111.6	18.8	40.8	1.06	1.25	0.95	1.24
20	2290	107.9	18.8	40.7	1.06	1.25	0.95	1.24

Table 17. Physical characteristics of polymers 1a–1c and 2

Polymer	n	M	Van der Waals volume, $Å^3$	Glass transition temperature, K	Molar volume, cm^3/mol	Solubility parameter, $(J/cm^3)^{0.5}$	Surface tension, mN/m
Polymer 1a	2	310	234	380	207	23.0	46.5
Polymer 1b	5	352	285	322	252	22.0	41.6
Polymer 1c	8	394	336	292	304	21.2	38.3
Polymer 2		265	248	374	219	20.2	35.6

Table 18. Physical characteristics of polymers with different degrees of branching

Degree of branching	Glass transition temperature, K	Van der Waals volume, $Å^3$	Molar volume, cm^3/mol	Solubility parameter, $(J/cm^3)^{0.5}$	Surface tension, mN/m
0	380	234	207	23.0	46.5
20	347	254	225.5	22.6	44.3
30	335	265	235.9	22.3	43.3
35	330	270	241.1	22.2	42.9
40	325	275	245.7	22.1	42.4
60	310	295	265.4	21.8	40.9
80	299	316	284.2	21.5	39.5
100	292	336	304	21.2	38.3
Polymer 2	374	248	219	20.2	35.6

Table 19. Left- and right-hand sides of criterion (79) for blends of polymers with different degrees of branching and polymer 2

Degree of branching, %	μ_1 Copolymer is introduced into polymer 2	$1.374\beta_1$ Copolymer is introduced into polymer 2	μ_1 Polymer 2 is introduced into the copolymer	$1.374\beta_2$ Polymer 2 is introduced into the copolymer	Miscibility (copolymer is introduced into polymer 2)	Miscibility (polymer 2 is introduced into the copolymer)
0	–	–	–	–	Immiscible	Immiscible
20	–	–	–	–	Immiscible	Immiscible
30	–	–	–	–	Immiscible	Immiscible
35	1.21	1.24	0.83	1.20	Miscible	Miscible
40	1.20	1.25	0.84	1.26	Miscible	Miscible
60	1.16	1.27	0.86	1.28	Miscible	Miscible
80	1.13	1.29	0.88	1.30	Miscible	Miscible
100	1.10	1.31	0.91	1.32	Miscible	Miscible

7.3. Criterion for Solubility of Polymers in Organic Solvents

The problem of predicting the solubility of polymers in one solvent or another has been continually discussed in the literature over many years. One way of preliminarily estimating the solubility of a polymer is by comparing the Hildebrand solubility parameters of the polymer (δ_p) and solvent (δ_s).

It is often believed that the polymer would be expected to be soluble in the given solvent if $\delta_p \approx \delta_s$. However, experience demonstrates that this comparison only allows one to "discard" the organic liquids in which the polymer will certainly be insoluble. These are the liquids for which $\delta_p \gg \delta_s$ or $\delta_p \ll \delta_s$. This esti-

Table 20. Molar heat capacity of polymers at 298 K

Polymer	Chemical structure	C_p, J/(mol K)
Polyethylene	$-CH_2-CH_2-$	49.6
Polypropylene: atactic isotactic	$-CH_2-CH-$ $\vert$ CH_3	68.3 90.7
Polystyrene	$-CH_2-CH-$ $\vert$ C_6H_5	128.2
Polytetrafluoroethylene	$-CF_2-CF_2-$	96.2
Poly(methyl methacrylate)	CH_3 $\vert$ $-CH_2-C-$ $\vert$ $C-O-CH_3$ $\Vert$ O	138.6
Poly(ε-caprolactam) (polyamide 6)	$-C-NH-(CH_2)_5-$ $\Vert$ O	164.2
Polyrthylene terephthalate	$-O-(CH_2)_2-O-C-p-C_6H_4-C-$ $\Vert$ $\Vert$ O O	218.4

mation makes it possible to considerably reduce the number of possible polymer solvents to be tested. Estimates and experience [4–7, 23, 34] demonstrate, for example, that, of 160 solvents, it is possible to exclude at once 130−140 organic liquids that are obviously unsuitable for dissolving the given polymer. Among the remaining solvents, which obey the $\delta_p \approx \delta_s$ rule, half will actually dissolve the polymer. It is therefore desirable to have a more accurate way of preliminarily estimating the solubility of a given polymer in those solvents for which $\delta_p \approx \delta_s$. A specific feature of the problem of dissolution is that here, as distinct from the determination of some of the simplest properties, it is necessary to take into account both the chemical structure and particular physical structure of the polymer.

Our criterion for polymer solubility in organic solvents [4–7, 23, 24] is based on an analysis of the surface forces arising from the introduction of a polymer material (powder, film, monolith, etc.) into a solvent.

The physical meaning of this solubility criterion is as follows. A solid (globule)/liquid interface forms at the instant a polymer (powder or film) is immersed into a solvent. The formation of this interface involves the work of adhesive wetting, $W_A = \gamma_{sp} - (\gamma_p + \gamma_s)$, where γ_p and γ_s are the surface tensions of the polymer and solvent, respectively, and γ_{sp} is the interfacial tension. The existence of this work generates forces acting on the globule and depending on the magnitude and sign of the surface curvature (according to the Laplace law).

One of these forces presses the globule to the polymer because of the positive curvature of the globule surface, and the other exerts a disjoining effect in the place where the globule is connected with the polymer because of the negative curvature. This force causes the globule to separate from the polymer material. Two conditions necessary for globule detachment are analyzed here: (1) the force acting from the solvent side must be stronger than the force pressing the globule to the material; (2) the work done by the surface tension forces of the solvent must exceed the dissociation energy of the intermolecular bonds in the place of globule−material contact.

We analyzed [23, 24] cases in which the polymer swells before dissolving and in which the polymer dissolves almost without swelling.

The polymer solubility condition is written as

$$\mu \le 2\rho\beta, \tag{75}$$

where

Table 21. $C_{p,i}^{s}$ and $C_{p,i}^{l}$ data for some atoms

Atom	$C_{p,i}^{s}$, (cal/(mol K))/Å^3	$C_{p,i}^{l}$, (cal/(mol K))/Å^3
Carbon	0.232030	0.345640
Hydrogen	0.714129	0.622889
Oxygen	0.634726	0.929977
Nitrogen	0.314997	2.099874
Fluorine	0.543367	0.464909
Chlorine	0.368819	0.284693
Sulfur	0.273109	0.303031

$$\mu = \frac{\delta_p^2}{\delta_s^2}, \quad \rho = \frac{\varepsilon_{max}^{p} \, r_s}{\varepsilon_{max}^{s} \, r_p}, \quad \beta = \Phi\left(\frac{\gamma_p}{\gamma_s}\right)^{1/2}.$$

Here, ε_{max}^{p} is the maximum relative strain of the intermolecular bonds in the polymer at the instant they break and the polymer passes into solution; ε_{max}^{s} is the maximum strain of the liquid, i.e., the strain at which continuity violation occurs; r_s is the characteristic length of the bond between Frenkel layers of the solvent; and r_p is the characteristic bonding globule radius for the polymer. These concepts are detailed in our monographs [4−7].

The following form of criterion (75) is more convenient for practical applications:

$$\mu \leq 1.374\Phi(\Phi - \sqrt{\Phi^2 - 1 + a}) \tag{76}$$

Here, $a = \gamma_{ps}/\gamma_s$, γ_p and γ_s are the surface tensions of the polymer and solvent, and γ_{ps} is the interfacial tension calculated via the relationships

$$\gamma_{sp} = \gamma_s + \gamma_p - 2\Phi(\gamma_s \gamma_p)^{1/2} \tag{77}$$

$$\Phi = \frac{4\left(V_s V_p\right)^{1/3}}{(V_s^{1/3} + V_p^{1.3})^2} \tag{78}$$

where V_s and V_p are, respectively, the molar volumes of the solvent and polymer per repeating unit.

In view of relationship (77), solubility criterion (76) can be rewritten as

$$\mu \leq 1.374\Phi\left(\Phi - \sqrt{\Phi^2 + \frac{\gamma_p}{\gamma_s} - 2\Phi\left(\frac{\gamma_p}{\gamma_s}\right)^{0.5}}\right). \tag{79}$$

According to criterion (76), solubility will be observed if the calculated $1.374\Phi(\Phi - \sqrt{\Phi^2 - 1 + a})$ value is larger than, or equal to, $\mu = (\delta_p/\delta_s)^2$. Here, both experimental and calculated δ_s and δ_p values may be used.

The plot of μ as a function of $\beta = \Phi(\Phi - \sqrt{\Phi^2 - 1 + a})$ is a straight line (Fig. 3, dashed line).

The points indicating the absence of solubility (dark circles) are typically above the aforementioned straight line, while points indicating the possibility of dissolution (open circles) are below this line. Thus, the μ data array is divided into the insolubility and solubility fields. However, either field contains a small number of "foreign" points, the proportion of which is ~15%. Therefore, the predicting power of criterion (76) is ~85%.

When developing the solubility criterion, we took into consideration the degree of polymerization of the polymer. Even if the polymer has a globular structure, the solubility condition may vary with the degree of polymerization, N. With N taken into account, the solubility criterion is written as

$$\mu^* \leq 1.374\beta, \tag{80}$$

where $\mu^* = \mu(N/N_0)^{1/6}$; μ has the same meaning as in formulas (75) and (76) and $N_0 = 200000/M$ (standard degree of polymerization at which the solubility of polymers was considered in our monographs [4−7]).

As for the supramolecular structure effect on polymer solubility, the solubility condition for polymers with a fibrillar (oriented) structure is more stringent than for globular polymers. Criterion (80) is valid for fibrillar polymers, but with a smaller ρ value: for the globular supramolecular structure, $\rho = 1.374$; for the

Table 22. Atomic constants and parameters characterizing specific intermolecular interactions

Atom and type of intermolecular interaction	Designation	Value
Carbon in the main chain	$a_{C, m}$	1.990
Carbon in a side chain	$a_{C, s}$	1.699
Hydrogen in the main chain	$a_{H, m}$	−0.205
Hydrogehn in a side chain	$a_{H, s}$	−0.017
Oxygen in the main chain	$a_{O, m}$	3.706
Oxygen in a side chain	$a_{O, s}$	−1.693
Nityrtogen in the main chain	$a_{N, m}$	8.88
Nitrogen in a side chain	$a_{N, s}$	1.108
Chlorine	a_{Cl}	1.548
Fluorine	a_F	0.114
Silicon	a_{Si}	2.016
Sulfur	a_S	15.226
Polymers containing only $-CH_2-$ or $-CF_2-$	$b_{-CH_2-(-CF_2-)}$	3.504
Dipole−dipole interaction	b_d	4.83
Aromatic ring (backbone)	$b_{ar.r}$	−2.755
Double bond	$b_=$	0.954

fibrillar supramolecular structure, $\rho = 1.25$. There is experimental evidence that an oriented polymer is poorly soluble or even insoluble, while the initial polymer is quite soluble (for example, poly(vinyl alcohol) in water).

It should also be taken into consideration that the solubility of a polymer is temperature-dependent. The solubility criterion described in our monographs [4–7] takes into account this significant factor as well. Indeed, the cohesion energy appearing in relationship (61) depends on temperature according to a linear law, like surface tension. The temperature dependence of the solubility parameter δ_T^2 is described the following equation:

$$\delta_T^2 = \frac{V\delta^2 + R(298 - T)}{V_T},\tag{81}$$

where V is the molar volume of the polymer at room temperature (298 K), V_T is the molar volume at temperature T, and δ is the solubility parameter at room temperature.

The temperature dependence of the surface tension $\gamma_{p, T}$, is described by the equation

$$\gamma_{n,T} = D_i \frac{V\delta^2 + R(298 - T)}{V_{n,T}} \left(\frac{\sum_i \Delta V_i}{m}\right)^{1/3}\tag{82}$$

This leads to changes in the parameters of criteria (76) and (80), implying changes in the solubility conditions.

