

INFLUENCE OF CHEMICAL STRUCTURE ON THE PROPERTIES OF POLYMERS

A. A. ASKADSKII

Institute of Element-organic Compounds of Acad. of Sciences USSR, Vavilov's street B-312, Moscow, USSR

Abstract—The influence of chemical structure of the amorphous polymers of different classes on the physical properties (density, coefficient of thermal expansion, glass transition temperature, refractive index, optical-sensitivity index, solubility parameter) has been studied. Relations enabling the calculation of these properties exclusively on the basis of the chemical structure of the repeating unit are proposed.

At present the problem of synthesis of polymers with desired properties has become more acute due to a greatly increased range of chemical compounds involved in polymerization and polycondensation processes. Among these properties are the glass transition temperature, the density and the coefficient of thermal expansion, the refractive index, etc. Of special importance is the problem of polymer solubility, i.e. the prediction of solubility of the polymer in a particular solvent. The aforesaid properties of polymers are the most important, and they largely determine all other properties. It is shown in this paper that all the above-mentioned characteristics can be determined prior to polymer synthesis exclusively on the basis of the chemical structure of the repeating unit.

We will first discuss the problem of the packing of the macromolecules in the monolithic polymers and then pass to the calculation of their density.

1. PACKING OF MACROMOLECULES AND DENSITY OF POLYMERS

The coefficient of packing k representing the ratio of the van der Waals volume of atoms and atom groups included in the molecule to the true volume determined from the experimental data is taken as the measure of density.¹⁻³ In calculations of the coefficient of packing of polymers we will proceed from the molar volumes of the repeating unit. Then

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

where ΔV_i are the increments of the van der Waals volumes of the atoms of the repeating unit of the polymer, M : the molecular weight of the repeating unit, d : the polymer density, and N_A : the Avogadro number. For the calculation of the coefficient of packing, k , the volume increments, ΔV_i , were calculated for a large number of atoms valency-connected with a variety of atoms.

Since we may further need the ΔV_i values for calculating not only the density but also all the other polymer characteristics, they are listed in detail in Table 1.

Independent of the chemical structure of the polymer, the coefficients of packing of amorphous monolithic polymers proved to be approximately the same and equal ~ 0.681 at $T = 20^\circ\text{C}$. In order to illustrate this experimental fact, Fig. 1 shows the dependence of the density of structurally different polymers on $M/N_A \sum_i \Delta V_i$. It is clear

that this is a linear relationship, and that the experimental d values fit it well. The slope of the line represents the coefficient of packing, $k = 0.681$. Because the k value in the first approximation represents the constant of the amorphous monolithic polymers, the polymer density can be calculated from the chemical structure of the repeating unit alone. For this purpose we rewrite the relation (1) as follows:

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

where $k_{av} = 0.681$.

Our calculations showed that the density of an amorphous polymer could be calculated, as a rule, within 0.01 g/cm^3 .

It should be noted at once, that the coefficients of packing of crystalline polymers are dependent on the chemical structure of polymers, and their values lie in a broad range.

In this study we calculate the coefficients of packing of the crystalline polymers using the crystallographic values of density defined from the X-ray analysis data proceeding from the volume of the elementary cell and the mass of the atoms included in it. The calculations were made for 80 polymeric systems with very different chemical structures. The crystalline polymers were found to have a rather broad curve of distribution of the coefficients of packing (Fig. 2). Figure 2 shows a similar curve for the amorphous polymers. It is clearly seen that the curve of k distribution for amorphous systems is rather narrow.

Let us now analyse the temperature dependence of the coefficient of packing. This was calculated from the

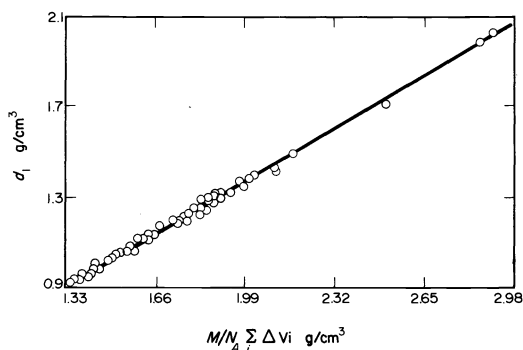


Fig. 1. Dependence of the density of amorphous and amorphous-crystalline polymers of the ratio $M/N_A \sum_i \Delta V_i$.

