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Computational Procedures for the Determination of the Physical Characteristics of Polymers

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Methods are described for the calculation of the principal physical characteristics of polymers from data for the chemical structure of the repeating polymer unit. These characteristics include the density, coefficient of thermal expansion, glass point, melting point, refractive index, coefficient of optical sensitivity to stress, and the solubility parameters of low-molecular-weight liquids and polymers. A consistent relation between these characteristics and the chemical structure of polymers has been traced.
The bibliography includes 27 references.

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I. INTRODUCTION

As a consequence of the extension of the range of chemical substances involved in polymerisation and polycondensation processes, the problem of the synthesis of polymers with specified properties has now become even more acute. Such properties include the glass point, the density, the coefficient of volume expansion, the refractive index, etc. The solution of the problem associated with the solubility of the polymer in a particular solvent is particularly important. The above properties of polymers are the most important ones and in many respects they determine the many other properties. It is shown in the present review that all the parameters enumerated above can be determined even before synthesising the polymer solely on the basis of the chemical structure of the repeating unit.

We shall examine primarily problems associated with the packing of macromolecules in monolithic polymeric materials and with the calculation of their densities.

II. THE PACKING OF MACROMOLECULES AND THE DENSITIES OF POLYMERS

The packing coefficient k, which is defined as the ratio of the van der Waals volume of atoms and groups of atoms in the molecule to the true volume determined from experimental data, serves as a measure of the packing density of the macromolecules[1-3]. The calculation of the packing coefficients of molecules is usually based on the molar volumes of the repeating units. Then

$$k = \frac{N_A \sum_i \Delta V_i}{M/d}, \qquad (1)$$

where ΔV_i are the increments of the van der Waals volumes of the atoms in the repeating unit of the polymer, m the molecular weight of the repeating unit, d the density of the polymer, and N_A the Avogadro number. In order to evaluate the packing coefficients k, the volume increments ΔV_i for a large number of atoms, linked by valence bonds with a wide variety of other atoms, have been calculated in a number of studies[1-8]. Since the values of ΔV_i will be convenient subsequently for the calculation not only of the densities but also of other properties of polymers, a detailed table of their values is included (Table 1).

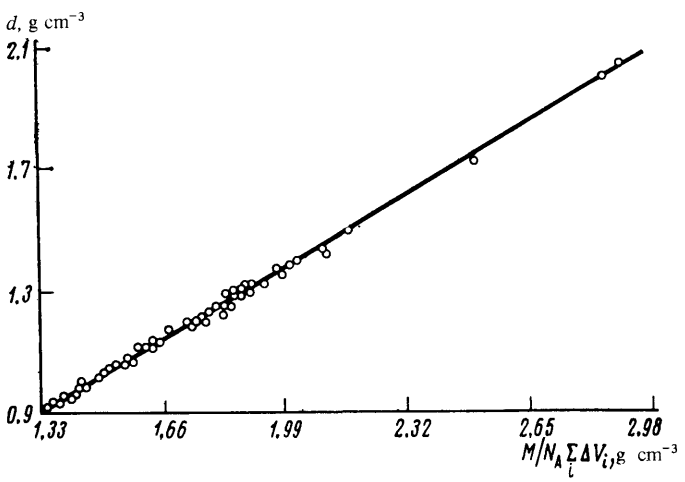


Figure 1. Variation of the densities of amorphous and amorphous-crystalline polymers with the ratio $M/N_A \sum_i \Delta V_i$.

In the calculation of the packing coefficients of amorphous monolithic polymers, it was found[2] that, regardless of the chemical structure of the polymers, their packing coefficients are approximately the same and amount to 0.681 at 20°C. In order to demonstrate this experimental finding, Table 2 lists the values of k for a number of amorphous polymers and Fig. 1 illustrates the variation of the densities of polymers having different chemical structures with the ratio $M/N_A \sum_i \Delta V_i$. Evidently this relation is described by a straight line on which the experimental

values of d fit satisfactorily. Its slope is equal to the packing coefficients $k = 0.681$. Since k is to a first approximation a constant for amorphous monolithic bodies, the density of the polymer may be calculated solely from the chemical structure of the repeating unit by the equation

$$d = \frac{k_{av} M}{N_A \sum_i \Delta V_i}, \qquad (2)$$

where $k_{av} = 0.681$.

Table 1. The van der Waals volumes of atoms and atomic groups.

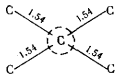
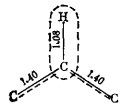
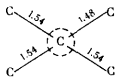
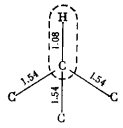
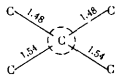
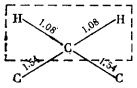
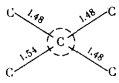
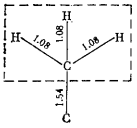
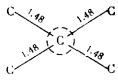
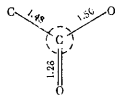
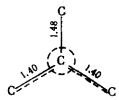
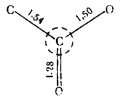
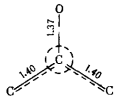
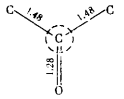
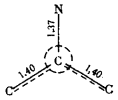
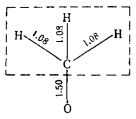
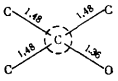
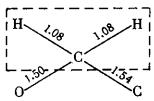
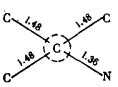
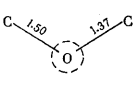
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	8.4		15.9
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	5.8		2.7
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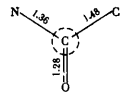
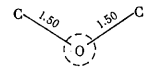
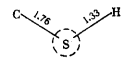
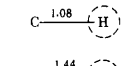
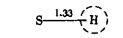
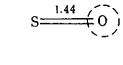
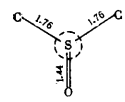
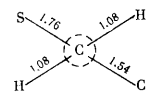
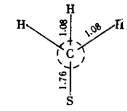
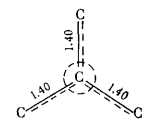
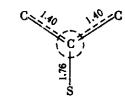
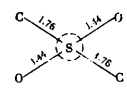
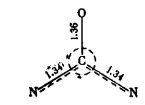
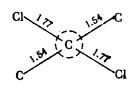
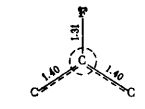
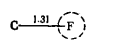
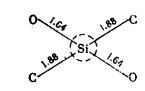
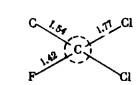
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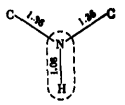
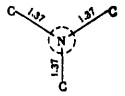
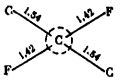
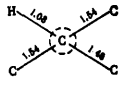
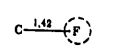
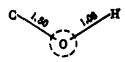
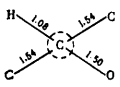
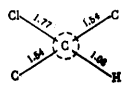
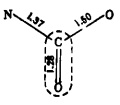
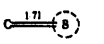
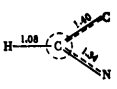
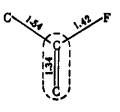
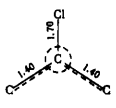
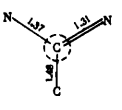
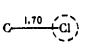
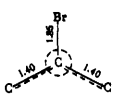
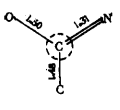
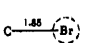
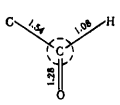
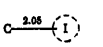
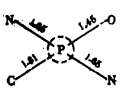
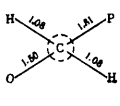
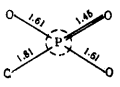
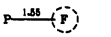
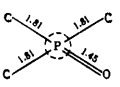
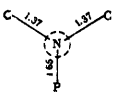
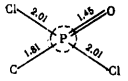
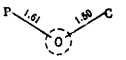
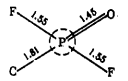
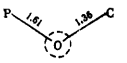
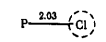
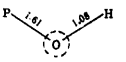
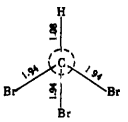
Group	Δ v_i, Å³	Group	Δ v_i, Å³
	8.3		15.9
			10.0
	0.9		9.4
	8.6		9.6
	5.6		
	12.2		10.1
	4.7		19.85
	23.3		20.2
			14.8
	20.7		10.5
	12.6		19.5
			9.9
	14.1		27.1
	6.1		10.5
	16.9		37.9
			17.4
	16.4		
	19.6		9.3
	14 8		1.55

Table 1 (continued).