7.4. Polymer−Polymer Miscibility Prediction

The polymer miscibility problem is topical because new polymer materials are now being commonly produced by blending known polymers. Not only do polymer blends consist of comparable amounts of prepared components, but the introduction of polymer microadmixtures, surface modification, and other methods are also used. A number of issues arise here, including the issue of the occurrence of microphase separation and the controlling of the microphase particle size and composition.

The miscibility of two polymers can be approximately predicted by the following familiar equation:

$$\chi_{12} = \frac{V}{RT}(\delta_1 - \delta_2)^2,\tag{83}$$

Table 23. Chemical structure of polymers, parameters necessary for calculations, and experimental and calculated thermal conductivity (λ) data

Polymer	ρ, g/cm^3	c_p, J/(g K)	M	m	$\sum_i \Delta V_i$, Å^3	λ_{calc}, W/(m K)	λ_{exp}, W/(m K)
PA-12	1.073	1.60	197	37	218	0.203	0.25
							0.19
PA-6	1.169	1.49	113	19	116	0.245	0.24
PA-6,6	1.159	1.50	226	38	232	0.244	0.24
PA-6,12	1.103	1.57	310	56	334	0.216	0.22
PA-6,10	1.118	1.55	282	50	300	0.224	0.22
PA-11	1.082	1.59	183	34	201	0.206	0.23
Polyacetal	1.309	1.80	30	4	26.6	0.435	0.23
							0.30
							0.44
Polybutylene terephthalate	1.309	1.22	220	29	200	0.165	0.29
							0.16
Polycarbonate	1.265	1.19	254	33	239	0.198	0.20
Poly(2,6-dimethyl-1,4-phe-nylene ether)	1.216	1.22	120	17	117	0.185	0.12
							0.23
Polyether ether ketone	1.305	1.51	288	34	262	0.252	0.25
PET	1.378	1.15	192	22	166	0.25	0.15
							0.24
Poly(chlorotrifluororethylene)	2.145	0.90	116	6	64.5	0.140	0.146
PTFE	2.121	1.02	100	6	54.9	0.261	0.25
PVC (plasticate)	1.517	1.08	62.5	6	48.9	0.191	0.17
							0.21
Polyvinylidene chloride	1.783	0.92	96.9	6	63.7	0.138	0.13
PVDF	1.674	1.27	64	6	44.5	0.163	0.13
							0.17
Polybutene	0.960	2.14	56.1	12	68.3	0.196	0.22
PB	0.973	2.03	54.1	10	64.2	0.222	0.22
Polychloroprene	1.304	1.40	88.5	10	79.0	0.189	0.19
PE	0.955	2.19	28.1	6	34.1	0.40	0.33
							0.42
PIB	0.884	2.14	56.1	12	68.3	0.186	0.13
Polyisoprene	0.972	2.04	68.1	13	81.3	0.219	0.13
							0.22
Poly(4-methyl-1-pentene)	0.963	2.12	84.2	18	102	0.196	0.167
PP	0.964	2.16	42.1	9	51.2	0.199	0.12
							0.20
PS	1.07	1.30	104	16	110	0.155	0.16
Poly(p-xylylene)	1.131	1.30	104	16	109	0.144	0.12
Cellulose	1.464	1.36	162	21	132	0.186	0.071
							0.13
							0.17
PDMS	1.135	1.58	74.2	10	71.8	0.20	0.20
PAN	1.168	1.22	53.1	7	54.0	0.259	0.26

Table 23. (Contd.)

Polymer	ρ, g/cm^3	c_p, J/(g K)	M	m	$\sum_i \Delta V_i$, Å^3	λ_{calc}, W/(m K)	λ_{exp}, W/(m K)
Poly(isobutyl methacrylate)	1.09	1.49	142	24	148	0.155	0.13
Poly(ethyl acrylate)	1.14	1.83	100	15	96.4	0.196	0.213
PMMA	1.17	1.38	100	15	96.4	0.156	0.16
							0.167
							0.17
							0.19
							0.2
							0.21
							0.23
Polyvinyl acetate	1.23	1.32	86.1	12	79.4	0.1540	0.159
PVS	1.26	1.54	44.1	7	41.5	0.075	0.106
							0.20
Poly(N-vinylcarbazole)	1.18	1.15	193	26	186	0.126	0.126
Polyvinyl fluoride	1.391	1.27	46	6	39.3	0.147	0.16
Polyvinyl formal	1.23	1.29	100	15	92.3	0.255	0.27
Poly(phenylene sulfide)	1.36	0.993	108	11	94.4	0.29	0.29

where χ_{12} is the interaction parameter for polymers 1 and 2, V is the molar volume of the repeating unit of one of the polymers, δ_1 and δ_2 are the solubility (Hildebrand) parameters of polymers 1 and 2, R is the universal gas constant, and T is absolute temperature.

The smaller χ_{12} is, the higher is the miscibility between the two polymers. Complete miscibility is reached at a negative χ_{12} value.

The thermodynamics of polymer blends and the methods of predicting the miscibility of polymers are detailed in monographs [25–27]. Most of the methods are based on Flory–Huggins theory and its modifications. The most popular method of prediction is polymer reference interaction site model (PRISM) theory, which has been computerized [28]. This model is based on the consideration of an ensemble of interacting cells and involves a number of structural features of polymers and their blends. Another development of Flory–Huggins theory is the lattice cluster theory (LCT) model [29, 30]. This model also makes it possible to take into account fine structural features of the polymers blended, including the effect of branching, the unit connection type, etc. The polymer–polymer miscibility prediction methods, which are based on Flory–Huggins theory, are also considered in a monograph by Kochnev et al. [31].

A possible way of predicting the miscibility of polymers involves the use of a criterion intended for the solubility of polymers in organic solvents (see Eq. (79)). This miscibility analysis was carried out in our earlier work [37]. The following cases are possible in an analysis of the miscibility of two polymers. If a small amount of one polymer is introduced into the other polymer, then the former is considered in terms of criterion (79) as a polymer and the latter is considered as a solvent, and vice versa. Let us introduce the following designations:

$$\beta_1 = \Phi\left(\Phi - \sqrt{\Phi^2 + \frac{\gamma_{p,1}}{\gamma_{p,2}} - 2\Phi\left(\frac{\gamma_{p,1}}{\gamma_{p,2}}\right)^{0.5}}\right), \tag{84}$$

$$\beta_2 = \Phi\left(\Phi - \sqrt{\Phi^2 + \frac{\gamma_{p,2}}{\gamma_{p,1}} - 2\Phi\left(\frac{\gamma_{p,2}}{\gamma_{p,1}}\right)^{0.5}}\right), \tag{85}$$

where $\gamma_{p,1}$ and $\gamma_{p,2}$ are the surface energies of polymers 1 and 2;

$$\Phi = \frac{4\left(V_{p,1} \cdot V_{p,2}\right)^{1/3}}{\left(V_{p,1}^{1/3} + V_{p,2}^{1/3}\right)^2}, \tag{86}$$

Table 24. Atomic constants and parameters characterizing specific intermolecular interactions

Atom and type of intermolecular interaction	Designation	$\Delta E_i^{**}/RT_{298}$, Å^3	ΔE_i^{**}, kJ/mol Å^3
Carbon	$\Delta E_{\mathrm{C}}^{**}$	42.75	105.85
Hydrogen	$\Delta E_{\mathrm{H}}^{**}$	−36.65	−90.75
Oxygen	$\Delta E_{\mathrm{O}}^{**}$	−8.20	−20.3
Hydrogen bond for the -NHCO-group	$\Delta E_{\mathrm{NHCO}}^{**}$	−385.2	−953.7
Double bond	$\Delta E_{=}^{**}$	−182.8	−452.6
Chlorine	$\Delta E_{\mathrm{Cl}}^{**}$	44.1	109.2
Fluorine	$\Delta E_{\mathrm{F}}^{**}$	−60.1	−148.8
Hydrogen bond	ΔE_{h}^{**}	−28.3	−70.1
Aliphatic ring (backbone)	$\Delta E_{\mathrm{al.c}}^{**}$	−234.5	−580.6
Dipole−dipole interaction	ΔE_{d}^{**}	−109.8	−271.9
Aromatic ring (backbone in the main chain)	$\Delta E_{\mathrm{ar.c},\,b}^{**}$	−203	−502.6
Nitrogen	$\Delta E_{\mathrm{N}}^{**}$	29.8	73.8
Silicon	$\Delta E_{\mathrm{Si}}^{**}$	−156.9	−388.5
Sulfur	$\Delta E_{\mathrm{S}}^{**}$	−621	−1538
Aromatic ring (backbone) in a side chain	$\Delta E_{\mathrm{ar.c},\,s}^{**}$	−326.3	−808

where $V_{\mathrm{p,1}}$ and $V_{\mathrm{p,2}}$ are the molar volumes of polymers 1 and 2.

The following situations can take place here:

(1) If, when criterion (79) is used, the left-hand side of the criterion is larger than the right-hand side in all cases, the polymers are absolutely immiscible. Here, we mean that a small amount of polymer 1 is introduced into polymer 2 or a small amount of polymer 2 is introduced into polymer 1. The miscibility criterion will then appear as follows:

for the introduction of polymer 1 into polymer 2,

$$\mu_1 = \frac{\delta_{\mathrm{p,1}}^2}{\delta_{\mathrm{p,2}}^2} > 1.374\beta_1 \tag{87}$$

for the introduction of polymer 2 into polymer 1,

$$\mu_2 = \frac{\delta_{\mathrm{p,2}}^2}{\delta_{\mathrm{p,1}}^2} > 1.374\beta_2 \tag{88}$$

Here, $\delta_{\mathrm{p,1}}$ and $\delta_{\mathrm{p,2}}$ are the solubility parameters of polymers 1 and 2.

Since the left-hand side of criteria (87) and (88) is larger than their right-hand side, the polymers are immiscible.

(2) For the introduction of a small amount of polymer 1 into polymer 2, criterion (79) appears as

$$\mu_1 = \frac{\delta_{\mathrm{p,1}}^2}{\delta_{\mathrm{p,2}}^2} < 1.374\beta_1, \tag{89}$$

that is, the polymers are miscible. However, in the introduction of polymer 2 into polymer 1 the polymers can be immiscible because

$$\mu_2 = \frac{\delta_{\mathrm{p,2}}^2}{\delta_{\mathrm{p,1}}^2} > 1.374\beta_2. \tag{90}$$

This seemingly paradoxical situation can really take place, as was demonstrated in our earlier work [20]. For the case in which polymer 1 is miscible with polymer 2 but polymer 2 is immiscible with polymer 1, the temperature dependence of the glass transition temperature is schematically represented in Fig. 4 (curve *1*).

The curves presented in Fig. 4 were analyzed in detail [20]. The difference between curves *1* and *2* is due to phase separation and to the miscibility of the microphases being enhanced as a result of variation of the proportions of the initial polymers therein.