Table 1. Van-der-Waals volumes

Group	ΔV_i (\AA^3)	Group	ΔV_i (\AA^3)	Group	ΔV_i (\AA^3)	Group	ΔV_i (\AA^3)
	5-0		5-8		4-7		7-0
	4-7		5-85		14-7		7-2
	4-5		14-1		15-9		9-1
	4-2		15-9		10-0		3-5
	4-0		12-3		9-4		19-5
	8-4		26-3		9-6		14-7
	14-7		20-2		10-1		18-4
	11-1		2-7		7-1		9-6
	17-1		3-4		8-2		12-9
	23-5		2-0		13-1		6-6
	8-3		2-1		9-0		14-3
	15-7		8-3		17-1		8-1
	11-65		0-9		10-0		5-8
	10-2		8-6		27-6		15-8
	7-25		5-6		16-0		10-65
			12-2		0-49		9-0

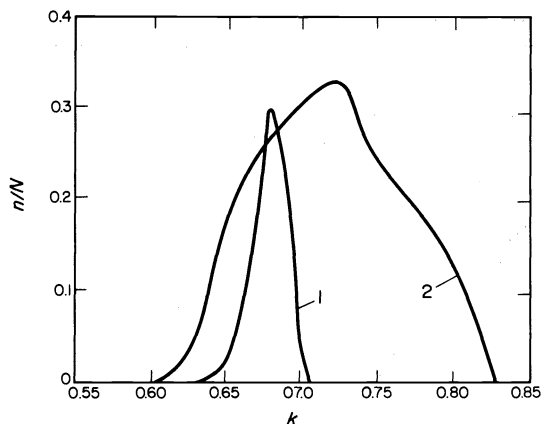


Fig. 2. Curves of distribution of packing coefficient for amorphous (1) and crystalline (2) polymers.

formulae (3) and (4) which were directly derived from eqn (1):

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

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

where V_g is the specific volume of the polymer at glass transition temperature, T_g ; α_G and α_L are the coefficients of thermal expansion of the polymer before and after glass transition temperature, respectively. Calculations from the formulas (3) and (4) show that the temperature dependences of the coefficient of packing for polymers have a form given in Fig. 3. A noteworthy property of this temperature dependence is that the coefficient of packing, in the first approximation, is the same for all polymers at any temperature below the glass transition temperature. In the second, more accurate approximation, the coefficient of packing is the same for each polymer at its glass transition temperature and equals $k_g = 0.667$.

At low temperatures ($T_0 \approx 6^\circ\text{K}$) the coefficients of packing of polymers are also approximately the same and, as shown by our calculations, are equal to $k_0 = 0.731$.

2. CALCULATIONS OF THE GLASS TRANSITION TEMPERATURE OF POLYMERS

Let us now derive a calculation scheme for the

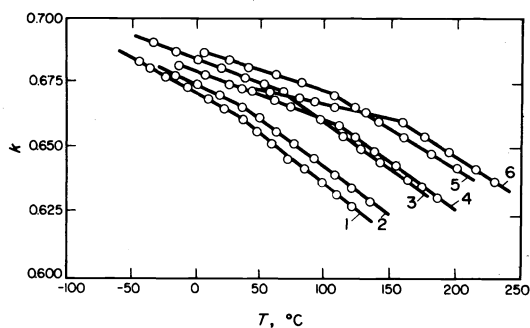


Fig. 3. Temperature dependence of coefficient of packing for the polymers: 1-poly(*n*-butyl methacrylate), 2-poly(*n*-propyl methacrylate), 3-poly(ethyl methacrylate), 4-polystyrene, 5-poly(methyl methacrylate), 6-polycarbonate of 4,4-diphenylpropane.

determination of the glass transition temperature. According to eqn (1), $k_g/k_0 = V_0/V_g$, where V_0 is the specific volume of the polymer at T_0 . Taking this relation into consideration, as well as the equation $V_g = V_0[1 + \alpha_G(T_g - T_0)] \approx V_0(1 + \alpha_G T_g)$ we can write:

$$1 + \alpha_G T_g = \frac{k_0}{k_g} \quad (5)$$

or

$$T_g = \frac{k_0/k_g - 1}{\alpha_G} \quad (6)$$

Due to the additivity of the volume, the coefficient of thermal expansion, α_G , can naturally be considered as

$$\alpha_G = \frac{\sum_i \alpha_i \Delta V_i}{\sum_i \Delta V_i} \quad (7)$$

where α_i is partial coefficient of thermal expansion of the i -atom or the atom group of the repeating unit of the polymer, ΔV_i —the volume increment of the i -atom or the atom group.