Group	Δ v_i, Å³	Group	Δ v_i, Å³
	16.5		6.0
			3.15
	17.9		2.4
	20.0		5.4
	10.5		9.25
	27.3		
	13.6		13.3
	10.0		9.3
	9.6		17.4
			13.3
	17.7		14.1
	2.0		14.2
	11.0		14.7
	13.5		14.9
	38.4		7.0
	17.3		

The calculations[2] have shown that the density of an amorphous polymer may be calculated as a rule to within 0.01 g cm^{-3}. Table 3 presents as an example the experimental and calculated densities d at 20°C for representatives of various classes of polymers in the amorphous monolithic state. It can be seen that these agree with adequate accuracy. We may note immediately that the

packing coefficients for crystalline polymers depend significantly on the chemical structure of the polymers and their values lie within very broad limits. It should also be noted that calculations of the densities of polymers have been performed in a study[9] where the increments of the van der Waals volumes obtained by different workers were used.

Table 2. The packing coefficients k for amorphous monolithic polymers.

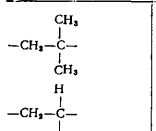
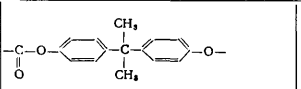
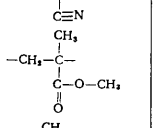
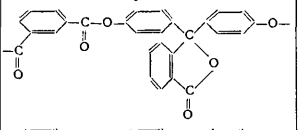
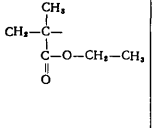
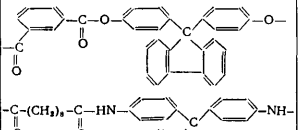
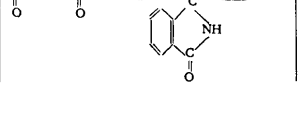
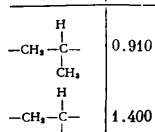
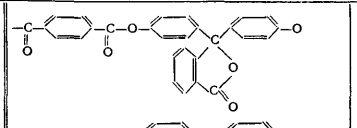
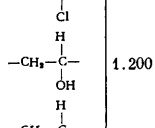
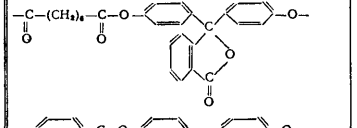
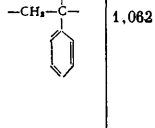
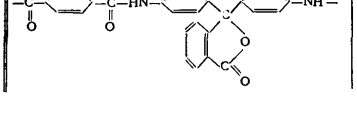
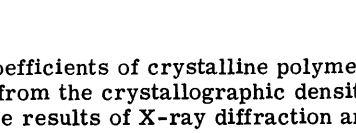
Polymer unit	Volume of unit, Å^3	k	Polymer unit	Volume of unit, Å^3	k
	41.6	0.678		144.3	0.679
	32.6	0.682		234.7	0.679
	58.5	0.684		263.1	0.680
	69.1	0.680		277.5	0.688

Table 3. The calculated and experimental densities of amorphous monolithic polymers.

Polymer unit	d_{exp}, g cm^{-3}	d_{calc}, g cm^{-3}	Polymer unit	d_{exp}, g cm^{-3}	d_{calc}, g cm^{-3}
	0.910	0.905		1 307	1.301
	1.400	1.380		1,213	1 213
	1.200	1.201			
	1.062	1.051		1 253	1.256
				1.302	1.280

The packing coefficients of crystalline polymers have been calculated[4] from the crystallographic densities evaluated from the results of X-ray diffraction analysis, namely the unit cell volumes and the masses of the atoms in the unit cell. Calculations were performed for 80 polymeric systems with a wide variety of chemical structures. It was found as a result that crystalline polymers have a very broad distribution curve with regard to the packing coefficients, which depend on the chemical structure of the polymer (Table 4). The distribution curve with respect to the packing coefficients is illustrated in Fig. 2, which also shows an analogous curve for amorphous polymers. It can be seen that the distribution curve with respect to the values of k for amorphous systems is extremely narrow.

Table 4. The packing coefficients k for crystalline polymers.

Polymer	Type of unit cell	d, g cm^{-3}	$N_A \sum_i \Delta V_i$, cm^3 mole^{-1}	M	k
1	2	3	4	5	6
Polyethylene	orthorhombic	1.0	20.6	28	0.736
		1.014	20.6	28	0.746
	pseudomonoclinic	0.965	20.6	28	0.710
	triclinic	1.013	20.6	28	0.745
Polypropylene					
isotactic	monoclinic	0.936	31.1	42	0.693
syndiotactic	monoclinic	0.910	31.1	42	0.674
Polystyrene	rhombohedral	1.12	66.0	104	0.711
Polybut-1-ene	rhombohedral	0.95	41.2	56	0.699
Polyisobutylene	orthorhombic	0.937	41.6	56	0.696
Polybuta-1,2-di-ene					
syndiotactic	orthorhombic	0.963	38.8	54	0.692
isotactic	rhombohedral	0.960	38.8	54	0.690
trans-Polybuta-1,4-diene	pseudohexagonal	1.02	38.8	54	0.733
cis-Polybuta-1,4-diene	monoclinic	1.01	38.8	54	0.726
cis-Poly-1,4-isoprene	monoclinic	1.00	49.3	68	0.725
trans-β-Poly-1,4-isoprene	orthorhombic	1.11	49.3	68	0.805
trans-Penta-1,4-diene	pseudohexagonal	0.98	49.3	68	0.710
Poly-3-methylbut-1-ene	monoclinic	0.93	51.5	70	0.684
Poly-4-methylpent-1-ene	tetragonal	0.813	61.8	84	0.598
Polyvinylcyclopentane	triclinic	0.986	64.9	96	0.666
Polyvinylcyclohexane	tetragonal	0.95	75.2	110	0.649
	triclinic	0.982	75.2	110	0.671
Poly-*o*-methylstyrene	tetragonal	1.071	76.1	118	0.691
Poly-*m*-methylstyrene	tetragonal	1.010	76.1	118	0.651
Poly-α-vinylnaphthalene	tetragonal	1.124	93.6	154	0.683
Poly(vinyl chloride)	orthorhombic	1.44	29.5	62.5	0.680
	orthorhombic	1.522	29.5	62.5	0.718
	monoclinic	1.455	29.5	62.5	0.687
Poly(vinylidene chloride)	monoclinic	1.949	38.5	97	0.773
	monoclinic	1.959	38.5	97	0.777
Polytetrafluoroethylene	pseudohexagonal	2.40	33.1	100	0.794
	hexagonal	2,36	33.1	100	0.781
Polychlorotrifluoroethylene	hexagonal	2.10	39.6	116.5	0.714
Poly(vinyl alcohol)	monoclinic	1.35	25.1	44	0.770
Poly(methyl methacrylate)					
isotactic	pseudo-orthorhombic	1.23	58.5	100	0.719
Poly(vinyl fluoride)	hexagonal	1.44	23.7	46	0.742
Polyacrylonitrile	orthorhombic	1.11	32.6	53	0.677
Polychloroprene	orthorhombic	1.657	47.7	88.5	0.893
Poly-*o*-fluorostyrene	rhombohedral	1.526	63.2	122	0.790
Poly(*NN*-dibutylacryl-amide)	hexagonal	1.06	121.7	183	0.705
Poly(ethylene terephthalate)	triclinic	1.455	102.4	192	0.776
Poly(hexamethylene terephthalate)	triclinic	1.131	143.6	249	0.652
Poly(decamethylene terephthalate)	triclinic	1.012	184.8	304	0.615
Poly(ethylene isophthalate)	triclinic	1.358	102.4	192	0.724
Poly(tetramethylene isophthalate)	triclinic	1.309	123	220	0.732
Poly(ethylene succinate)	triclinic	1.175	75.2	128	0.690
Poly(ethylene adipate)	triclinic	1.274	95.8	156	0.782
Poly(ethylene sebacate)	monoclinic	1.187	137	212	0.767
	triclinic	1.120	137	212	0.724
Poly(trimethylene sebacate)	tetragonal	1.090	147.3	226	0.710
Nylon 6,6					
α	triclinic	1.240	139.2	226	0.764
β	triclinic	1.248	139.2	226	0.769
Nylon 6, 10	triclinic	1.157	180.4	282	0.740
	triclinic	1.196	180.4	282	0.765
Nylon 7,7	pseudohexagonal	1.108	159.8	254	0.693
Nylon 6	monoclinic	1.23	69.9	113	0.758
	monoclinic	1.23	69.9	113	0.745
Nylon 7	triclinic	1.211	79.9	127	0.762
Nylon 8	hexagonal	1.038	90.2	141	0.664
Nylon 10	hexagonal	0.019	110.8	169	0.668
Nylon 11	triclinic	1.192	121.1	183	0.789
	triclinic	1.228	121.1	183	0.813
Poly(isobutyl vinyl ether)	orthorhombic	0.940	68.1	100	0.640
Cellulose					
I	monoclinic	1.592	79.5	162	0.781
II	monoclinic	1.625	79.5	162	0.797
Cellulose triacetate	pseudo-orthorhombic	1.30	148.8	288	0.672
Polyoxymethylene	hexagonal	1.506	16.1	30	0.808
Poly(ethylene oxide)	hexagonal	1.205	26.4	44	0.723
Poly(propylene oxide)	orthorhombic	1.096	34.9	58	0.659
	orthorhombic	1.102	34.9	58	0.663
	orthorhombic	1.154	34.9	58	0.694