Table 25. Experimental and calculated water npermeability data for some polymers

Polymer	$-\ln P\left(N_A\sum_i \Delta V_i\right)_{calc}$	$-\ln P\left(N_A\sum_i \Delta V_i\right)_{exp}$
Polyethylene	122.8	125
Polypropylene	184.2	188
Polyisoprene	409.2	379
Polychloroprene;	293.8	324
Polytetrafluoroethylene	254.2	150
Polyvinyl fluoride	155.7	142
Regenerated cellulose	709	680
Cellulose acetate	853.4	828
Ethyl cellulose	807	885
Cellulose nitrate	773	760
Benzyl cellulose	1098	1117
Polystyrene	476.4	457
Polycarbonate	801.5	990
Polyvinylidene chloride	14.8	12.9
Polyvinyl chloride	68.7	147
Poly(methyl methacrylate)	380	375
Poly(methyl acrylate)	318.6	283
Polyacrylonitrile	159.3	185
Poly(phenylene oxide)	374	584
Polyvinyl alcohol	172.6	141
Polyvinyltrimethylsilane	590.4	574
Nylon 6	720	720
Polyethylene terephthalate	621.2	560
Polyvinyl butyral	682.3	652
Polyimide BPDA-ODA	1025	1011
Polyimide PMDA-ODA	794.7	942
Polyimide 6FDA-ODA	1406	1530
Polyimide Ultem	1462	1199
Polydimethylsiloxane	429	446
Polyimide BPDA-DDS	1801	1890
Polyimide DSDA-TPEP	2078	1989
Ftorlon 3M	167.1	62.5

It is also possible that the polymers are totally miscible. In this case, the miscibility criterion takes the following form:

$$\mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} < 1.374\beta_1 \tag{91}$$

for the introduction of polymer 1 into polymer 2 and

$$\mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} < 1.374\beta_2 \tag{92}$$

for the introduction of polymer 2 into polymer 1.
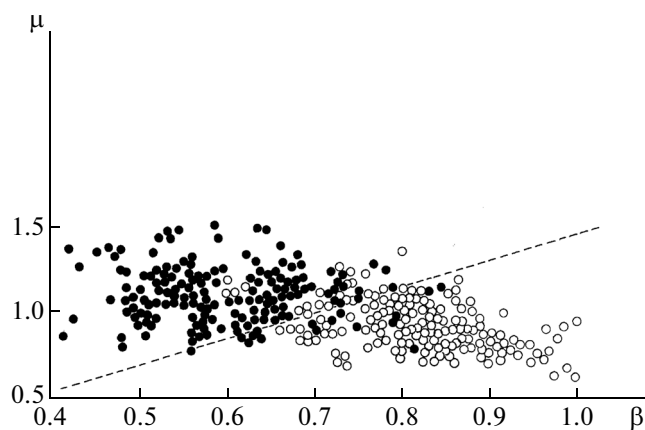
Fig. 3. μ versus β for a number of polymer−solvent pairs.
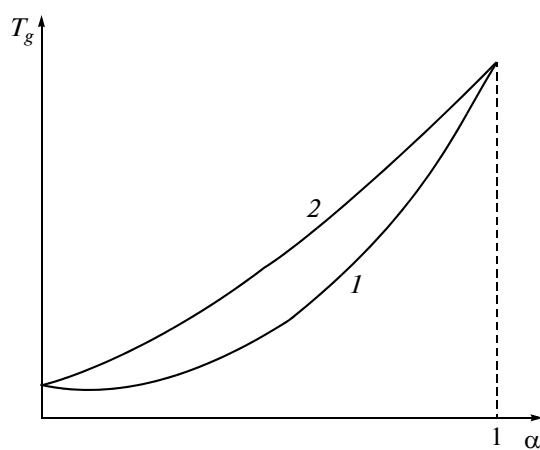
Fig. 4. Scematic representation of the glass transition temperature as a function of the blend composition: (*1*) partially miscible polymers and (*2*) totally miscible polymers. α is the mole fraction of one of the components.
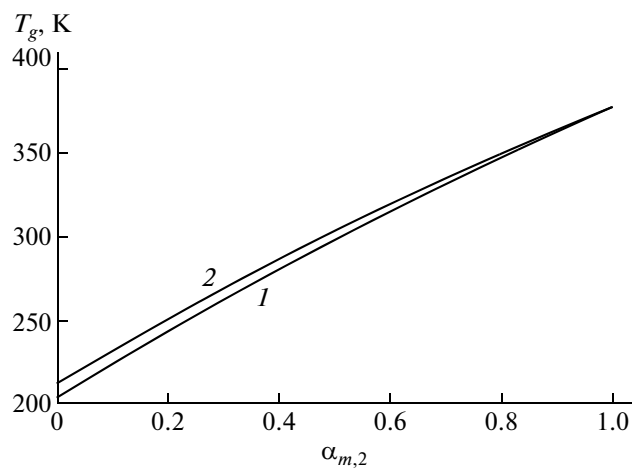
Fig. 5. Glass transition temperature T_g as a function of the mole fraction αw of PMMA in the PEO−PMMA blend: (*1*) curve calculated without involving experimental data; (*2*) experimental data were used in the T_g calculation.
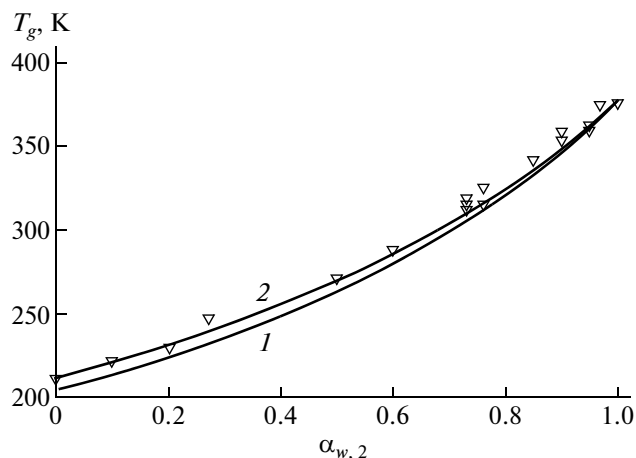
Fig. 6. Glass transition temperature T_g as a function of the weight fraction αw of PMMA in the PEO–PMMA blend: (*1*) curve calculated without involving experimental data; (*2*) experimental data were used in the T_g calculation.

In this situation, one glass transition temperature T_g is observed, and the dependence of T_g on the mixture composition is schematized in Fig. 4 (curve *2*)

Now we will consider the behavior of some well-studied polymer blends. The most detailed set of miscible polymer blends was presented by Schneider [32].

Miscible PEO (polymer 1) + PMMA (polymer 2) blends. The physical parameters that are necessary for the calculations are listed in Table 12. (These parameters were calculated using the Cascade software.)

For criterion (91), when polymer 1 is viewed as a polymer and polymer 2 is viewed as a solvent, we have $\mu_1 = 0.98$ and $1.374\beta_1 = 1.33$. The polymers are miscible, since $\mu_1 < 1.374\beta_1$. The interfacial tension is very low and is 0.91 mN/m. For criterion (92), when polymer 2 is considered as a polymer and polymer 1 is considered as a solvent, we have $\mu_2 = 1.02$ and $1.374\beta_2 = 1.29$. The polymers show complete miscibility, since μ_2 is smaller than $1.374\beta_2$ as well.

The glass transition temperature as a function of the mole fraction of polymer 2, $\alpha_{m,2}$, for miscible blends is derived from the following simplified relationship [4–7]:

$$T_g = \frac{(1 - \alpha_{m,2})\left(\sum_i \Delta V_i\right)_1 + \alpha_{m,2}\left(\sum_i \Delta V_i\right)_2}{(1 - \alpha_{m,2})\dfrac{\left(\sum_i \Delta V_i\right)_1}{T_{g,1}} + \alpha_{m,2}\dfrac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}}}, \tag{93}$$

where $\left(\sum_i \Delta V_i\right)_1$ and $\left(\sum_i \Delta V_i\right)_2$ are the van der Waals volumes of the repeating units of polymers 1 and 2

and $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of polymers 1 and 2.

If calculated $T_{g,1}$ and $T_{g,2}$ values are used, the substitution of all parameters into formula (93) yields

$$T_g = \frac{43.7 + \alpha_{m,2}52.7}{0.214 + \alpha_{m,2}0.0417} \tag{94}$$

If experimental $T_{g,1}$ and $T_{g,2}$ values are substituted into formula (93), we will obtain

$$T_g = \frac{43.7 + \alpha_{m,2}52.7}{0.206 + \alpha_{m,2}0.0497} \tag{95}$$

These relationships for the glass transition temperature are plotted in Fig. 5.

The mole fraction α_m and the weight fraction α_w are known to be related by the formula
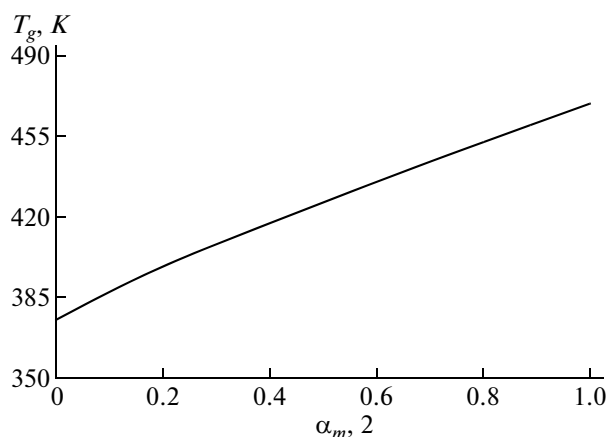
Fig. 7. Glass transition temperature T_g as a function of the mole fraction α_m of PC in the PS−PC blend. The curve was calculated without involving any experimental data.

$$\alpha_m = \frac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)} \tag{96}$$

where M_1 and M_2 are the molecular weights of the repeating units of polymers 1 and 2.

We will then obtain

$$T_g = \frac{43.7 + \dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)} 52.7}{0.214 + \dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)} 0.0417} \tag{97}$$

and

$$T_g = \frac{43.7 + \dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)} 52.7}{0.206 + \dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)} 0.0497} \tag{98}$$

Relationships (97) and (98) describe the dependences of the glass transition temperatures on the weight fraction of polymer 2 (Fig. 6).

Figure 6 also shows experimental data points from the work [32]. The experimental and calculated data can be seen to be in good agreement. (It is natural that this agreement is somewhat better when experimental glass transition temperature data are used for both polymers.)

Miscible PS (polymer 1) + tetramethyl-substituted PC (polymer 2) blends. The chemical structure of PC is shown below:
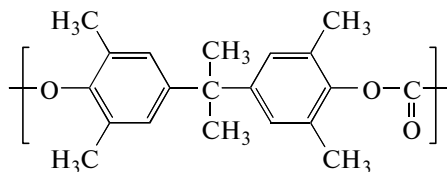
The physical parameters necessary for the calculation are presented in Table 13.

Criteria (91) and (92) were calculated using the Cascade software. Note that the molar volume of PC should be divided by 2, since this quantity is calculated for a chain containing two base elements (as PS).
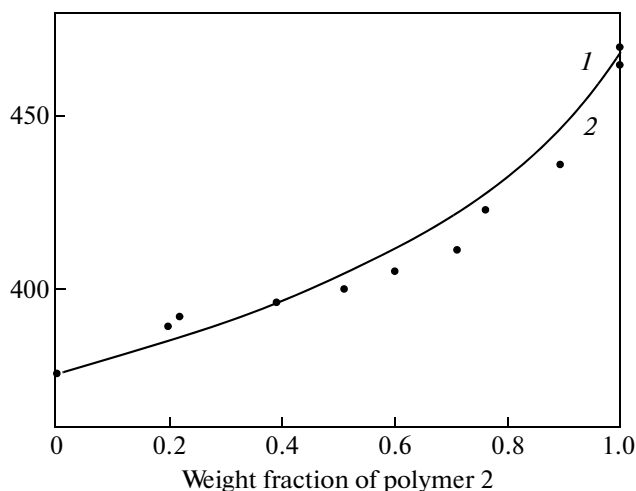
Fig. 8. Glass transition temperature T_g as a function of the weight fraction α_w of PC in the PS−PC blend: (*1*) curve calculated without involving any experimental T_g data for PS or PC; (*2*) experimental data.

For criterion (91), when PS is the polymer and PC is the solvent, we obtain $\mu_1 = 0.99$ and $1.374\beta_1 = 1.15$. The polymers considered are miscible, since $\mu_1 < 1.374\beta_1$. The interfacial tension is 0.94 mN/m. For criterion (92), when PC is the polymer and PS is the solvent, we obtain $\mu_2 = 1.04$ and $1.374\beta_2 = 1.18$. The polymers are totally miscible, since $\mu_2 < 1.374\beta_2$ as well.