The starting equation relating T_g to the structure of the repeating unit is obtained by substitution of (6) for (7):

$$T_g = \frac{\sum_i \Delta V_i}{\sum_i K_i \Delta V_i} \quad (8)$$

where

$$K_i = \alpha_i / (k_0/k_g - 1). \quad (9)$$

The values of K_i characteristic of each atom and each type of intermolecular interaction were determined by means of statistical treatment of the experimental data by the method of "least squares". These data are given in Table 2.

Let us now relate the coefficients α_i of the eqn (9) to the parameters of intermolecular interaction (the intermolecular bond energy and the distance between the interacting atoms). It is known that the coefficient of thermal expansion can be represented as follows:

$$\alpha_i = \frac{3R\beta_i}{\gamma_i^2 \tau_{0i}} \quad (10)$$

where β_i is the coefficient of anharmonism, $\beta_i = (1/2)(\partial^3 \varphi / \partial \tau^3)|_{\tau_{0i}}$; γ_i is the harmonic force constant, $\gamma_i = (\partial^2 \varphi / \partial \tau^2)|_{\tau_{0i}}$; τ_{0i} is the equilibrium distance between the given i -atom and the adjacent atoms, φ is the interaction potential of the i -atom with the adjacent.

When using Lennard-Jones' potential in determination of β_i and γ_i ,

$$\varphi(\tau) = D \left[\left(\frac{\tau_0}{\tau} \right)^{12} - 2 \left(\frac{\tau_0}{\tau} \right)^6 \right]$$

where D is the bond energy (the depth of the potential well), τ_0 —the equilibrium distance between the atoms,

$$\gamma_i = \frac{72D_i}{\tau_{0i}^2}; \quad \beta_i = \frac{666D_i}{\tau_{0i}^3}; \quad (11)$$

and

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

Table 2. K_i , α_i , and D_i constants for different atoms and interactions

Atom and interaction type	Symbol	$K_i \cdot 10^3$ (deg ⁻¹)	$\alpha_i \cdot 10^3$ (deg ⁻¹)	D_i (cal/mol)
C	K_C	0.021	—	—
O (backbone)	$K_{O,b}$	22.95	2.21	0.39
O (side group)	$K_{O,s}$	7.03	0.68	1.28
H	K_H	19.98	1.92	0.45
N (backbone)	$K_{N,b}$	8.62	0.83	1.04
N (side group)	$K_{N,s}$	6.35	0.61	1.43
Cl	K_{Cl}	4.01	0.39	2.25
S (backbone)	$K_{S,b}$	3.53	0.34	2.56
Dipole-dipole interaction	K_d	-55.73		
Hydrogen bond:				
aliphatic polyamides	K'_h	-206.78		
all other cases	K_h	-139.6		
Coefficient of symmetry†	K_p	-90.5		
Coefficient for polydienes	K_w	92.22		

†Used when all aromatic main-chain cycles are substituted in p-position.

An evaluation of the D_i value for bonds of various types shows that the bond energy values resulted from the handling of the experimental data conform to the energies of intermolecular interaction (rather than to chemical bonds).

Calculations from the formula (12) shows that the averaged bond energies, D_b , have the values given in Table 2.

As, according to the data,^{5,6} the values of bond energies, D_{0i} , for different atoms given in Table 2 are several times as low as the found D_i values, it should be written

$$D_i = L_i D_{0i} \quad (13)$$

where L_i is the coordination number.

Then the starting eqn (8) can be written as

$$1/T_g = 4.55R \left\langle \frac{1}{LD_0} \right\rangle \quad (14)$$

where

$$\left\langle \frac{1}{LD_0} \right\rangle = \frac{\sum_i \frac{1}{L_i D_{0i}} \cdot \Delta V_i}{\sum_i \Delta V_i}$$

The relation (14) for calculating T_g has a form similar to that for definition of the Kuri temperature in ferromagnetics.

For calculating the glass transition temperature of polymers, relation (8) is very useful. Checking of eqn (8) for applicability showed that the calculated and experimental glass transition temperatures agree well for a great number of the investigated polymers with very different chemical structures. Figure 4 shows the dependence of T_g on $\sum_i \Delta V_i / \sum_i K_i \Delta V_i$ for 80 polymers. In Fig. 4 a theoretical line adhering to eqn (8) is drawn, while the points correspond to the experimental values of T_g . It is seen that eqn (8) is valid over a very broad temperature interval. Thus, it is possible to calculate the glass transition temperature prior to synthesis independent of the class of polymer.