Table 4 (continued).

Polymer	Type of unit cell	d, g cm^{-3}	$N_A \sum \Delta V_i$, cm^3 mole^{-1}	M	k
1	2	3	4	5	6
Polyacetaldehyde	tetragonal	1.14	26.6	44	0.689
Polypropionaldehyde	tetragonal	1.05	36.9	58	0.668
Poly-n-butyraldehyde	tetragonal	1.00	47.2	72	0.655
Polybisphenol	orthorhombic	1.30	144.3	254	0.738
Poly(hexamethylene sulphone)	monoclinic	2.77	78.7	148	0.736
Poly(hexamethylene pentaethylene sulphone)	monoclinic	2.83	116.1	282	0.583
Poly(hexamethylene tetramethylene sulphone)	monoclinic	2.92	136.7	268	0.745
Poly(pentamethylene sulphone)	monoclinic	2.95	68.4	134	0.753
Poly(pentamethylene tetramethylene sulphone)	monoclinic	3.06	126.4	254	0.761

*In the crystallographic data [3] for polymers containing the sulphone group, an error was made in the calculation of the density, which is too high by a factor of two.

We shall now consider the temperature variation of the packing coefficient. It was calculated [10] by Eqns. (3) and (4), which follow directly from Eqn. (1):

$$k(T) = \frac{N_A \sum_i \Delta V_i}{MV_g[1 + \alpha_G (T - T_g)]}; \quad T < T_g, \tag{3}$$

and

$$k(T) = \frac{N_A \sum_i \Delta V_i}{MV_g[1 + \alpha_L (T - T_g)]}; \quad T > T_g, \tag{4}$$

where V_g is the specific volume of the polymer at the glass point T_g and α_G and α_L are the coefficients of volume expansion of the polymer below and above the glass point respectively. The calculations carried out using Eqns. (3) and (4) have shown [10] that the temperature variation of the packing coefficients of a number of polymers is of the form shown in Fig. 3. A remarkable properties of these temperature variations is that the packing coefficients are the same to a first approximation for all polymers at any selected temperature below their glass points. To a second, more accurate approximation, the packing coefficient is the same for each polymer at its glass point and amounts to $k_g = 0.667$.

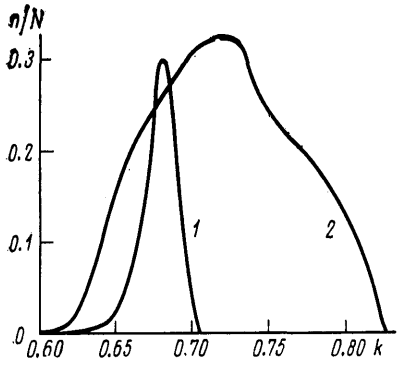


Figure 2. Distribution curves with respect to packing coefficients for amorphous (curve *1*) and crystalline (curve *2*) polymers.

At low temperatures ($T_0 \simeq 6$ K), the packing coefficients of polymers, determined by the extrapolation of the temperature variations of k to $T \to 0$, are also approximately the same and calculations have shown [10] that they can be estimated as $k_0 = 0.731$.

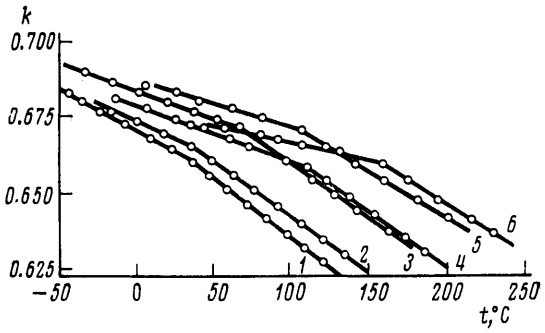


Figure 3. Temperature variation of the packing coefficients of polymers: 1) poly(n-butyl methacrylate); 2) poly(n-propyl methacrylate); 3) poly(ethyl methacrylate); 4) polystyrene; 5) poly(methyl methacrylate); 6) polycarbonate of di-(4-hydroxyphenyl)propane.

III. CALCULATION OF THE GLASS POINTS, COEFFICIENTS OF THERMAL EXPANSION, AND MELTING POINTS OF POLYMERS

An empirical relation has been proposed [11] whereby one can calculate the glass points T_g of polymers from the chemical structure of the repeating unit of the macromolecule and the density of the polymer:

$$\lg T_g = \frac{d}{M} \sum_i K_i' + A, \tag{5}$$

where M is the molecular weight of the repeating unit, d the density of the polymer, and $\sum_i K_i'$ the effective volume of the repeating unit, which consists of the effective volumes of the atoms and groups of atoms in this unit, and the parameter A is constant for a given class of polymers. Eqn. (5) holds satisfactorily for several classes of polymers (aromatic polyesters and polyamides, polymethacrylates).

Subsequently a more accurate universal computational scheme was proposed [12], which is valid for polymers of different classes. According to this scheme, the glass point is determined from the relation

$$\lg T_g = \frac{\sum_i K_i^*}{N_A \sum_i \Delta V_i} + A^*, \tag{6}$$

where $A^* = 1.435$ for any polymer and $\sum_i K_i^*$ is the effective volume of the repeating unit, differing from $\sum_i K_i'$ in Eqn. (5) by the fact that the values of K_i^* are determined by solving the excess system of equations based on Eqn. (6), which includes the van der Waals volume, while the K_i' are determined by the same procedure on the basis of Eqn. (5), which includes the molar volume.

In order to calculate the glass points of polymers, it is necessary to know the parameters K_i^* characterising the contributions of each atom and type of intermolecular interaction to the glass point. These quantities are listed in Table 5. Knowing them, it is easy to calculate the glass points of many polymers using Eqn.(6).

Table 5. The increments K_i^* for various atoms and types of intermolecular interaction.

Element or type of interaction	Designation	Value
Carbon	K_C^*	10.739
Oxygen in side group	$K_{O,s}^*$	3.925
Oxygen in main chain	$K_{O,m}^*$	−5.244
Hydrogen	K_H^*	−1.248
Hydrogen in side group	$K_{N,s}^*$	9.520
Hydrogen in main chain	$K_{N,m}^*$	2.185
Chlorine	K_{Cl}^*	7.242
Silicon	K_{Si}^*	19.570
Hydrogen bond	K_h^*	7.333
Dipole-dipole interaction	K_d^*	7.333
Symmetry coefficient	K_p^*	10.500

Note. The coefficient K_d^* is introduced in all cases when a hydrogen atom is replaced by a group of any type other than phenyl. This rule does not extent to polyisoprene and polychloroprene. When two hydrogen atoms are replaced by identical groups, the quantity $0.5K_d^*$ is introduced. The coefficient K_p^* is introduced when all the aromatic rings in the main chain are substituted in the *p*-position.

Table 6. The increments a_i, b_i, α_i, and D_i for various atoms and types of intermolecular interaction.