In order to express the glass transition temperature T_g as a function of the mole fraction of polymer 2, it is possible for totally miscible polymers to use complete equation (19), which is valid for copolymers [4−7]:

$$T_g = \frac{(1 - \alpha_{m,2})\left(\sum_i \Delta V_i\right)_1 + \alpha_{m,2}\left(\sum_i \Delta V_i\right)_2}{(1 - \alpha_{m,2})\dfrac{\left(\sum_i \Delta V_i\right)_1}{T_{g,1}} + \alpha_{m,2}\dfrac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}} + 0.06(1 - \alpha_{m,2})\alpha_{m,2}}. \tag{99}$$

Equation (99) more precisely relates T_g to the mole fraction of polymer 2. If we take into account the calculated values of $T_{g,1}$ and $T_{g,2}$ and substitute all parameters into formula (99), we will obtain

$$T_g = \frac{110 + \alpha_{m,2}195}{0.293 + \alpha_{m,2}0.357 + 0.06\alpha_{m,2} - 0.06\alpha_{m,2}^2} \tag{100}$$

The calculated and experimental glass transition temperature values are in good agreement. For this reason, we will use only the calculated data. The dependence of T_g on $\alpha_{m,2}$ is plotted in Fig. 7.

In order to derive T_g as a function of the weight fraction α_w of PC, it is necessary to substitute Eq. (96) into Eq. (100):

$$T_g = \frac{110 + \dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)}195}{0.293 + \dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)}0.357 + 0.06\dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)} - 0.06\left[\dfrac{1}{1 + \dfrac{M_2}{M_1}\left(\dfrac{1}{\alpha_w} - 1\right)}\right]^2} \tag{101}$$

Relationship (101), which is plotted in Fig. 8, describes the dependence of the glass transition temperature on the weight fraction of polymer 2 (PC). This relationship is juxtaposed in Fig. 8 with experimental data [32]. It can be seen that the experimental and calculated data are in good agreement.
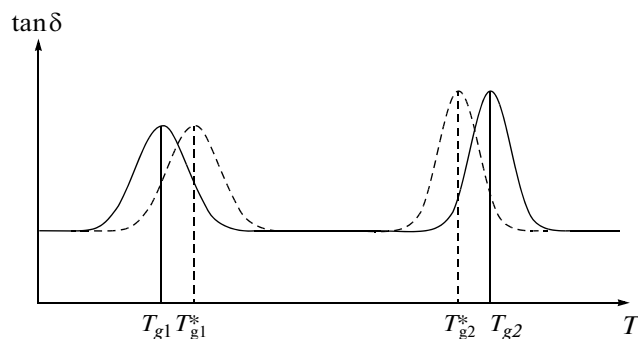
Fig. 9. Schematic representation of the temperature dependence of $\tan\delta$ for a blend of partially miscible polymers.

7.5. Determining the Composition of the Microphases of Partially Miscible Polymers

The miscibility of two polymers is commonly judged from the glass transition temperature of their blend. A single glass transition temperature of the blend is observed for totally miscible polymers, and this temperature is between the glass transition temperatures of the initial components. For absolutely immiscible polymers, two distinct glass transition temperatures are observed, each corresponding to the glass transition temperature of one of the components. In the case of partial miscibility, when both components are present in a microphase but in different proportions, two glass transition temperatures are observed again; however, as compared to those of the initial components, they are shifted toward one another.

The most popular experimental procedure used to determine the glass transition temperature of a blend is dynamic mechanical analysis (DMA). In this method, the temperature dependences of the storage modulus E', loss modulus E'', and mechanical loss tangent $\tan\delta = E''/E'$ are measured. If the blend is totally miscible, there will be a single glass transition temperature and it will depend on the blend composition. If the polymers of the blend are absolutely immiscible, the temperature dependence of E'' or $\tan\delta$ will display two peaks pertaining to two microphases, one consisting of polymer 1 and the other of polymer 2 (Fig. 9).

For a blend of two partially miscible polymers, the temperature dependence of E'' or $\tan\delta$ indicates two peaks pertaining to two microphases, both consisting of a mixture of polymers 1 and 2. The first phase contains some amount of polymer 2, and the second contains some amount of polymer 1. This causes the peaks to shift relative to the glass transition temperature of either component. The solid lines in Fig. 9 represent data for an absolutely immiscible polymer blend; the dashed lines, for a partially miscible polymer blend.

By way of example, we will present the results of an analysis of a blend of two polyesters. One of them is based on terephthalic acid and phenolphthalein (polyester 1):
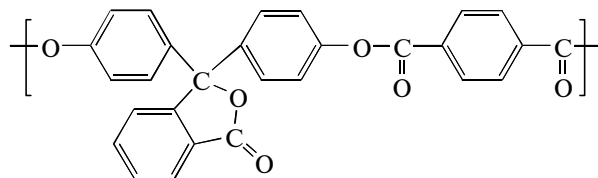
the other polymer is an aromatic polyester based on terephthalic acid and dimethyl-substituted bisphenol A (polymer 2).
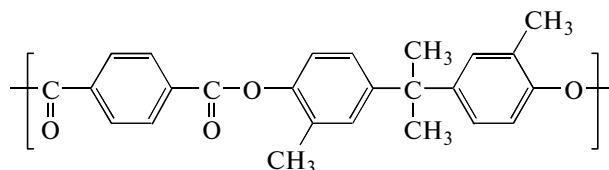
These polymers were synthesized for the first time by Korshak et al. [33, 34].
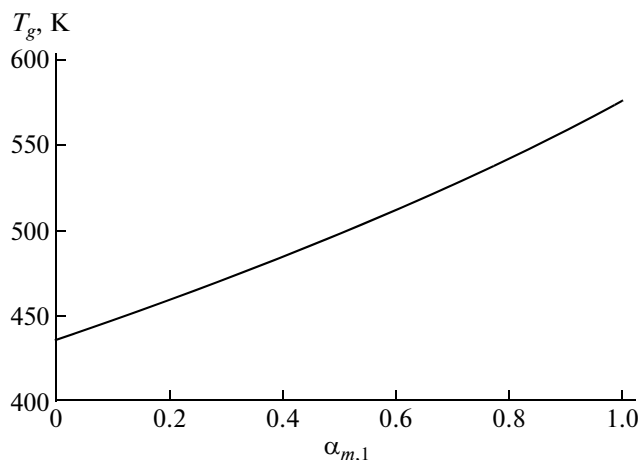
Fig. 10. Glass transition temperature of the polyether 1 + polyether 2 blend as a function of the mole fraction of polyether 1.

In order to plot the glass transition temperature curve for the two-component miscible blend, one may use a simplified relationship. It is necessary to describe the dependence of T_g on the mole fraction of polyester 1. Since $\alpha_{m,2} = 1 - \alpha_{m,1}$, we obtain

$$T_g = \frac{\alpha_{m,1}\left[\left(\sum_i \Delta V_i\right)_1 - \left(\sum_i \Delta V_i\right)_2\right] + \left(\sum_i \Delta V_i\right)_2}{\alpha_{m,1}\left[\dfrac{\left(\sum_i \Delta V_i\right)_1}{T_{g,1}} - \dfrac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}}\right] + \dfrac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}}}. \tag{102}$$

The dependence of T_g on $\alpha_{m,1}$ is plotted in Fig. 10.

This plot provides the means to determine the composition of the microphases corresponding to each peak in the $\tan \delta$ versus the temperature curve (Fig. 11).

The first peak, which indicates the glass transition temperature of the first microphase, is observed at 205°C (478 K), while the glass transition temperature of polyester 2 is 436 K. Therefore, the first microphase contains some amount of polyester 1. The second peak, which is due to the glass transition in the second microphase, occurs at 280°C (553 K), while the glass transition temperature of polyester 1 is 576 K. Therefore, the second microphase contains some amount of polyester 2.

In order to estimate the compositions of these microphases ($\alpha_{m,1}$ and $\alpha_{m,2}$), we will modify formula (102):

$$\alpha_{m,1} = \frac{B - T_g D}{T_g C - A}, \quad \alpha_{m,2} = 1 - \frac{B - T_g D}{T_g C - A}, \tag{103}$$

where $A = \left[\left(\sum_i \Delta V_i\right)_1 - \left(\sum_i \Delta V_i\right)_2\right]$; $B = \left(\sum_i \Delta V_i\right)_2$; $C = \left[\dfrac{\left(\sum_i \Delta V_i\right)_1}{T_{g,1}} - \dfrac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}}\right]$; and $D = \dfrac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}}$.

Using expression (103) and the experimental measured temperatures of either peak (Fig. 11), we obtain the following $\alpha_{m,1}$ and $\alpha_{m,2}$ values. For the first peak, $\alpha_{m,1} = 0.345$ and $\alpha_{m,2} = 0.655$; for the second peak, $\alpha_{m,1} = 0.86$ and $\alpha_{m,2} = 0.14$. Thus, the first microphase contains not only polyester 2 but also a considerable amount of polyester 1, while the second microphase is dominated by polyester 1 and contains a very small amount of polyester 2.
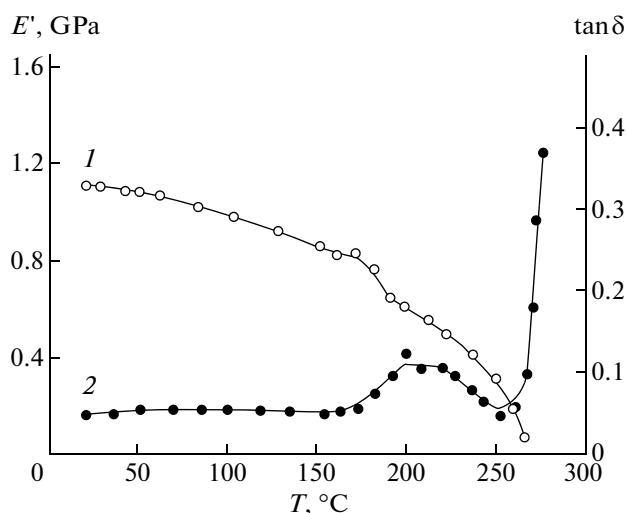
Fig. 11. Temperature dependence of the (*1*) storage modulus E' and (*2*) $\tan\delta$ for the equimolar polyether 1 + polyether 2 blend.

7.6. Factors in the Miscibility of Polymers

Here, we will consider the effects of a number of parameters of polymer–polymer miscibility and on the properties of polymer blends. These parameters include variations in temperature, composition, molecular weight, and polymer chain architecture (linear, branched, and other chains).

Temperature effect. To apply the solubility and miscibility criteria at different temperatures, it is necessary to take into account the temperature dependence of the solubility parameter for both polymers and those of the molar volume and surface tension. The temperature dependence of the solubility parameter δ_T^2 is described by the equation

$$\delta_T^2 = \frac{V\delta^2 + R(298 - T)}{V_T},\qquad(104)$$

where V is the molar volume of the polymer at room temperature (298 K), V_T is the molar volume at temperature T, and δ is the solubility parameter at vroom temperature.

The temperature dependence of surface tension $\gamma_{p,T}$ is expressed as

$$\gamma_{p,T} = D_j \frac{V\delta^2 + R(298 - T)}{V_{p,T}} \left(\frac{\sum_i \Delta V_i}{m} \right)^{1/3} \qquad(105)$$

Here, $\left(\sum_i \Delta V_i \right)$ is the van der Waals volume of the repeating unit of the polymer; m is the number of atoms in this unit; for group I nonpolar polymers (hydrocarbons, perfluorinated polymers, polyethers), $D_{In-p} = 0.0769$; for group II polar polymers, (polyesters, polymers containing a nitro group or an acetyl group), $D_{IIp} = 0.0452$; for polymers containing alcohol, acid, amide, and urethane groups (all are polar and show hydrogen bonding), $D_{III} = 0.0287$; for polymers containing nitrile groups (all are polar), $D_{IV} = 0.0361$; for polymers containing only aromatic rings (e.g., polystyrene and polyphenylene), $D_V = 0.061$.