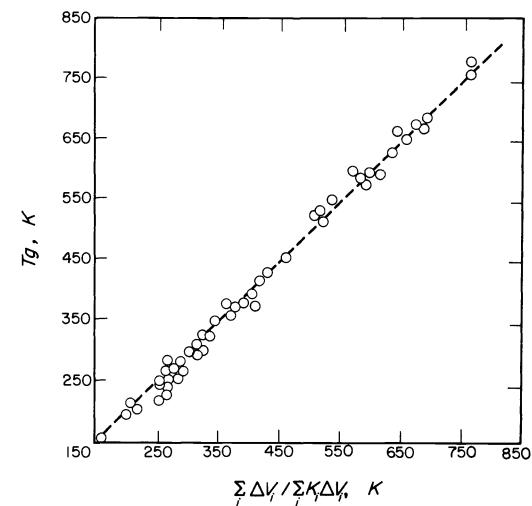


Fig. 4. Dependence of T_g on the ratio $\sum_i \Delta V_i / \sum_i K_i \Delta V_i$.

dence of T_g on $\sum_i \Delta V_i / \sum_i K_i \Delta V_i$ for 80 polymers. In Fig. 4 a theoretical line adhering to eqn (8) is drawn, while the points correspond to the experimental values of T_g . It is seen that eqn (8) is valid over a very broad temperature interval. Thus, it is possible to calculate the glass transition temperature prior to synthesis independent of the class of polymer.

The coefficient of thermal expansion, α_G , can simultaneously be calculated for an amorphous solid polymer from eqn (7). For a number of polymers there is a reasonable agreement between the calculated and experimental data (Table 3).

Table 3. The coefficients of thermal expansion (α_G) for some polymers

Polymer	$\sum_i \Delta V_i$ (Å ³)	$\sum_i \alpha_i \Delta V_i \cdot 10^4$ (Å ³ /grad)	$\alpha_G \cdot 10^4$ exp. (deg ⁻¹)	$\alpha_G \cdot 10^4$ calc. (deg ⁻¹)
Poly(methyl methacrylate)	97.0	208.5	2.15	2.73
Poly(ethyl methacrylate)	114.4	314.6	2.75	2.99
Poly(<i>n</i> -propyl methacrylate)	131.5	414.2	3.15	3.19
Poly(<i>n</i> -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

Let us now ascertain the effect of changes in the density of packing of the macromolecules on the melting point of the polymer when passing from the amorphous to crystalline state. It should be noted preliminary that, for many polymeric systems, according to the Beaman data,⁷ the relation between the glass transition temperature, T_g , and the melting point, T_m , is approximately constant ($T_g/T_m \approx 0.67$). But a detailed analysis shows⁸ that this common tendency is not always fulfilled. The relation $\beta = T_g/T_m$ can take on very different values (from 0.25 to 0.97).

Our calculations showed that the β value depends on the relation of the coefficients of packing for completely amorphous and fully crystallized polymers, k_{am}/k_{cr} . This dependence is shown in Fig. 5. It can be seen that with an increase in k_{am}/k_{cr} the β value increases approximately linearly. Consequently, the relation between the glass transition temperature and the melting point depends on the difference in densities of packing of the macromolecules in the amorphous and crystalline state. A higher density of packing on polymer crystallization results in a more profound difference between the melting points and glass transition temperature.

3. OPTICAL PROPERTIES

Among the parameters of optical properties the refractive index, n , is the most important. For calculation of this characteristic we derived a relationship based on the Lorenz-Lorentz equation (2)

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{N_A \sum_i \Delta V_i}{k_{av}} = R = \sum_i m_i A_i \tau_i \quad (15)$$

where k_{av} is the mean coefficient of molecular packing (for monolithic polymers $k_{av} = 0.681$, for films $k_{av} = 0.695$), R —the molar refraction, m_i —the number of the i -type atoms in the repeating unit, τ_i —the specific refraction of the i -type atoms, A_i —the atomic weight.

Our investigation pointed to a good agreement of the calculated and experimental values for refractive index exemplified by aromatic systems (Table 4).