Atom or type of interaction	Designation	$a_i \cdot 10^3$ ($b_i \cdot 10^3$), K^{-1}	$\alpha_i \cdot 10^4$, K^{-1}	D_i, kcal mole^{-1}
Carbon*	a_C	0.021	—	—
Hydrogen	a_H	10.98	1.92	0.45
Oxygen in main chain	$a_{O,m}$	22.95	2.21	0.39
Oxygen in side chain	$a_{O,s}$	7.03	0.68	1.28
Nitrogen in main chain	$a_{N,m}$	8.62	0.83	1.04
Nitrogen in side chain	$a_{N,s}$	6.35	0.61	1.43
Chlorine	a_{Cl}	4.01	0.39	2.25
Sulphur in main chain	$a_{S,m}$	3.53	0.34	2.56
Dipole-Dipole interaction	b_d	−55.37	—	—
Hydrogen bond**	b_h'	−206.78	—	—
Symmetry coefficient***	b_h	−139.60		
Coefficient for polydienes taking into account the greater freedom of rotation in the presence of double bonds in the main chain	b_C $b_{=}$	−90.50 92.22		

*α_i and $1/D_i$ are negligibly small.
**b_h' is introduced for aliphatic polyamides.
***b_h is introduced in all other instances when the polymer contains hydrogen bonds.

Eqn.(6) makes it possible to estimate with adequate accuracy the glass points of polymers, but the physical significance of its parameters has not been established. An attempt was therefore made[10] to construct a computational scheme based on the previously proposed[12] principle of the additivity of the contributions of the individual atoms to the glass point, taking into account the physical ideas concerning volume expansion.

We shall now consider this scheme. According to Eqn. (1), $k_g/k_0 = V_0/V_g$, where V_0 is the specific volume of the polymer at the temperature T_0. Taking into account this equation, it was found[10] that

$$T_g = \frac{k_0/k_g - 1}{\alpha_G}. \tag{7}$$

The coefficient of volume expansion α_G can be expressed[10] in terms of the equation

$$\alpha_G = \frac{\sum_i a_i \Delta V_i}{\sum_i \Delta V_i} + \frac{\sum_i \beta_i}{\sum_i \Delta V_i}, \tag{8}$$

where α_i is the partial coefficient of volume expansion of the ith atom or groups of atoms in the repeating unit of the polymer, ΔV_i the volume increment of the ith atom or atomic group, and β_i are increments taking into account the contribution of strong intermolecular interactions to the coefficient of volume expansion (hydrogen bonds, dipole−dipole interaction, etc.; see Table 6).

The initial expression establishing the relation between T_g and the structure of the repeating unit has been obtained[10] by substituting Eqn.(8) in Eqn.(7):

$$T_g = \frac{\sum_i \Delta V_i}{\sum_i a_i \Delta V_i + \sum_i b_i}. \tag{9}$$

where

$$a_i = \alpha_i/(k_0/k_g - 1); \quad b_i = \beta_i/(k_0/k_g - 1). \tag{10}$$

The numerical values of a_i and b_i characteristic of each atom and of each type of intermolecular interaction have been determined[10] by a statistical treatment of the experimental data using the method of least squares. These results are presented in Table 6.

We shall now trace the relation between the coefficient α_i in Eqn.(10) and the intermolecular interaction parameters (the intermolecular bond energy and the distance between the interacting atoms). It is known[13] that the coefficient of volume expansion is described by the expression

$$\alpha_i = 3R\beta_i'/\gamma_i^2 r_{0i}, \tag{11}$$

where $\beta_i' = -\frac{1}{2}\partial^3\varphi/\partial r^3|_{r_{0i}}$ is the anharmonic coefficient, $\gamma_i = \partial^2\varphi/\partial r^2|_{r_{0i}}$ the harmonic force constant, r_{0i} the distance between the given ith and neighbouring atoms, φ the potential of the interaction of the ith atom with a neighbouring atom, and R the gas constant.

When the Lennard-Jones potential is used in the form for the determination of β_i' and γ_i [14]

$$\varphi(r) = D\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^6\right],$$

where D is the bond energy (the depth of the potential well) and r_0 the equilibrium distance between the atoms, then

$$\gamma_i = 72D_i/r_{0i}^2, \quad \beta_i' = 666D_i/r_{0i}^3;$$

or

$$\alpha_i = \frac{7}{16}\cdot\frac{R}{D_i}, \quad D_i = \frac{7}{16}\cdot\frac{R}{\alpha_i}. \tag{12}$$

Estimates of the values of D_i for bonds of different types have shown[10] that the bond energies derived from experimental data correspond to the intermolecular interaction energies (and not to chemical bonds).

Calculations carried out by Eqn.(12) demonstrated[10] that the average bond energies D_i assume the values listed in Table 6. Since, according to the literature[15,16] the bond energies D_i^0 for different atoms, included in Table 6, are several times smaller than the observed values of D_i, it follows that[10]

$$D_i = zD_i^0, \qquad (13)$$

where z is the coordination number.

Table 7. The calculated and experimental glass points of polymers.

Polymer	$\sum_i \Delta V_i$, Å³	T_g, K (calc.)	T_g, K (expt.)
Polyisoprene	81.8	198	200
Polychloroprene	79.15	213	225
Polydimethylsiloxane	72.1	150	150
Polypropylene	51.7	278	258, 293
Polyisobutylene	69.1	215	199
Polybutene	68.8	259	248
Poly(methyl vinyl ether)	61.0	292	258
Poly(ethyl vinyl ether)	78.4	270	248
Poly(n-butyl vinyl ether)	112.6	250	221
Poly(vinyl propionate)	97.1	260	266
Poly(vinyl acetate)	79.65	318	298
Poly(vinyl chloride)	49.05	340	355
Poly(vinylidene chloride)	69.3	267	256
Poly(methyl methacrylate)	97.0	353	378
Poly(ethyl methacrylate)	114.45	322	338
Poly(n-propyl methacrylate)	131.55	302	308
Poly(n-butyl methacrylate)	148.65	288	293
Poly(n-hexyl methacrylate)	182.85	270	268
Poly(n-octyl methacrylate)	217.05	259	253
Poly(methyl acrylate)	79.65	318	293
Poly(ethyl acrylate)	97.1	293	261
Poly(n-butyl acrylate)	131.7	267	233
Polystyrene	109.9	413	378
Poly-α-methylstyrene	127.2	437	435
Poly(vinyl alcohol)	41.6	366	358
Poly(ethylene terephthalate)	165.9	369	353
Polyacrylonitrile	54.1	420	418
Nylon 6,6	232.3	332	325
Nylon 6	116.15	332	335
Polyacrylamide	64.05	428	426
Polyacrylic acid	60.25	388	379; 439
Polycarbonate based on 2,2-di-(4-hydroxyphenyl)propane	239.25	422	411
Polyarylate of sebacic acid and phenolphthalein	450.5	367	363
Polyarylate of isophthalic acid and phenolphthalein	388.9	522	543
Polyarylate of terephthalic acid and phenolphthalein	388.9	594	583
Polyarylate of isophthalic acid and phenolphthalein anilide	470.9	532	563
Polyarylate of terephthalic acid and phenolphthalein anilide	470.9	593	593
Polyarylate of diphenylphthalide-4,4'-dicarboxylic acid phenolphthalein	571.6	581	598
Polyarylate of biphenyl-4,4'-dicarboxylic-acid and phenolphthalein	464.5	569	603
Polyarylate of isophthalic acid and phenolfluorene	436.8	516	543
Polyarylate of biphenyl-4,4'-dicarboxylic acid and phenolfluorene	512.5	558	587
Polyarylate of diphenylphthalidedicarboxylic acid and 4,4'-dihydroxybiphenyl	465.2	569	585
Polyarylate of oxydi(4-carboxybenzene) and phenolphthalein	473.8	547	573
Polyarylate of terephthalic acid and dimethyldian	367.8	412	423
Polyamide of terephthalic acid and anilinephthalein imide	399.6	590	618
Polyamide of sebacic acid and anilinephthalein imide	460,7	458	451
Polyamide of diphenylphthalidedicarboxylic acid and anilinephthalein imide	582,9	637	641
Polyimide of the dianhydride of oxydi(3,4-dicarboxybenzene) and anilinefluorene	537.9	640	670
Polyimide of the dianhydride of oxydi(3,4-dicarboxybenzene) and anilinephthalein	490.6	658	664
Polyimide of the dianhydride of 3,3',4,4'-tetracarboxybiphenyl and anilinefluorene	530.1	669	687
Polypyromellitimide of anilinephthalein	407.2	766	789