Now we will consider the effect of temperature on the miscibility of polymers 1 and 2 (Table 13), the chemical structure of which is presented below.
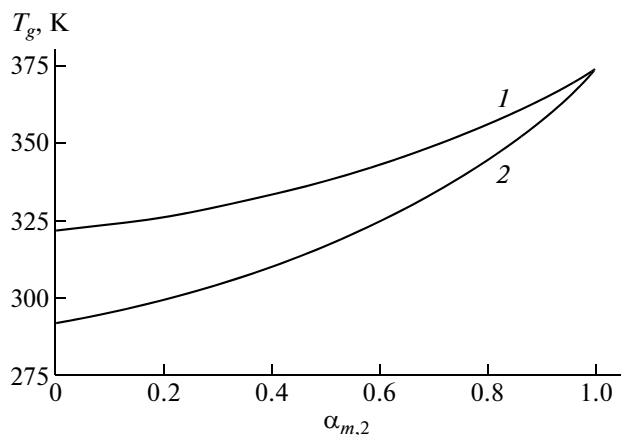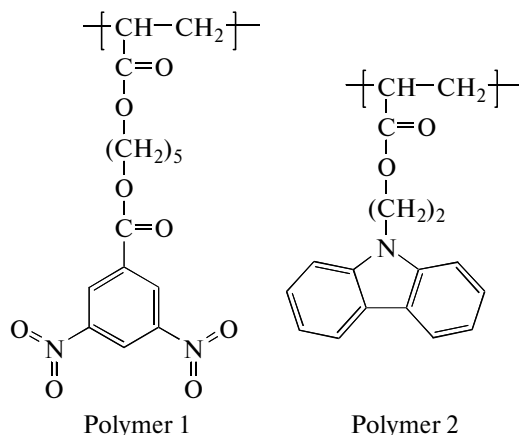
Fig. 12. Glass transition temperature T_g as a function of the mole fraction $\alpha_{m,2}$ of polymer 2: (*1*) polymer 1b + polymer 2 and (*2*) polymer 1c + polymer 2.

Polymer 1   Polymer 2

The molar volume, solubility parameter, and surface energy data for polymers 1 and 2 are listed in Tables 14 and 15. These tables contain the values of both sides of the miscibility criterion: μ_1 and $1.374\beta_1$; μ_2 and $1.374\beta_2$.

It follows from these data that the miscibility of the polymers increases with an increasing temperature when polymer 1 is introduced into polymer 2, since the difference between μ_1 and $1.374\beta_1$ increases. If polymer 2 is introduced into polymer 1, the miscibility of the polymers decreases with an increasing temperature, since the difference between μ_2 and $1.374\beta_2$ decreases slightly. The general conclusion is that the miscibility of polymers in the solid state depends very weakly on temperature.

Molecular weight effect. Here, there are at least two issues to be analyzed. The first issue is the effect of terminal groups in a polymer with a very low molecular weight. These groups can have an intermolecular interaction energy and molar volume other than those of the repeating unit of the polymer. The second issue is the effect of the molecular weight of the blended polymers, which alters the polymer solubility criterion. The effect of the molecular weight of a polymer on its solubility was analyzed in our monographs [5−7], according to which the solubility criterion takes the following form:

$$\mu^* \leq 1.374\Phi\left(\Phi - \sqrt{\Phi^2 + \frac{\gamma_p}{\gamma_s} - 2\Phi\left(\frac{\gamma_p}{\gamma_s}\right)^{0.5}}\right) = 1.374\beta, \tag{106}$$

where $\mu^* = \mu(N/N_0)^{1/6} = \mu(M/M_0)^{1/6}$; N is the degree of polymerization of the polymer, M is the molecular weight of the polymer, M_0 is the molecular weight of the polymers for which the method was calibrated ($M_0 = 2 \times 10^5$), and N_0 is the corresponding degree of polymerization.

The first of the above-mentioned issues will be considered for PS containing the terminal groups shown below,
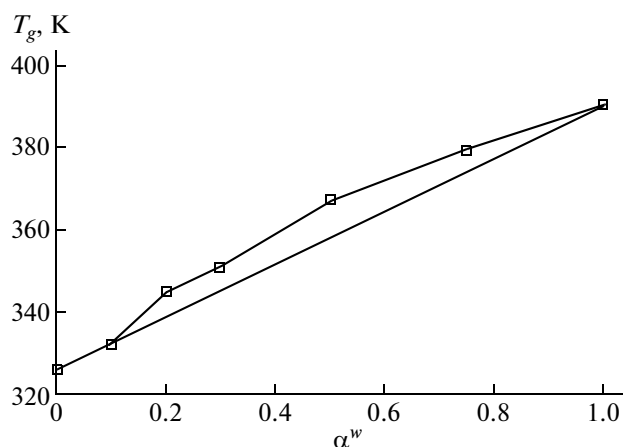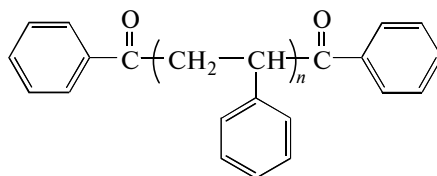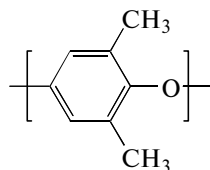
Fig. 13. Glass transition temperature T_g as a function of the weight fraction α_w of polymer 2.

and for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO),

as an example.

The physical parameters necessary for calculating criterion (106) and the results of assessing the miscibility of the polymers are presented in Table 16.

Note that the larger the difference is between μ^* and 1.374β in criterion (106) the better the miscibility is (obviously, the $\mu^* < 1.374\beta$ condition must be satisfied). It follows from the data presented in Table 15 that the miscibility increases with an increasing PS molecular weight when PS is introduced into PPO, since the difference between μ_1^* and $1.374\beta_1$ increases. However, the miscibility worsens as the PS molecular weight is increased when PPO is introduced into PS, since the difference between μ_2^* and $1.374\beta_2$ decreases. All of this is due to the variation of three factors: surface tension, solubility parameter, and molar volume.

The second of the aforementioned issues will be considered for mixtures of polymer 1 and polymer 2 (PPO) as an example. Calculations demonstrated that, when polymer 1 is introduced into PPO, miscibility is observed within a polymer 1 molecular weight range of 500 to 2.8×10^5. If the molecular weight of polymer 1 is above 2.8×10^5, the polymers are immiscible. When PPO is introduced into polymer 1, miscibility is observed in a PPO molecular weight range of 500 to 2.3×10^5. If the molecular weight of PPO is above 2.3×10^5, the polymers are immiscible. Thus, microphase separation takes place when the molecular weigh of PPO is very high.

7.7. Effect of the Molecular (Linear, Branched, Other) Architecture of the Polymer

The chemical structure of the branched polymers to be considered is shown below:
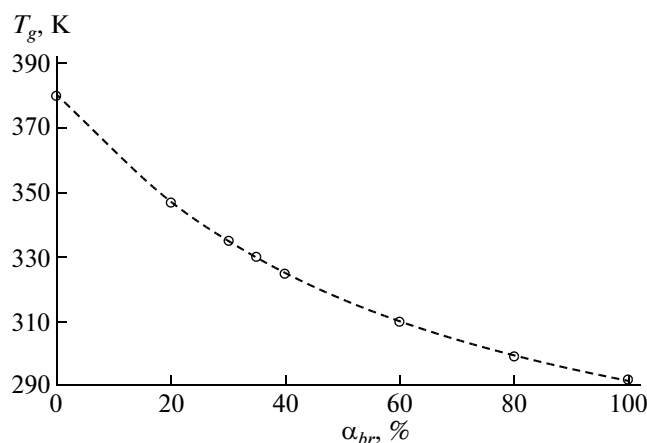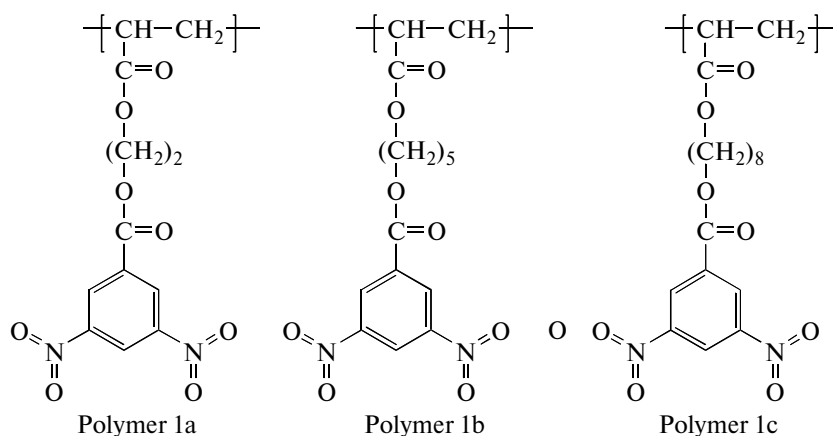
Fig. 14. Glass transition temperature T_g as a function of the degree of branching, α_{br}.

Polymer 1a   Polymer 1b   Polymer 1c

Some of these polymers are miscible with polymer 2 (see above). The physical parameters necessary for the calculations are listed in Table 17.

When polymer 1a is introduced into polymer 2, the polymers are immiscible. When polymer 2 is introduced into polymer 1a, the polymers are immiscible as well ($\mu > 1.374\beta$). When polymer 1b is introduced into polymer 2, the polymers are miscible ($\mu < 1.374\beta$; $\mu = 1.19$, $1.374\beta = 1.26$), as in the case of polymer 2 introduced into polymer 1b ($\mu < 1.374\beta$; $\mu = 0.84$, $1.374\beta = 1.27$). The same behavior is displayed by the polymer 1c + polymer 2 blend.

Thus, the changes in the chemical structure of the side chain (length of the pendant substituent) for the polymers considered above improve the miscibility of the polymers.

The dependence of the glass transition temperature on the mole fraction of polymer 2, $\alpha_{m,2}$ for miscible blends is described by relationship (99). If the physical parameters listed in Table 16 are used, for the polymer 1b + polymer 2 blend we will obtain

$$T_g = \frac{285 - \alpha_{m,2}37}{0.885 - \alpha_{m,2}0.222 + 0.06\alpha_{m,2} - 0.06\alpha_{m,2}^2}. \tag{107}$$

For the polymer 1c + polymer 2 blend, we have

$$T_g = \frac{336 - \alpha_{m,2}88}{1.151 - \alpha_{m,2}0.488 + 0.06\alpha_{m,2} - 0.06\alpha_{m,2}^2}. \tag{108}$$

The dependences of the glass transition temperature on the mole fraction of polymer 2 for the blends considered are plotted in Fig. 12.

We will use formula (96) to obtain the relationship between the glass transition temperature and the weight fraction of polymer 2. Again, experimental data points [32] are juxtaposed with the plot of this relationship (Fig. 13).
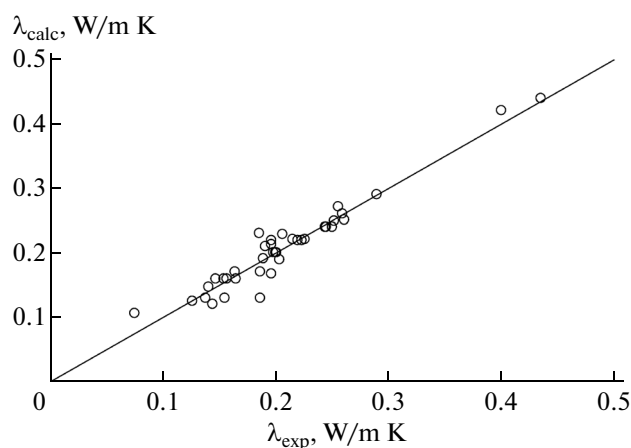
λ_calc, W/m K

Fig. 15. Thermal conductivity correlation diagram.

We will now estimate the physical properties of polymers with different degrees of branching. By way of example, we will consider blends composed of polymer 2 and polymer 1c. Since the pendant group in polymer 1c is much longer than in polymer 2, it can be conventionally accepted that the larger the mole fraction of polymer 1c is, the higher the degree of branching will be. The calculated values of parameters of the polymers are presented in Table 18.