Another important parameter of the optical properties of polymers is the optical-sensitivity index, C_σ , which represents the constant of proportionality between the magnitude of birefringence, Δn , and the stress, σ , that gives rise to birefringence:

$$\Delta n = C_\sigma \cdot \sigma. \quad (16)$$

The coefficient C_σ is rather sensitive to the chemical structure of the polymer. Our investigations showed that the optical sensitivity, for instance, of aromatic systems is higher by one order than that of all polymers previously studied. Table 5 gives, as an example, the values of C_σ for various classes of polymers. The high optical sensitivity of aromatic systems results from a great amount of condensed cycles characterized by considerable anisotropy of polarizability. On the basis of a great number of experimental data, we derived a relation between C_σ and the

Table 4. Refractive indices of some aromatic polymers

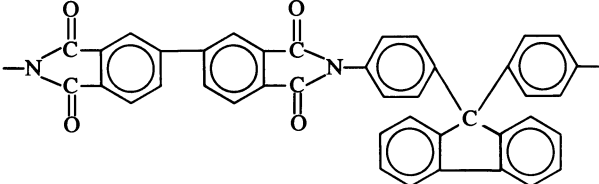
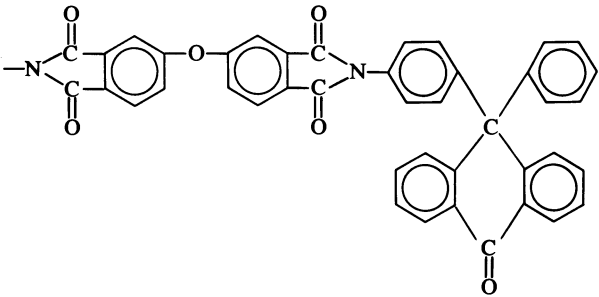
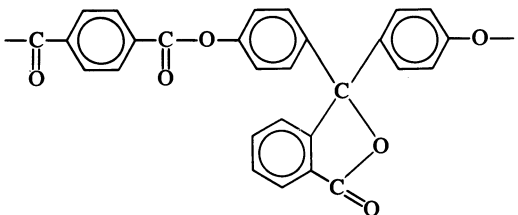
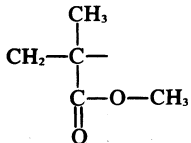
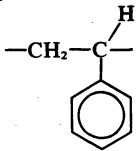
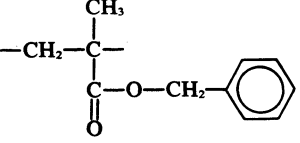
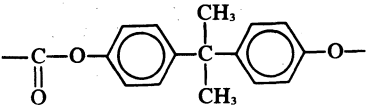
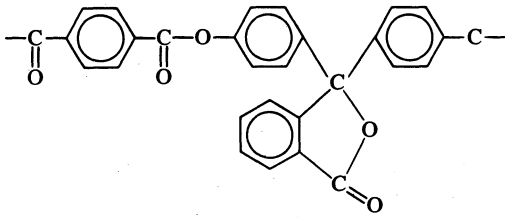
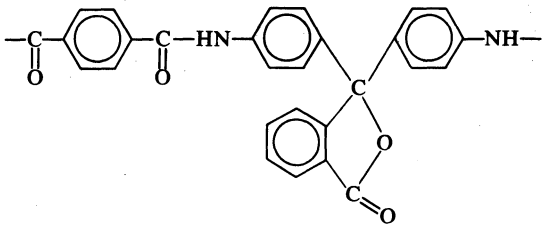
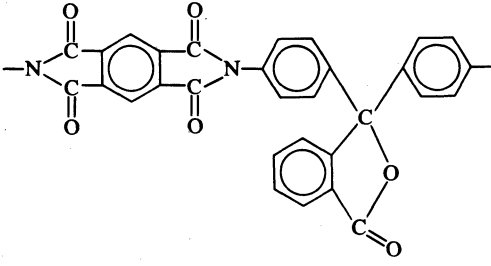
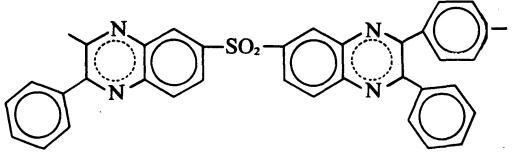
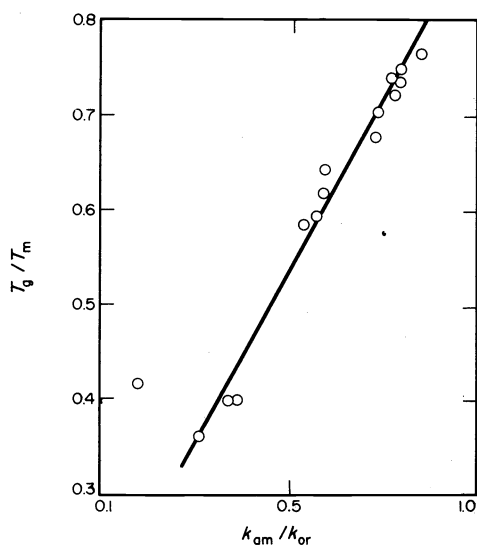
Repeating unit	Calc. density (g/cm ³)	Refractive index	
		Calc.	Exp.
	1.314	1.491	1.493
	1.346	1.553	1.552
	1.326	1.516	1.512