The initial Eqn.(9) can then be written in the form

$$1/T_g = 4.55R\left\langle \frac{1}{zD_0} \right\rangle, \qquad (14)$$

where

$$\left\langle \frac{1}{zD_0} \right\rangle = \sum_i \frac{1}{z_i D_i^0} \Delta V_i \Big/ \sum_i \Delta V_i.$$

Eqn.(9) can be used conveniently for the calculation of the glass points of polymers. A test of the applicability of Eqn.(9) has shown[10] that, for many polymers with a wide variety of chemical structures, the calculated and experimental values of T_g agree satisfactorily. These data are compiled in Table 7. Fig.4 illustrates the variation of T_g with $\sum_i \Delta V_i/(\sum_i a_i \Delta V_i + \sum_i b_i)$ for a number of polymers. The figure also includes the theoretical straight line based on Eqn.(9), the points corresponding to the experimental values of T_g. Fig.4 shows that Eqn.(9) holds over a very wide range of temperatures. Thus there is a possibility, in principle, of calculating the glass point of a polymer before its synthesis, regardless of the class to which it belongs. It is possible to calculate at the same time the coefficient of volume expansion α_G of the solid amorphous polymer from Eqn.(8). Calculations for a number of polymers showed a satisfactory agreement between the calculated and experimental data (Table 8).

Table 8. The volume expansion coefficients of polymers.

Polymer	$\sum_i \Delta V_i$, Å³	$\sum \alpha_i \Delta V_i \cdot 10^4$, Å³K⁻¹	$\alpha_G \cdot 10^4$, K⁻¹	
			calc.	expt.
Poly(methyl methacrylate)	97.0	208.5	2.15	2.73
Poly(ethyl methacrylate)	114.4	314.6	2.75	2.99
Poly(n-propyl methacrylate)	131.5	414.2	3.15	3.19
Poly(n-butyl methacrylate)	148.6	564.7	3.80	3.34
Poly(methyl acrylate)	79.6	214.9	2.70	3.03
Polystyrene	109.9	274.7	2.50	2.34

We shall now consider how the change in the packing density of the macromolecules on passing from the amorphous to the crystalline state of the polymer affects its melting point. We note first that, according to Beaman's data[17], the ratio of the glass point T_g to the melting point T_m is approximately constant for many polymeric systems and can be estimated as $\gamma = T_g/T_m \simeq 0.67$. However, a detailed analysis[18] showed that this relation does not always hold. The ratio $\gamma = T_g/T_m$ can assume a wide variety of values (ranging from 0.25 to 0.97).

Calculations have shown[4] that γ depends on the ratio of the packing coefficients of the fully amorphous and fully crystalline polymers (k_{am}/k_{cr}). This dependence is illustrated in Fig. 5, from which it follows that γ increases approximately linearly with increase of k_{am}/k_{cr}. Consequently γ depends on the difference between the packing densities of the macromolecules in the amorphous and crystalline states. The greater the increase of packing density on crystallisation of the polymer, the greater the difference between the melting and glass points.

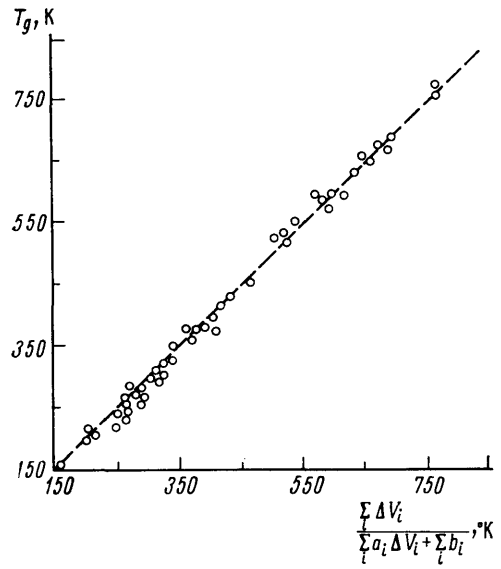


Figure 4. Variation of T_g with the ratio $\sum_i \Delta V_i / (\sum_i a_i \Delta V_i + \sum_i b_i)$.

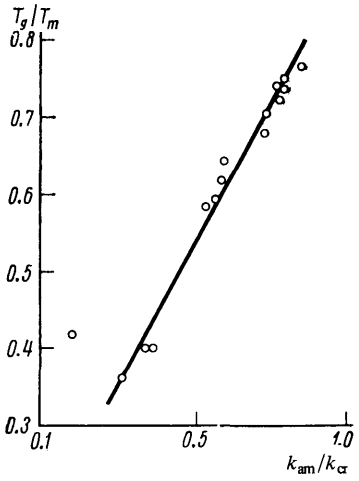


Figure 5. Variation of T_g/T_m with k_{am}/k_{cr}.

An attempt has been made [19] to establish a relation between γ and the parameters of the chemical structure of the repeating units of the polymer. The approach developed by Askadskii et al. [10] in devising a computational scheme for the estimation of the glass points of polymers was used. The initial relation for the determination of the melting point T_m can be written in the form [19]

$$V_m = V_0[1 + \alpha_{cr}(T_m - T_0)] \approx V_0(1 + \alpha_{cr} T_m), \quad (15)$$

where V_m is the specific volume of the polymer at the melting point, determined by the extrapolation of the dilatometric relation from temperatures $T < T_m$ to T_m, V_0 the specific volume of the crystalline polymer at the characteristic temperature T_0, which is approximately 6 K according to Askadskii et al. [10], and α_{cr} the coefficient of volume expansion of the crystalline polymer in the range of temperatures below the melting point.

Bearing in mind that $V_m/V_0 = k_{0,cr}/k_{m,cr}$, where $k_{0,cr}$ and $k_{m,cr}$ are the coefficients of molecular packing of the crystalline polymer at the temperatures T_0 and T_m respectively, we find from Eqn. (15)

$$\frac{T_g}{T_m} = \frac{k_{0,a} - k_{g,a}}{k_{0,cr} - k_{g,a}}. \quad (16)$$

Eqn. (16) was obtained [19] from the familiar experimental observation that the coefficients of volume expansion of amorphous and crystalline polymers having the same structure are virtually identical. The quantities $k_{0,a} = 0.731$ and $k_{g,a} = 0.667$ in Eqn. (16) are constant [10].

Taking into account the additivity of the volume, the packing coefficients of crystalline polymers can be expressed in the form [19]

$$k_{0,cr} = \sum_i \Delta V_i / V = \sum_i \Delta V_i / \sum_i \frac{1}{k_i} \Delta V_i, \quad (17)$$

where k_i is the partial packing coefficient of the ith atom, ΔV_i the increment of the van der Waals volume of the ith atom, and V the total volume of the given body.

When account is taken of Eqn. (8), Eqn. (16) becomes

$$\frac{T_g}{T_m} = \left[\frac{\sum_i \Delta V_i}{\sum_i \delta_i \Delta V_i} - A \right]^{-1}, \quad (18)$$

where

$$A = k_{g,a}/(k_{0,a} - k_{g,a}) = \text{const}, \quad (19)$$

$$\delta_i = (k_{0,a} - k_{g,a})/k_i. \quad (20)$$

Table 9. The parameters δ_i and γ_i for various atoms and types of intermolecular interaction.

Atom or type of interaction	Designation	δ_i	γ_i, Å³
Silicon	δ_{Si}	0.0840	—
Carbon	δ_C	0.08685	—
Hydrogen	δ_H	0.0740	—
Oxygen in main chain	$\delta_{O,m}$	0.0621	—
Oxygen in side chain	$\delta_{O,s}$	0.0963	—
Nitrogen in main chain	$\delta_{N,m}$	−0.0212	—
Dipole-dipole interaction	γ_d	—	−0.0727
Hydrogen bond	γ_h	—	−0.0188

It follows from the computational scheme described that fusion of a crystalline polymer and the transition from the vitreous state to the viscoelastic state occur when the same molecular packing coefficient $k_{g,a} = k_{m,a}$, which is equal to 2/3 for all polymers, is attained. Consequently, the fusion of crystalline and the softening of amorphous polymers of any chemical structure require a definite fraction of the free volume, equal to 0.333. The difference between T_g and T_m (or their ratio T_g/T_m) will then be determined by the difference between (or the ratio) of the packing coefficients of the amorphous (k_{am}) and crystalline (k_{cr}) polymers, which has been demonstrated independently in another study [4].