Figure 14 plots the glass transition temperature as a function of the degree of branching α_{br}.

The results of the analysis of miscibility between polymer 2 and polymers with different degrees of branching are presented in Table 19.

Clearly, when the copolymer is introduced into polymer 2, miscibility is observed starting at a degree of branching of 35%. If the degree of branching is below 35%, the polymers are immiscible. When polymer 2 is introduced into the copolymer, the miscibility of the polymers is better ($\mu \ll 1.374\beta$) at any degree of branching above 35%. This behavior is due to the fact that the values of the solubility parameter δ are very different within the 0−35% range of the degree of branching.

Thus, the miscibility of two polymers depends very weakly on temperature if both are in the glassy state. At the same time, the degree of branching and molecular weight exert very strong effects on the polymer−polymer miscibility.

The computational scheme for predicting polymer−polymer miscibility makes possible a miscibility analysis based on the chemical structure of the repeating units. To make a prediction, it is insufficient to know only the Hildebrand solubility parameters involved in the interaction parameter $\chi_{1,2}$. Not only the solubility parameters but also surface forces and surface tension in polymer blending, the molecular weights of the polymers, their degree of branching, the intermolecular interaction energy, temperature, and the van der Waals volume and molar volume of the repeating units should be taken into account. The miscibility of polymers is depends most strongly on their molecular weights and degree of branching. The molecular weight effect arises from two factors. When a polymer has a low molecular weight, there is a considerable effect of the terminal groups, which differ in chemical structure from the repeating unit. At a high molecular weight, the key role is played by the size of the so-called bond globules and by the character of intermolecular interaction between the polymers. The effect of the degree of branching on the miscibility of polymers is dual in character. If the chemical structure of the side groups is radically different from that of the main chain, its effect on the miscibility is dominant.

As was demonstrated by calculations, the temperature effect on the solubility parameter of polymers and on their surface energy and molar volume is insufficiently strong to significantly change the parameters appearing in solubility criteria (84) and (85). As a consequence, if a polymer blend is in the glassy state, the temperature effect on the miscibility of its components is not strong.

The Cascade software, which includes a *miscibility of polymers* option, enables one to determine all of the physical characteristics involved in the solubility criterion and to predict the miscibility of polymers in the online mode once the chemical structures of the components are displayed.
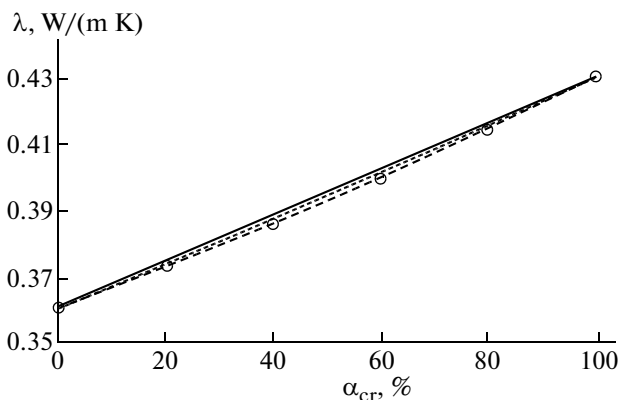
Fig. 16. Thermal conductivity of PE as a function of its degree of crystallinity. The solid line represents the data calculated via formula (115), the dotted line represents the data calculated via formula (116), and the dashed line represents the data calculated via formula (113).

8. THERMOPHYSICAL PROPERTIES OF POLYMERS

8.1. Heat Capacity

The heat capacity of polymers depends on their chemical structure (Table 20).

Among the hydrocarbon polymers, polyethylene has the lowest heat capacity. The substitution of polar groups for hydrogen atoms in polyethylene enhances its heat capacity. On passing from aliphatic polymers to aromatic ones, the heat capacity increases markedly.

There have been many attempts to calculate the heat capacity of polymers that started from the chemical structure of the repeating unit. We will consider a computational method based on the assumption that the molar heat capacity of a polymer body is proportional to the van der Waals volume of the atoms constituting the repeating unit of the polymer [4−7]:

$$C_p^s = \Sigma C_{p,i}^s \Delta V_i + A_s \qquad (109)$$

and

$$C_p^l = \Sigma C_{p,i}^l \Delta V_i + A_l, \qquad (110)$$

where C_p^s and C_p^l are the molar heat capacities of the polymer in the glassy and rubbery states, respectively; $C_{p,i}^s$ and $C_{p,i}^l$ are constants for each atom, which have the meaning of heat capacity per unit van der Waals volume and refer to the glassy and rubbery states, respectively; and A_s and A_l are parameters, the values of which are $A_s = 0.77$ cal/(mol K) and $A_l = 0.69$ cal/(mol K).

The $C_{p,i}^s$ and $C_{p,i}^l$ values were determined by applying regression analysis to the overdetermined system of equations based on relationship (109) or (110) with the use of experimental heat capacity data for comprehensively studied polymers (so-called polymer standards, namely, polyethylene, polystyrene, poly(methyl methacrylate), etc.).

The C_p^s and C_p^l values obtained in this way for each kind of atom are listed in Table 21.

Using these values and van der Waals volumes, one can easily calculate the molar heat capacities C_p^s and C_p^l for a great number of polymers.

8.2. Thermal Conductivity

Thermal conductivity is among the important thermophysical properties of amorphous and crystalline polymers. A theory relevant to this subject is most comprehensively described in monographs [38, 39]. For amorphous polymers, which are dielectrics, the mechanism of heat conduction and the temperature dependence of conductivity are related with the basic kinetic equation

$$\lambda = \frac{1}{3}\rho C_V \langle c \rangle \langle l \rangle, \qquad (111)$$

where λ is thermal conductivity, C_V is heat capacity, $\langle c \rangle$ is the average phonon velocity, and $\langle l \rangle$ is the phonon mean free path.

Since the heat capacity of polymers at the glass transition temperature T_g increases abruptly, it would be expected that the heat capacity will as well, according to Eq. (111). In fact, this kind of temperature dependence of heat capacity is not observed for polymer glasses. (The best-studied polymer in this respect is PMMA.) It was hypothesized [40] that energy transfer near the T_g point is due to intramolecular and intermolecular interactions. This heat conduction mechanism is typical of liquids. Since amorphous polymers are liquids in phase state terms, their thermal conductivity can be described by the Vargaftik equation [41], which applies to the thermal conductivity of organic liquids:

$$\lambda = A \frac{c_p \rho^{4/3}}{M^{1/3}} \qquad (112)$$

Here, c_p is heat capacity at constant pressure, ρ is density, M is the molecular weight of the liquid, and A is a constant.

There has been an attempt [42] to devise a computational scheme to estimate the thermal conductivity of a polymer by starting from its chemical structure. In this estimate, all of the physical parameters involved in Eq. (112) are taken into account. For polymers, Eq. (112) should be modified, because otherwise there will be some uncertainty, even if the molecular weight of the repeating unit is used. We will illustrate this point using polyamides as an example. The chemical structure of PA-6 is

$$-NH-(CH_2)_5-CO-$$

The molecular weight of the repeating unit of PA-6 is 113.

The chemical structure of PA-6,6 is

$$-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-$$
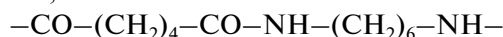
The molecular weight of the repeating unit of PA-6,6 is 226.

By substituting these values into Eq. (112), we obtain different thermal conductivity values, while the observed values are equal. It is therefore necessary to reduce the molecular weight of the repeating unit of the polymer, M, to one atom; that is, it is necessary to divide M by the number of atoms in the repeating unit, m. Relationship (112) will then take the following form:

$$\lambda = A \frac{c_p \rho^{4/3}}{\left(\dfrac{M}{m}\right)^{1/3}} \qquad (113)$$

The value of A, which depends on the chemical structure of the polymer, was expressed follows [42]:

$$A = \frac{\sum_i a_i + \sum_j b_j}{N_A \sum_i \Delta V_i}, \qquad (114)$$

where a_i represents the atomic constants of each atom, b_j designates the constants for the polar groups giving rise to dipole−dipole interaction or hydrogen bonding, N_A is the Avogadro constant, and ΔV_i is the van der Waals volume of the ith atom.

Calibration of the computational scheme (finding the constants a_i and b_j) was carried out in the following way. Based on the measured values of thermal conductivity λ for well-studied polymers (so-called polymer standards) and on the calculated values of all of the parameters appearing in Eq. (113), we estimated the A value. Experimental thermal conductivity data were taken from a handbook [43]. Next, an overdetermined system of equations based on the relationship

$$A N_A \sum_i \Delta V_i = \frac{\lambda \left(\dfrac{M}{m}\right)^{1/3}}{c_p \rho^{4/3}} N_A \sum_i \Delta V_i = \sum_i a_i + \sum_j b_j, \qquad (115)$$

was composed, and the system was solved by a standard method.

For example, the parameters of Eq. (115) for PMMA are written as

$$\sum_i a_i + \sum_j b_j = 2a_{C,\text{main}} + 3a_{C,\text{side}} + 2a_{H,\text{main}} + 6a_{H,\text{side}} + 2a_{O,\text{side}} + b_d$$

A number of variants of the computational scheme were developed [42] to take into account the role of various types of intermolecular interactions, the degree of crystallinity, and the positions of atoms in the

main chain or in the side chains. The best variant, which led to a correlation coefficient of $r = 0.993$, was obtained on the basis of the following propositions.

(1) The atoms belonging to the main chain of the polymer were distinguished from the atoms of the side chains. The atomic constants a_i of the main-chain atoms were given the subscript *main*, and those of the side-chain atoms were given the subscript *side* (Table 22).

(2) A polymer density at 60% crystallinity was used in the calibration of the computational scheme for crystallizing polymers. This density value was determined by the Cascade software. In the subsequent calculation of thermal conductivity, the polymer density at any preset degree of crystallinity can be used (see below).

(3) The effect of the dipole−dipole interaction and those of aromatic rings and double bonds in the main chain on thermal conductivity were taken into account by introducing b_j parameters. The hydrogen bond effect turned out to be very weak. At the same time, heat transfer is enhanced for polymers containing the same groups of atoms that are only in the main chain, and such polymers are always crystallizable, so they need a special parameter to be introduced (see Table 21). These polymers include PE and PTFE.

The results of the thermal conductivity calculations are presented in Table 23.

Note that different experimental thermal conductivity values are reported for the same polymer in some cases. For example, $\lambda_{\text{эксп}}$ for PVA is reported to be 0.20 W/(m K) [43] and 0.1063 W/(m K) [44]. The thermal conductivity correlation diagram is presented in Fig. 15.

Equation (113) in combination with relationship (114) provides the means to estimate the effects of temperature and degree of crystallinity on the thermal conductivity. The thermal conductivity as a function of the degree of crystallinity, α_{cr}, can be estimated with the following two relationships:

$$\lambda = \alpha_{\text{cr}}\lambda_{\text{cr}} + (1 - \alpha_{\text{cr}})\lambda_{\text{am}}, \tag{116}$$

$$\lambda = \frac{2\lambda_{\text{am}} + \lambda_{\text{cr}} + 2\alpha_{\text{cr}}(\lambda_{\text{cr}} - \lambda_{\text{am}})}{2\lambda_{\text{am}} + \lambda_{\text{cr}} - \alpha_{\text{cr}}(\lambda_{\text{cr}} - \lambda_{\text{am}})}\lambda_{\text{am}}, \tag{117}$$

where λ_{cr} is the thermal conductivity of the crystalline sample and λ_{am} is the thermal conductivity of the amorphous sample.

The thermal conductivity versus degree of crystallinity curves obtained with formulas (116) and (117) are plotted in Fig. 16. These curves are close together and are close to the same curve obtained using formula (113).

The thermal conductivity is calculated in the following way.

(1) Initially, the c_p value is calculated. This value depends on whether the polymer is in the glassy or rubbery state at room temperature. In order to decide which of the heat capacity values is to be used, it is necessary to determine the glass transition temperature. If this temperature is above 298 K, the c_p value characterizing the glassy state should be used; if this temperature is below 298 K, then the heat capacity value for the rubbery state should be taken. The M, m, and ρ values are also calculated here. It is necessary to know the polymer density for 60% crystallinity.