Table 5. Constants for different polymers

Polymer	$NA \sum_i \Delta V_i$ (cm ³ /mol)	$\sum_i C_i$ (cm ² /kg · cm ³ /mol · 10 ⁷)	$C_\sigma \cdot 10^7$ (cm ² /kg calc.)	$C_\sigma \cdot 10^7$ (cm ² /kg exp.)
	58.5	-20.97	-3.99	-3.27
	66.0	-22.27	16.9	10.7
	103.9	-34.54	22.0	24.5
	144.3	-34.47	115.5	111.0
	234.7	-63.11	85.5	92.7
	237.7	-63.56	87.0	90.4
	245.1	-59.73	110.7	111.2
	276.6	-56.2	150.8	150.1

Fig. 5. Dependence of T_g/T_m on k_{am}/k_{er} .

chemical structure of the repeating unit of polymer:

$$C_\sigma = \frac{\sum_i C_i}{N_A \sum_i \Delta V_i} + \Pi \quad (17)$$

where C_i are the increments characterizing the contribution of each atom and the type of intermolecular interaction to the optical-sensitivity index; $N_A \sum_i \Delta V_i$ is the van der Waals volume of the repeating unit, N_A —the Avogadro number, Π —the parameter universal for all polymers.

The C_i values are given in Table 6. Using them the C_σ value can easily be calculated for many polymers. Checking by means of (17) showed good agreement between the calculated and experimental values of C_σ (Table 5).

Table 6. C_i constants for different atoms and interactions

Atom and interaction type	Symbol	$C_i \cdot 10^7$ ($\text{cm}^2/\text{kg} \cdot \text{cal/mol}$)
C	C_C	-2.0492
H	C_H	-0.5227
O (backbone)	$C_{O,b}$	3.198
O (side group)	$C_{O,s}$	-0.7568
N (backbone)	$C_{N,b}$	7.175
N (side group)	$C_{N,s}$	1.303
Cl	C_{Cl}	-3.476
S (backbone)	$C_{S,b}$	-0.790
Dipole-dipole interaction†	C_d	-2.512
Hydrogen bond for aromatic polyamides	C_h	-6.21
Coefficient of symmetry‡	C_σ	6.791
Universal constant	Π	0.3544

†When any atom has two polar groups only one it should be used in calculating. For polystyrene and its derivatives $C_{O=}$ = -1.70.

‡Used when all aromatic main-chain cycles are substituted in p-position.

†Developed together with L. K. Kolmakova, A. A. Tager, G. L. Slonyski and V. V. Korshak.

4. ENERGY OF INTERMOLECULAR INTERACTION AND SOLUBILITY†

The density of cohesive energy equal to the energy of intermolecular interaction of 1 cm^3 of substance, E/V , is one of the most important parameters for evaluating the intermolecular interaction in liquids. This parameter for liquids is determined from the heat of evaporation, ΔH_{ev} , and calculated by the formula

$$\delta^2 = E/V = (\Delta H_{ev} - RT)/V \quad (18)$$

where δ is the Hildebrandt solubility parameter, V —the molar volume of liquid.

The value of ΔH_{ev} can be experimentally determined only for low molecular weight substances capable of evaporation without decomposition, which cannot naturally be obtained for polymers. Some authors⁹⁻¹² have attempted, therefore, to calculate the value of δ by separating the values E and V into component increments; other approaches have also been proposed. It is, however, evident that such a separation would not be correct, because the volume occupied by the same atom in different molecules would vary due to the difference in the coefficient of molecular packing in liquids. The same is valid for the cohesive energy, E .