In order to determine the parameters δ_i,[19] the excess system of equations derived from Eqn.(18) was solved by least squares. The results showed that a satisfactory calculation of T_g/T_m (or T_m) requires the introduction of the parameters listed in Table 9. These parameters take into account the influence of the type of atom on the melting point. Knowing the parameters δ_i, it is possible to calculate T_g/T_m (or T_m) for a large number of polymers. The results of the analysis showed that the calculated and experimental values of T_m agree as a rule to within 2–3% and that the error reaches a higher value only in a few instances (see Table 10).

Table 10. The melting points T_m of polymers (T_g obtained from dilatometric data).

Polymer	$\sum_i \Delta V_i$, Å³	T_g, K	T_m, K	
			calc.	expt.
Polypropylene	51.7	263	449	449
Polystyrene	109.9	378	544	513; 523
Polybut-1-ene	68.8	249	412	405; 398
Poly-4-methylpent-1-ene	103.4	302	515	523; 508
Poly-α-vinylnaphthalene	155.4	453	626	633
Poly(ethylene adipate)	159.1	223	342	323
Nylon 6,6	232.3	351	541	539
Nylon 6,10	300.7	323	495	499; 488
Nylon 6	116.15	323; 348	498	488; 499
Nylon 11	201.65	319	467	467; 455; 448
Poly(isobutyl vinyl ether)	113	246	396	438
Poly(ethylene oxide)	43.8	206	348	339
Poly(propylene oxide)	61.3	198	323	340; 348
Poly(styrene oxide)	119.5	310	442	422
Poly(tetramethylene oxide)	77.8	194	312	309
Poly(methyl methacrylate)	97.05	318	466	433
Poly(tetramethylene adipate)	193.3	205	314	332
Poly(trimethylene adipate)	176.2	214	315	311
Poly(ethyl vinyl ether)	78.4	254	387	359
Poly(methyl vinyl ether)	61.0	260	399	417
Polydimethylsiloxane	72.09	150	234	234

IV. OPTICAL PROPERTIES

Among the parameters of the optical properties of polymers, the refractive index n is most important. The relation

$$\frac{n^2-1}{n^2+2}\cdot\frac{N_A\sum_i \Delta V_i}{k_{av}} = R = \sum_i m_i A_i r_i, \qquad (21)$$

where k_{av} is the average molecular packing coefficient (for monolithic block materials, $k_{av} = 0.681$ and for films, $k_{av} = 0.695$), R the molar refraction, m_i the number of atoms of the ith kind in the repeating unit, r_i the specific refraction of atoms of the ith kind, and A_i the atomic weight, was derived[20]. It is based on the Lorenz–Lorentz equation and Eqn.(2). The relevant investigation[21] demonstrated a satisfactory agreement between the calculated and experimental refractive indices for aromatic systems (Table 11).

Another important parameter is the coefficient of optical sensitivity to stress C_σ, which is defined as the proportionality coefficient between the double refraction Δn and the stress σ responsible for it:

$$\Delta n = C_\sigma \sigma . \qquad (22)$$

The coefficient C_σ is extremely sensitive to the chemical structure of the polymer. Heat resistant card polymers are particularly interesting in this respect. It was found[21] that the optical sensitivity of such systems is an order of magnitude higher than the optical sensitivity of all the polymers investigated previously. Table 12 lists the optico-mechanical properties of many polymers.

Table 11. The refractive indices of certain aromatic polymers.

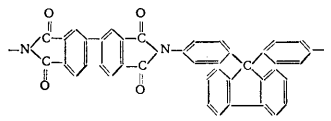
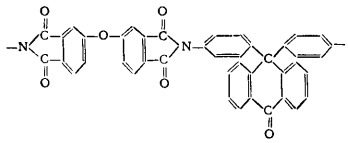
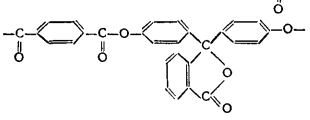
Structure of repeating unit	Density (calc.), g cm⁻³	n	
		calc.	expt.
	1.314	1.491	1.493
	1.346	1.553	1.552
	1.326	1.516	1.512

Table 12. The optico-mechanical properties of polymers (E is the modulus of elasticity and T_s the softening temperature).

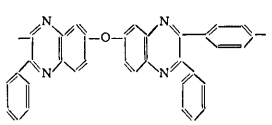
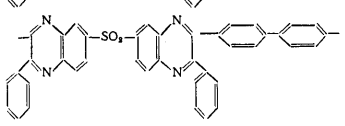
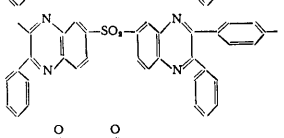
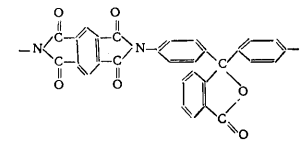
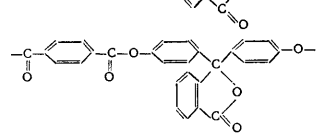
No.	Structure of repeating unit	T_p, °C	$10^{-4}E$, kgf cm⁻²	$10^7 C_\sigma$, cm² kgf⁻¹		$N_A \cdot \sum_i \Delta V_i$, cm³ mole⁻¹
				expt.	calc.	
1		—	1.9	161.1	156.9	276
2		—	1.45	152.0	142.8	334
3		—	1.1	150.1	150.8	288
4		515	3.1	111.2	110.7	245
5		320	2.9	92.7	85.5	234

Table 12 (continued).

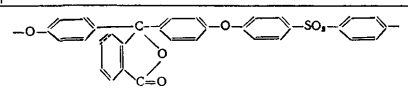
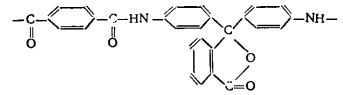
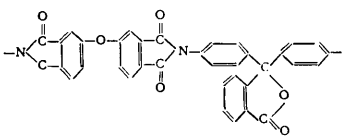
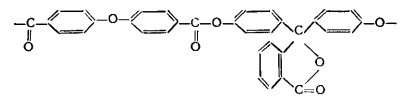
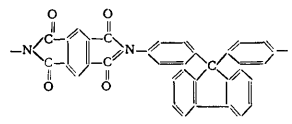
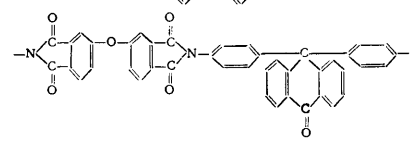
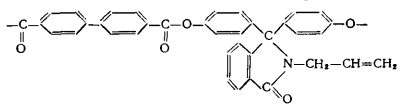
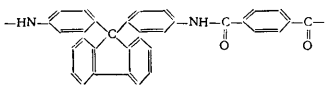
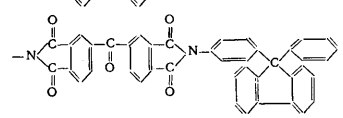
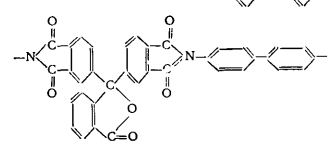
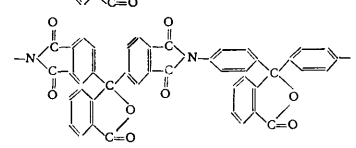
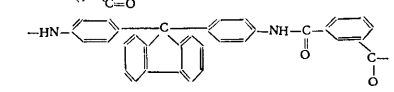
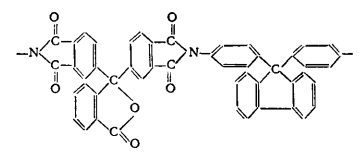
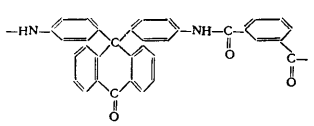
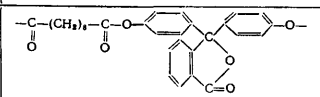
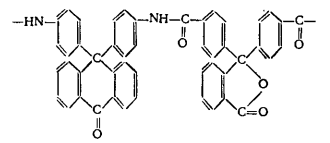
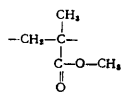
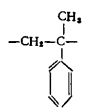
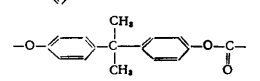
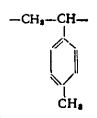
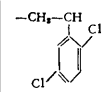
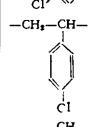
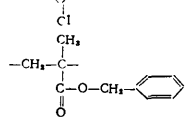
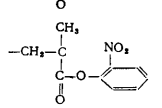
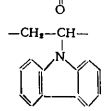
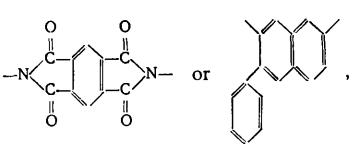
No.	Structure of repeating unit	T_p, °C	$10^{-4}E$, kgf cm^{-2}	$10^7 C_\sigma$, cm^2 kgf^{-1} expt.	$10^7 C_\sigma$, cm^2 kgf^{-1} calc.	$N_A \cdot \sum \Delta V_i$, cm^3 mole^{-1}
6		—	1.63	72.8	72.0	262
7		—	1.25	90.4	87.0	237
8		350	2.4	88.9	91.8	296
9		320	2.45	89.4	94.0	285.4
10		450	3.67	86.6	75.0	319.3
11		350—400	4.3	82.5	82.1	335.4
12		250—280	1.57	82.1	73.6	310.0
13		—	1.26	77.4	84.0	266.4
14		350—400	3.75	75.3	75.6	330.1
15		500	2.7	73.0	76.2	290.8
16		450	3.52	67.2	63.6	355.7
17		—	1.25	62.0	59.0	266.4
18		520	1.93	56.2	63.6	384,2
19		—	1.28	61.5	51,0	277,3