(2) The A value is determined via relationship (114) with the a_i and b_j values listed in Table 21. The van der Waals volume of the repeating unit of the polymer or that of the repeating fragment of the polymer network $\sum_i \Delta V_i$ and the densities of the amorphous and totally crystalline samples are determined as was described above. The thermal conductivity for different degrees of crystallinity can be calculated via formula (116) or (117). With these data, the λ_{am} and λ_{cr} values are calculated via Eq. (113).

This computational scheme provides means to estimate, with a sufficient degree of accuracy, the thermal conductivity of polymers from their chemical structure. Note that experimental determination of thermal conductivity involves some difficulties, and, as a consequence, different experimental λ values for the same polymer can be found in the literature. The above scheme enables one to estimate the thermal conductivity of a polymer as a function of its degree of crystallinity and temperature.

Note that thermal conductivity appears in equations for other thermophysical properties of polymers, including thermal diffusivity:

$$\alpha = \frac{\lambda}{c_p \rho} \tag{118}$$

Since it is possible to calculate the specific heat capacity c_p and density ρ at different temperatures and degrees of crystallinity, it is also possible to calculate the thermal diffusivity as a function of these parameters.

9. MECHANICAL PROPERTIES

9.1. Elastic Modulus of Linear Polymers

The dependence of the elastic modulus on the chemical structure of the polymers in their blend will be described in terms of Eq. (119), which was suggested in our earlier works [4–6]. This equation is written as

$$E = \frac{\sum_i \Delta V_i}{\sum \dfrac{\Delta V_i S_i}{\kappa_i l_i}}, \tag{119}$$

where ΔV_i is the van der Waals volume of the ith atom in the repeating unit, S_i is the ith atom's van der Waals surface area through which intermolecular interaction takes place, κ_i is the coefficient of elasticity of the bond of the ith atom, and l_i is the characteristic bond length.

The energy of the intermolecular interaction of atoms, D, is described in terms of the London potential

$$\varphi = -2D\left(\frac{r_0}{r}\right)^6 \Bigg|_{r=2r_0}, \tag{120}$$

where r_0 is the equilibrium distance.

Since the distance between two atoms is $l_i = 2r_i$, we will express κ_i in terms of the parameters of the London potential:

$$\kappa_i = \frac{\partial^2 \varphi}{\partial r^2} = -\frac{84 z D_i}{r_0^2}\left(\frac{r_0}{r}\right)^8, \tag{121}$$

where z is the coordination number and D_i is the intermolecular interaction energy for the ith atom.

Now we will use the relationship between the melting point T_m of the polymer, the bond elasticity coefficient κ_i, and the anharmonicity coefficient δ_i, which was introduced in our earlier works [4–6]:

$$T_{m_i} = \frac{\kappa_i}{3R}\left(\frac{\kappa_i}{2\delta_i}\right)^2 = \frac{1}{K_i}, \tag{122}$$

where T_{m_i} is the critical temperature at which the ith oscillator loses its stability;

$$\delta_i = -\frac{1}{2}\frac{\partial^3 \varphi}{\partial r^3} = \frac{336 z D_i}{r_0^3}\left(\frac{r_0}{r}\right)^9 \tag{123}$$

Thus,

$$\kappa_i = \frac{192R}{K_i l_i}\Bigg|_{r=l_i}. \tag{124}$$

Substituting this expression into Eq. (119), we obtain

$$z D_i = \frac{16}{7}\left(\frac{r}{r_0}\right)^6 R \frac{1}{K_i}. \tag{125}$$

Based on Eq. (126), we write the following relationship for a polymer blend:

$$E = 192R \frac{\sum_i \Delta V_i}{\sum_i K_i S_i l_i \Delta V_i}. \tag{126}$$

$$E(\text{blend}) = \frac{192R\left[\alpha_{m,1}\left(\sum_i \Delta V_i\right)_1 + \alpha_{m,2}\left(\sum_i \Delta V_i\right)_2\right]}{\alpha_{m,1}\left(\sum_i K_i S_i l_i \Delta V_i\right)_1 + \alpha_{m,2}\left(\sum_i K_i S_i l_i \Delta V_i\right)_2}, \tag{127}$$

where $\alpha_{m,1}$ is the mole fraction of polymer 1 (elastomer), $\alpha_{m,2}$ is the mole fraction of polymer 2 (glassy polymer), $\left(\sum_i \Delta V_i\right)_1$ and $\left(\sum_i \Delta V_i\right)_2$ — are the van der Waals volumes of the repeating units of polymers 1 and 2, $\left(\sum_i K_i S_i l_i \Delta V_i\right)_1$ and $\left(\sum_i K_i S_i l_i \Delta V_i\right)_2$ are the sets of atomic constants for polymers 1 and 2.

The quantity $\left(\sum_i K_i S_i l_i \Delta V_i\right)$ can be represented as

$$\left(\sum_i K_i S_i l_i \Delta V_i\right) = \frac{\left(\sum_i \Delta V_i\right)}{E} \tag{128}$$

In view of expression (119), the relationship for the elastic modulus of a two-component polymer blend as a function of the component concentrations appears as

$$E(\text{blend}) = \frac{\alpha_{m,1}\left(\sum_i \Delta V_i\right)_1 + \alpha_{m,2}\left(\sum_i \Delta V_i\right)_2}{\alpha_{m,1}\dfrac{\left(\sum_i \Delta V_i\right)_1}{E_1} + \alpha_{m,2}\dfrac{\left(\sum_i \Delta V_i\right)_2}{E_2}} \tag{129}$$

Since $\alpha_{m,1} + \alpha_{m,2} = 1$,

$$E = \frac{1 + \alpha_{m,2}\left[\dfrac{\left(\sum_i \Delta V_i\right)_2}{\left(\sum_i \Delta V_i\right)_1} - 1\right]}{\dfrac{1}{E_1} + \alpha_{m,2}\left[\dfrac{\left(\sum_i \Delta V_i\right)_2}{\left(\sum_i \Delta V_i\right)_1 E_2} - \dfrac{1}{E_1}\right]} \tag{130}$$

9.2. Elastic Modulus of Network Polymers in the Rubbery State

The equation for estimating the equilibrium rubbery modulus E_∞ is described in our monographs [4–6]. The derivation of this equation is based on the theory of rotational isomerism and on an account of the total effect of liner fragments and network cross-linked points on the compressibility of a network polymer. (The latter factor is particularly significant for dense networks.) The equation has the following form:

$$E_\infty = E_0 \frac{2(m + \beta)}{\Phi m^2}, \tag{131}$$

where

$$E_0 = \frac{3\rho R \Phi T}{2 M_0} \tag{132}$$

Here, m is the number of repeating units in an average liner fragment, Φ is the functionality of the network (number of chains coming out of a cross-linked point), ρ is density, R is the universal gas constant, T is temperature, and M_0 is the molecular weight of the repeating unit in the internodal fragment.

The quantity β is defined as

$$\beta = \frac{\left(\sum_i \Delta V_i\right)_y}{\left(\sum_i \Delta V_i\right)_0}, \tag{133}$$

where $\left(\sum_i \Delta V_i\right)_y$ and $\left(\sum_i \Delta V_i\right)_0$ are the van der Waals volumes of the network cross-linked point and the repeating unit of the internodal fragment, respectively.

For high cross-linked networks, in which m is small, possibly below unity, the parameter β plays a great role and the equilibrium rubbery modulus calculated via Eq. (131) is substantially higher than the modulus estimated using the equation of the classical theory of high elasticity. However, it can readily be demonstrated that, for sparse networks, when $m \gg 1$ and $\beta \ll m$, expression (131) transforms into the classical equation

$$E_\infty = \frac{3\rho RT}{M_c} \tag{134}$$

Taking into account that $m = M_c/M_0$, we finally obtain the following relationship from formulas (131)–(133):

$$E_\infty = \frac{3\rho RT}{M_c}\left(1 + \frac{M_0}{M_c}\beta\right) \tag{135}$$

The generalized equation for E_∞, which is presented in our monographs, is valid for both high cross-linked and sparse networks [4–6].

10. BARRIER PROPERTIES

The barrier properties include the permeability of polymer membranes to various gases and liquids. The oxygen, nitrogen, and carbon dioxide permeabilities of polymers have long been calculated with various relationships. In recent years, it has become possible to predict the water permeability and to carry out a computer synthesis of polymers with a preset permeability.

10.1. Water Permeability

The basic equation for the permeability P of polymers is

$$P = P_0 e^{-\frac{\Delta E}{RT}}, \tag{136}$$

where P_0 is a constant, ΔE is the activation energy of permeation, R is the universal gas constant, and T is absolute temperature.

The activation energy ΔE is described by the following relationship [45]:

$$\Delta E = \frac{\sum_i \Delta E_i^{**}}{N_A \sum_i \Delta V_i}, \tag{137}$$

where N_A is the Avogadro number, $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit of the polymer,

$\sum_i \Delta E_i^{**}$ is the intermolecular interaction energy as the sum of the interaction energies of all atoms and specific atomic groups that give rise to dipole–dipole interactions or hydrogen bonding.

Then,

$$\ln P = \ln P_0 - \frac{\sum_i \Delta E_i^{**}}{N_A RT \sum_i \Delta V_i} \tag{138}$$

After slight rearrangements, we obtain

$$\frac{\sum_i \Delta E_i^{**}}{RT} - \left(N_A \sum_i \Delta V_i \right) \ln P_0 = -\left(N_A \sum_i \Delta V_i \right) \ln P \tag{139}$$

Next, we set up an overdetermined system of equations based on Eq. (139) with permeability values for so-called polymer standards, the permeability of which has been reliably determined [46–68]. Solving this system of equations yields a set of atomic constants and a number of parameters characterizing the energy of strong intermolecular interactions for some individual groups. These parameters are listed in Table 24. The value of $\ln P_0$ is 3.001 (barrers).

Experimental and calculated water permeability data are presented in Table 25.

The correlation coefficient here is 0.984.

The temperature dependence of the permeability P in a relatively narrow temperature range can be described by the Arrhenius equation

$$P = P_0 e^{-\frac{\Delta E}{RT}} = P_0 e^{-\frac{\Delta E_{cond} + \Delta E_s}{RT}}, \tag{140}$$

where ΔE_{cond} is the heat of solution and ΔE_s is the molar heat of mixing.

For gases that are above their critical point, such as H_2, O_2, and N_2 at room temperature, the ΔE_{cond} value is very small and ΔE is determined by ΔE_s. The ΔE_s values for rarefied gases are small and positive, so the permeability P increases slightly with an increasing temperature. For more condensable gases, such as SO_2, H_2O, and NH_3, ΔE is negative and is determined by ΔE_{cond} and the permeability P decreases with an increasing temperature. It is the combination of the ΔE_{cond} and ΔE_s values that determines whether the permeability increases or decreases with an increasing temperature.

11. COMPUTER SYNTHESIS OF POLYMERS WITH PRESET PROPERTIES

We demonstrated above that it is possible to calculate the most important physical properties of polymers by starting from the chemical structure of the repeating unit (for linear polymers) or repeating fragment (for polymer networks). At present, these problems are solved using a computer. Forward and inverse problems can be formulated here.

The forward problem is to calculate, starting from the chemical structure of the repeating unit of a polymer or from that of the repeating fragment of a network, one or several physical properties. The inverse, more complicated problem is to predict the chemical structure of the repeating unit of a polymer that would have one or several of the desired physical properties. The methods of solving both problems have already been described in detail [4–7], so we will not go into detail here. Note only that the computer programs PDTools, CHEOPS, and Cascade have been developed for this purpose. In these programs, the chemical structure of the repeating unit is represented as a structural formula of an organic compound on the computer display, just as a chemist would draw it on a piece of paper. Next, all of the physical properties of the polymer with the specified structure (listed below) are calculated and are outputted to the user. It is possible here to carry out a molecular design of the polymer by varying its chemical structure, introducing various groups, and so on, and to immediately calculate its physical characteristics.