Table 12 (continued).

No.	Structure of repeating unit	T_p, °C	$10^{-4}E$, kgf cm^{-2}	$10^7 C_\sigma$, cm^2 kgf^{-1} expt.	$10^7 C_\sigma$, cm^2 kgf^{-1} calc.	$N_A \cdot \sum \Delta V_i$, cm^3 mole^{-1}
20		100	1.50	55.8	58,7	271.5
21		—	1.40	53.0	60,0	387,6
22		80—90	—	10,7	16.9	66.0
23		135	2.10	—3.27	—3,99	58.5
24		—	3.50	—2.04	—9.6	76.6
25		150	1.40	111.0	115,5	144.3
26		—	—	15.7	21.5	76,2
27		—	3.52	7,3	13,2	82.6
28		—	2.65	22,9	15.3	74.4
29		—	—	24.5	22.0	103.9
30		—	—	22.4	20.0	104.6
31		—	—	57.5	57.8	111.7

The elastic mechanical behaviour of vitreous polymers, characterised by the modulus of elasticity E and the glass point T_g, can be influenced by two factors—the rigidity of the chains and the intermolecular interaction energy. If the polymer includes groups of the type



which lead to an increase of the skeletal and kinetic rigidity, it has as a rule a high modulus of elasticity.

The high optical sensitivity of these polymers is due to their structure—the presence of a large number of condensed rings, which are characterised by a considerable anisotropy of polarisability. Compounds saturated by nitrogen and sulphur atoms and aromatic rings have the highest values of C_σ, as can be seen from Table 12.

The optical sensitivity can also be greatly influenced by the type of substitution in the aromatic ring contained in the main chain. Thus a polymer where the aromatic ring in the main chain is substituted in the *p*-position has a higher optical sensitivity than a polymer where the ring is substituted in the *m*-position (see polymers 13 and 17 in Table 12).

The presence of a large number of polar groups leads to a decrease of optical sensitivity. For a given series of polymers, this behaviour is observed in relation to the C=O group. Having a high negative anisotropy of polarisability, it reduces the overall positive effect. The fact that the C=O group is a carrier of the negative effect has also been noted by Bazhenov et al.[21]

The data compiled in Table 12 show that there is a clearly defined relation between the structure of polymers and their optico-mechanical properties, which can be expressed in quantitative terms[21]. It has been shown[21] that the variation of C_σ with the parameters of the structure of the polymer chain can be determined by means of an additive scheme analogous to that used previously[11] to estimate the glass points.

Table 13. The increment C_i for various atoms and types of intermolecular interactions.

Atom or type of interaction	Designation	Value
Carbon	C_C	−2.0492
Hydrogen	C_H	−0.5227
Oxygen in main chain	$C_{O,\,m}$	3.198
Oxygen in side group	$C_{O,\,s}$	−0.7568
Nitrogen in main chain	$C_{N,\,m}$	7.175
Nitrogen in side group	$C_{N,\,s}$	1.303
Chlorine	C_{Cl}	−3.476
Sulphur	C_S	−0.790
Dipole-dipole interaction*	C_d	−2.512
Hydrogen bond in aromatic polyamides	C_h	−6.21
Symmetry coefficient**	C_n	6.791
Universal parameter	Π	0.3544

*The coefficient C_d is introduced for each polar group of any type; if there are two identical polar groups attached to the same atom, they are counted as one group. When the benzene ring is present in the substituent, the increment $C_{Ph} = -1.70$ is introduced instead of C_d.
**The symmetry coefficient is introduced if all the aromatic rings in the main chain are substituted in the *p*-position.

Interpretation of a large amount of experimental data led[21] to a relation between C_σ and the parameters of the chemical structure of the repeating unit of the polymer:

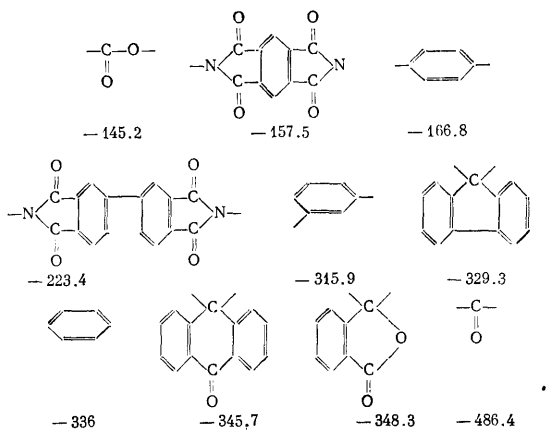
$$C_\sigma = \frac{\sum_i C_i}{N_A \sum_i \Delta V_i} + \Pi, \qquad (23)$$

where C_i are increments characterising the contribution of each atom and type of intermolecular interaction to the coefficient of optical sensitivity (see Table 13).

ΣV_i is the van der Waals volume of the repeating unit, consisting of the volumes of all the atoms in this unit, and $\Pi = 0.3544 \times 10^{-4}$ cm^2 kg^{-1} is a universal parameter.

In order to determine the increments C_i, an excess system of equations, derived on the basis of Eqn.(23) for the polymers listed in Table 12, was solved[21] by the method of least squares using the matrix theory. The calculation showed[21] that, for an adequate assessment of the influence of various atoms on C_σ, it is necessary to know at least 11 increments, which are listed in Table 13.

A test of the validity of Eqn.(23) showed that the calculated values of C_σ agree fairly satisfactorily with experimental data (Table 12). A separate calculation demonstrated that $C_{ph} = -1.700 \times 10^{-4}$ for a benzene ring in the side chain. Knowing the numerical values of C_i, which are listed in Table 13, it is possible to calculate the values of C_σ for polymers incorporating the corresponding atoms. A quantitative estimate of the contribution of each group of atoms to the coefficient of optical sensitivity is also possible on the basis of Eqn.(23). This contribution is characterised by the quantity $\sum_i C_i / N_A \sum_i \Delta V_i$, and, since this ratio is negative, the highest value of C_σ corresponds to the smallest absolute value of $\sum_i C_i / N_A \sum_i \Delta V_i$. Individual groups can be arranged in the following sequence in terms of the contribution of the ratio $\sum_i C_i / N_A \sum_i \Delta V_i$ to the coefficient of optical sensitivity (the ratios have been multiplied by 10^7):



Thus the computational scheme described for the determination of the coefficient of optical sensitivity makes it possible to estimate the expected optical sensitivity of the polymer and has a definite practical value for the synthesis of polymers with specified properties. It is also noteworthy that the high optical sensitivity of thermostable polymers can be of great practical value when the latter are used as models in a polarisation-optical study on stresses. The disadvantages of the usual polymeric materials are, on the one hand, the occurrence of distinct relaxation processes following the application of a mechanical load, and, on the other hand, a low optical sensitivity. In order to obtain a distinct pattern of the distribution of stresses in a given structure, it is necessary to employ fairly high stresses, which are undesirable owing to the intense relaxation processes (creep and relaxation of the stress). The availability of materials with an extremely high coefficient of optical sensitivity

permits their use with comparatively small loads, for which the relaxation processes are weak and Hooke's law virtually holds.

V. INTERMOLECULAR INTERACTION ENERGY AND SOLUBILITY

One of the principal parameters of the extent of intermolecular interaction in liquids is the density of cohesion energy, which is numerically equal to the potential energy E/V of 1 cm^3 of the substance. For a liquid, this parameter is usually estimated from its heat of evaporation ΔH_v and is calculated by the formula

$$\delta^2 = E/V = (\Delta H_v - RT)/V \ , \qquad (24)$$

where δ is the Hildebrand solubility parameter and V the molar volume of the liquid.

ΔH_v can be determined experimentally only for low-molecular-weight substances capable of evaporating without decomposition; naturally, this cannot be done for polymers. For this reason, many investigators [22-25] have attempted to calculate δ by resolving E and V into their constituent increments; other methods have also been proposed. However, evidently such resolution is not legitimate, since the volumes occupied by the same atom in different molecules are different owing to the differences between the molecular packing coefficients of liquids. This applies also to the cohesion energy E.

It has been shown [26] that the calculation of the increments of the cohesion energy density, when the latter is referred to the van der Waals (intrinsic) volume of the atoms and not to the molar volume, is physically justified in this case. For this purpose, Eqn. (24) is written [26] in the form

$$\delta^2 = \frac{Ek}{N_A \sum_i \Delta V_i} = \frac{E^*}{N_A \sum_i \Delta V_i} \ , \qquad (25)$$

where k is the molecular packing coefficient of the liquid and $\sum_i \Delta V_i$ the van der Waals volume of the molecule, consisting of the van der Waals volumes of the atoms ΔV_i.

Table 14. The values of ΔE_i^* for each atom and type of intermolecular interaction.

Atom	Designation	ΔE_i^* kcal/mole	Interaction	Designation	ΔE_i^* kcal/mole
Carbon	ΔE_C^*	550.67	dipole-dipole	ΔE_d^*	1623
Hydrogen	ΔE_H^*	47.71	dipole-dipole in dipolar aprotic solvents of the amide type	$\Delta E_{a,N}^*$	1623
Oxygen	ΔE_O^*	142.6	dipole-dipole in solvents of the dimethyl sulphoxide type	$\Delta E_{a,S}^*$	2600
Nitrogen	ΔE_N^*	1205	hydrogen bond	ΔE_h^*	3929
Fluorine	ΔE_F^*	24.2	aromatic ring (skeleton)	ΔE_{Ph}^*	713
Sulphur	ΔE_S^*	1750	double bond	$\Delta E_{\neq}^*$	−323

The quantity $E^* = Ek$ is in essence the molar cohesion energy of the liquid decreased by a factor equal to the factor by which the intrinsic molar volume of the molecule is smaller than the true molar volume. The quantity E^*, called the effective molar cohesion energy, has been expressed [26] as $E^* = \sum_i \Delta E_i^*$, where ΔE_i^* is the contribution of each atom and type of intermolecular interaction to E^*. Then

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \ . \qquad (26)$$

In order to calculate the values of ΔE_i^*, an excess system of equations was derived [26] on the basis of Eqn. (26) and was solved by least squares. The results show that a sufficiently accurate calculation of the solubility parameters δ requires the introduction of the increments ΔE_i^* listed in Table 14. Knowing ΔE_i^* and ΔV_i, it is possible to calculate the values of δ for organic liquids having different chemical structures. Table 15 presents as an example the calculated and experimental values of δ for many organic liquids, which are the same to a high degree of accuracy.

Table 15. The solubility parameters for solvents and polymers.

Name	$\sum_i \Delta E_i^*$, cal mole^{-1}	$N_A \sum_i \Delta V_i$, cm^3 mole^{-1}	δ, cal$^{1/2}$ cm$^{-3/2}$	
			calc.	expt.
Cyclohexane	3876	61.8	7.92	8.2
n-Octane	5264	90.1	7.6	7.55
Benzene	4303	53.1	9.0	9.15
Toluene	4949	63.3	8.8	8.9
Styrene	5177	69.8	8.61	8.66
Perfluoro-n-pentane	3044	96.4	5.6	5.5
Perfluorocyclohexane	3578	99.4	6.01	6.0
Glycol	9532	36.7	16.1	15.7
Methanol	4814	22.0	14.8	14.5
1-Propanol	6106	42.8	11.9	11.9
Acetic acid	5307	33.5	12.6	12.6
Ethyl formate	3847	45.1	9.2	9.4
Ethyl acetate	4493	55.6	9.0	9.1
Ethyl propionate	5139	65.9	8.8	8.9
Methyl acrylate	4074	52.8	8.8	8.9
Methyl methacrylate	4720	63.3	8.6	8.7
Acetone	3704	39.5	9.7	10.0
Acetamide	9984	35.8	16.6	16.7
Dimethylformamide	6808	46.5	11.9	12.1
Acrylonitrile	4084	37.4	10.7	10.45
Dimethyl sulphide	3183	39.3	8.9	9.0
Diethyl sulphone	10266	65.7	12.7	12.5
Poly(methyl methacrylate)	5043	58.5	9.3	9.1; 9.5 9.4
Poly(ethyl methacrylate)	5689	69.0	9.1	8.95
Poly(n-propyl methacrylate)	6335	79.3	8.9	—
Poly(n-butyl methacrylate)	6981	89.6	8.8	—
Poly(methyl methacrylate)	4397	48.2	9.55	10.1
Poly(ethyl acrylate)	5043	58.5	9.3	9.4
Polystyrene	5500	66.0	9.1	9.1; 8.6 8.7
Polyisobutylene	2584	41.6	7.9	7.85; 7.8 8.05
Polyacrylonitrile	4623	32.6	11.9	—
Poly(ethylene terephthalate)	10418	102.4	10.1	—
Nylon 6,6	18210	139.2	11.4	—

Fig. 6 illustrates the theoretical variation of δ with the [square root of the] ratio $\sum_i \Delta E_i^* / N_A \sum_i \Delta V_i$, on which the experimental points fit satisfactorily.

All the considerations described above permit the application of this method to the calculation of the cohesion energy density of polymers. Table 15 shows that the calculated [26] values of δ for many polymers agree with the available experimental data [27]. However, one should note that the experimental methods employed are not sufficiently accurate and the calculated values of δ may therefore prove to be more reliable.

Since the increments ΔE_i^* and ΔV_i have been determined (see above) for almost all atoms and groups in polymers of all structures, the proposed method can be used to calculate the values of δ for virtually any polymer, which is very important for the estimation of their solubilities and compatibilities with plasticisers and with one another.

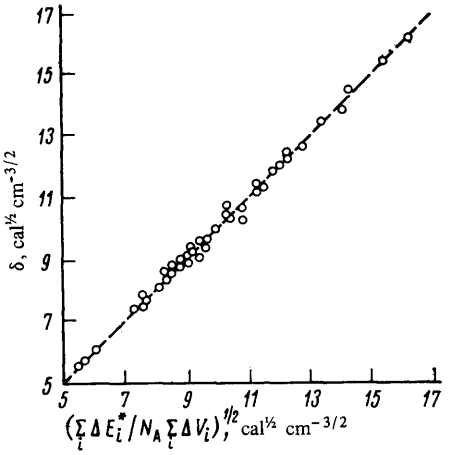


Figure 6. Variation of δ with [the square root of] the ratio $\sum_i \Delta E_i^* / N_A \sum_i \Delta V_i$ for low-molecular-weight liquids.

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