The approaches overviewed above and the corresponding computer programs provide the means to calculate over 120 properties of linear and network polymers. Thus, it is possible now to quantitatively estimate various physical properties of polymers on the basis of the chemical structure of their repeating unit (for linear polymers) or their repeating network fragment (for network systems).

The van der Waals volume and intermolecular interaction energy are also determined by these programs. When the properties of the polymer depend considerably on its molecular weight, this fact is taken into account in the corresponding equations and criteria. The properties of copolymers and homogeneous polymer blends can be calculated as well.

New opportunities are opened up by programs developed for the computer synthesis of polymers with preset properties. When solving the forward problem (estimation of the properties of a polymer from the

chemical structure of the repeating unit of the polymer entered into the computer), one can easily carry out a molecular design by varying the chemical structure of the repeating unit, adding new groups, replacing the existing groups with new ones, introducing various substituents, passing from one class of polymers to another, etc. The pictorial representation of the polymer structure in the form of a structural formula of the repeating unit and the high speed of computing in solving the forward problem enable the user to obtain a result quickly and to "design" the chemical structure of a polymer or copolymer in order to alter its properties in the desired way.

Solving the inverse problem (computer synthesis of polymers possessing the desired physical properties, whose allowable interval has been entered into the computer) may yield a variety of chemical structures even within a fixed class of polymers.

12. PRINCIPLES OF THE CASCADE SOFTWARE

At present, there are several computer programs for calculating the properties of polymers. One of them, SYNTHIA, implements the Bicerano method. As was mentioned above, the Bicerano approach is based on so-called connectivity indices and actually reduces to various correlations, such as the correlation between the glass transition temperature of polymers and the solubility parameter. The Bicerano method does not allow one to calculate the properties of network polymers or to correctly calculate the properties of copolymers and polymer blends. It does not cover many of the characteristics that can be calculated using the Cascade software (developed by the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences), including various kinds of intermolecular interaction energy and the stress-optic coefficient (basic constant in the photoelasticity method). The Bicerano approach is incapable of predicting the solubility and miscibility of polymers. In addition, it does not allow one to calculate a property of a polymer as a function of its molecular weight and degree of crystallinity.

The PDTools program provides the means to calculate the properties of polymers via the three existing methods: Askadskii–Matveev, Bicerano, and van Krevelen ones. As was mentioned above, the van Krevelen method is purely empirical, so it cannot serve as a basis for drawing scientific conclusions concerning the effects of different types of chemical and physical interactions on the properties of polymers. In addition, the van Krevelen method is invalid for copolymers and network systems. The aforementioned programs PDTools and SYNTHIA are not intended for computer synthesis of polymers with preset properties whose interval is inputted by the user.

The Cascade software, which is based on the Askadskii–Matveev method, enables the user to predict many physical properties of linear and network polymers by starting from their chemical structure and to carry out a computer synthesis of polymers with preset properties. The original variant of the software was presented in [69, 70]. In this program, the physical properties of polymers are calculated from the chemical structure of their repeating unit with the use of atomic physical constants, among which the fundamental characteristic is the van der Waals volume of the atoms constituting the repeating unit of a linear polymer or the repeating fragment of a network polymer. The repeating unit of a polymer is considered as a set of anharmonic oscillators formed by pairs of atoms belonging to this unit. The Cascade software is a computer implementation of an essentially atomistic approach. An average intermolecular interaction energy is inputted for each atom, and the effects of separate polar groups are taken into account by inputting a limited set of increments, which are the same for different types of dipole–dipole interactions and hydrogen bonds. Since each polar group has its own chemical structure and its own van der Waals volume, polar groups differ in their contribution to the intermolecular interaction.

The involvement of the minimum possible number of constants and increments makes it possible to calculate the physical characteristics of a great number of polymer structures, irrespective of how complex their chemical structures are. These calculations are helpful and even necessary, not only in solving the main problem of predicting the properties of polymers prior to their synthesis. The Cascade software enables one to analyze the solubility of polymers and polymer–polymer miscibility. It is possible to analyze the effects of various groups introduced into polymers by, e.g., the effects of a polymer-analog reaction on the properties of the resulting systems and on the composition of the microphases in the case of a microphase separation. It is also possible to analyze the effects of branching and structure defects in high cross-linked network polymers on their properties and to solve many other problems.

The Cascade software provides the means to calculate the dielectric loss tangent at various frequencies (10^2–10^6 Hz) and the softening point of polymers as a function of the plasticizer or solvent content. This program offers options for calculating various properties of a polymer of any chemical structure as a function of its molecular weight, microtacticity, degree of crystallinity, and temperature. It is also possible to calculate the temperature dependences of the density, molecular packing coefficient, and specific and molar volumes of polymers.

The Cascade software enables the user to calculate about 60 physical characteristics for linear and network polymers and for organic liquids that are used as polymer solvents. This program makes it possible to calculate the physical properties of polymer networks as well. The physical properties that can be calculated for network polymers include glass transition temperature, the onset temperature of intensive thermal degradation, refractive index, dielectric constant, equilibrium high-elasticity modulus, and many others. The program can predict the properties of copolymers, homogeneous polymer blends, etc.

Computer implementation of the method is based on modularity principles, on the developed user-friendly Windows interface, and on the principle of compatibility with the programs involved in computer-assisted organic synthesis planning (CAOSP) [71]. The first two principles are well known and commonly accepted, so we will briefly consider the third one. The structure of the compound that is the initial object to which CAOSP is to be applied should ensure the desired properties of the target compound. Since the search for this structure is among the problems of the method, it is necessary to ensure a consistent description of structures in the atomic constant method and CAOSP. The table of atoms and the table of connectivity, which specify the set of atoms and bond types in the structure of the compound, are the main programs in CAOSP. In the implementation of the method, it was found to be appropriate to compile these tables for each repeating unit formula considered. Special attention is paid to solving the problem of the dialog between the user and the program. The repeating unit structure is displayed using a planar representation of the arrangement of atoms connected by certain types of bonds. If necessary, a correspondence between this formula and the Wiswesser line notation [71] or Morgan formula [73] is established using the tables of atoms and connectivity. It seems important to ensure unambiguous interpretation of the repeating unit structure presented on the display. For this purpose, the program checks whether there is information about the atoms, atomic groups, and bonds in the database.

At present, the Cascade software enables the user to calculate about 60 physical characteristics for linear and network polymers and for organic liquids used as polymer solvents. This program is the only one that allows the physical properties of polymer networks to be calculated.

The Cascade software is applicable to the polymers and copolymers listed in Table 1. For liquids, the program can calculate the following properties:

(1) molecular weight;

(2) molar volume;

(3) van der Waals volume;

(4) density;

(5) Hildebrand solubility parameter;

(6) surface tension;

(7) refractive index;

(8) dielectric constant;

(9) molar heat capacity in the solid state;

(10) molar heat capacity in the liquid state;

(11) molar refraction;

(12) molar polarizability;

(13) total cohesion energy;

(14) cohesion energy fraction due to hydrogen bonding;

(15) cohesion energy fraction due to dipole−dipole interaction;

(16) cohesion energy fraction due to dispersion interaction.

The Cascade software is very simple for the user, who has only to draw, on the computer display, the chemical structure of the repeating unit for a linear polymer or that of the repeating fragment for a polymer network or the molecular structure of the organic liquid considered. For this purpose, the software includes a special-purpose editor, which allows the user to easily draw the structures. In addition, there is a Help option, in which it is described in detail how to use the program.

13. CONCLUSIONS

Here, we will overview recent works dealing with the prediction of various properties of polymers and their blends and properties of nanocomposites. Roy et al. [74] noted that the prediction and optimization of polymer properties is a complicated nonlinear problem. It was demonstrated in the cited work that the properties of modified monomers can be predicted using neural networks. These networks are divided into groups, and the existing databases are used. Afantitis Antreas et al. [75] suggested employing a neural network in the prediction of the glass transition temperature for high-molecular-weight rubbers.

Li et al. [76] considered the thermodynamic properties of polymers, including their enthalpy, entropy, and Gibbs energy. Experimental heat capacity data as a function of temperature were used for 15 polymers. The results of these calculations are presented in polynomial and graphical forms. These data provide the means to estimate the phase diagrams of binary, ternary, and other polymer systems.

Several works have been devoted to the prediction of properties of polymer blends. The elastic limit for blends of miscible glassy polymers was calculated by Engels et al. [77]. The mechanical properties of polymer blends were considered by Kunal et al. [78]. They analyzed predictions of the mechanical properties of various phase structures. Kate Kunal [79] discussed the prediction of properties of polymer blends prepared by pressure casting from powdered components.

The greatest number of works has been devoted to nanocomposites. A theoretical estimation of the mechanical properties of polymer nanocomposites was carried out by Valavala and Odegard [80]. There have been attempts to predict the limiting mechanical properties of composites based on metallic and polymer matrices and reinforced with short fibers [81–83]. Numerous works have detailed structure–property relationships for nanocomposites [84–105].

Ajloo Davood et al. [106] estimated the thermal degradation of polymers by the QSPR method. Bystritskaya et al. [107] predicted the aging behavior of polymer materials. A number of works deal with the properties of a solution. Miller-Chou and Koenig [108] presented a review on the solubility of polymers. Application of QSPR methods to polymer–solvent binary systems for calculating the Flory–Huggins interaction parameter χ_{12} was considered by Jie Xu et al. [109]. Singh Ramvir et al. [110] predicted the heat capacity of polymer composites.

There have been reviews on the application of QSPR methods. Salame Morris [111] considered the methods of estimating and predicting the polymer properties. Various approaches, and their industrial applications, that use thermodynamic information derived from databases or obtained by predictions based on thermodynamic models were analyzed. An analysis of data on the properties and modeling in polymer science was presented by Adams Nico and Schubert Ulrich [112]. The barrier properties (permeability of polymer membranes to various gases) were considered by Salame Morris [113].

Current computational methods applicable to the development of polymer dielectrics were analyzed by Wang et al. [114, 115]. A variety of methods, including *ab initio* quantum mechanical ones, were discussed. Some examples of computer synthesis applied to real polymer dielectrics were presented, and the increasing role of these computational methods in the design of the chemical structure of polymer dielectrics was emphasized.

Baldwin et al. [116] carried out experimental and theoretical studies of the dielectric constants of aromatic polyimides. Syntheses involving pyromellitic dianhydride and a short-chain amine can yield materials rich in imido groups. These materials have a high dielectric constant and are thermally stable up to 250°C. The synthesized homopolymers and copolymers had a dielectric constant of 3.96 to 6.57.

A series of recent works was devoted to estimation of the effect of plasticizers on the elastic modulus and glass transition temperature of polymers [117, 118] and to the effect of the degree of crystallinity on the same characteristics [119, 120]. Estimation of the microphase compositions in polymer blends was considered in our publication [121]. The problem of predicting the solubility of polymers in organic solvents was further discussed. A modified computational scheme was developed [121], which takes into account the effect of both the degree of polymerization and the lyophobic interaction on the polymer solubility conditions. This scheme is valid for polymers and copolymers consisting of nonpolar and polar moieties. In this case, the polymer cohesion energy ΔE^* appearing in the relationship for determining the polymer solubility parameter (61) is the sum of two parts, namely, the conventional cohesion energy of the "dry" polymer and an additional contribution from the lyophobic interaction to the cohesion energy. The lyophobic interaction arises from the nonpolar moiety of the polymer passing into a polar solvent and counteracts the dissolution of the polymer. The predicting power of the new criterion was tested on two systems: polyarylate of isophthalic acid phenolphthalein and polysulfone. An analysis of the solubility of these polymers in a wide variety of solvents demonstrated that the predicting power of the modified criterion is 93%.

All of the works reviewed in section 12 deal with particular issues of predicting the properties of polymers, their blends, and nanocomposites. They have made a considerable contribution to the state of the art in predicting the properties of polymers and polymer-based materials.

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