The calculation of increments of the density of cohesive energy by relating it, not to the molar, but to the van der Waals atom volume, is in this case physically well-grounded. For this purpose, eqn (18) should be rewritten:

$$\delta^2 = \frac{Ek}{N_A \sum_i \Delta V_i} = \frac{E^*}{N_A \sum_i \Delta V_i} \quad (19)$$

where k is the coefficient of molar packing in liquids, $\sum_i \Delta V_i$ —the van der Waals volume of the molecule composed from the van der Waals volumes of the atoms, ΔV_i ; N_A —the Avogadro number. The value $E^* = Ek$ is essentially the molar energy of cohesion of a liquid decreased as low as the van der Waals molar volume of the molecule in respect to the true molar volume. Let us designate the value E^* as the "effective molar energy of cohesion" and represent it as $E^* = \sum_i \Delta E_i^*$, where ΔE_i^* is the contribution of each atom and the type of intermolecular interaction E^* . Then

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \quad (20)$$

Table 7. ΔE_i^* constants for different atoms and interactions

Atom and interaction type	Symbol	ΔE_i^* (cal/mol)
C	ΔE_C^*	550.67
H	ΔE_H^*	47.71
O	ΔE_O^*	142.6
N	ΔE_N^*	1205.0
F	ΔE_F^*	24.2
S	ΔE_S^*	1750.0
Dipole-dipole interaction	ΔE_d^*	1623.2
Dipole-dipole interaction in dipolar aprotic solvents:		
Solvents of DMFA-type	$\Delta E_{d,N}^*$	1623.2
Solvents of DMSO-type	$\Delta E_{d,S}^*$	2600.0
Hydrogen bond	ΔE_h^*	3929.4
Aromatic cycle	ΔE_{ar}^*	713.1
Double bond	ΔE_{db}^*	-323.2

Table 8. Van der Waals volume ($N_A \sum_i \Delta V_i$) and solubility parameters (δ) of solvents and polymers

Solvents or polymers	$\sum_i \Delta E_i^*$ (cal/mol)	$N_A \sum_i \Delta V_i$ (cm ³ /mol)	δ , calc. (cal ^{0.5} /cm ^{1.5})	δ , exp. (cal ^{0.5} /cm ^{1.5})
cyclohexane	3876	61.8	7.9	8.2
<i>n</i> -octane	5264	90.1	7.6	7.55
<i>n</i> -decane	6656	110.7	7.75	7.75
benzene	4303	53.1	9.0	9.15
toluene	4949	63.3	8.8	8.9
styrene	5177	69.8	8.61	8.66
<i>n</i> -perfluoropentane	3044	96.4	5.6	5.5
perfluorocyclohexane	3578	99.4	6.0	6.0
glycol	9532	36.7	16.1	15.7
methanol	4814	22.0	14.8	14.5
<i>n</i> -proanol	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 sulfide	3183	39.3	8.9	9.0
diethyl sulfone	10,266	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(<i>n</i> -propyl methacrylate)	6335	79.3	8.9	
poly(<i>n</i> -butyl methacrylate)	6981	89.6	8.8	
poly(methyl acrylate)	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)	10,418	102.4	10.1	
nylon-6,6	18,210	139.2	11.4	

For calculation of the ΔE_i^* values we used the δ values for low-molecular weight liquids available in the literature.¹³ For this purpose we derived an excess system of equations on the basis of (20) which was solved by the method of the "least squares" on an electronic computer БЭСМ-4. For a more accurate calculation of solubility parameters, δ , it proved to be necessary to introduce 12 increments ΔE_i^* given in Table 7. Knowing the magnitude of ΔE_i^* and ΔV_i , we defined the δ value for 60 liquids having various chemical structures. As an example, Table 8 shows the calculated and experimental δ values coinciding with a high degree of accuracy.

Figure 6 represents theoretical dependence of δ on the ratio $E_i^*/N_A \sum_i \Delta V_i$; experimental points fit it well.

The above considerations permit to use this method for calculating cohesive-energy density of polymers. It is seen from Table 8 that the calculated δ values for a number of polymers agree with the available experimental data. It should be noted, nevertheless, that the experimental methods are not quite accurate, and the calculated δ values prove to be more reliable.

Since the increments ΔE_i^* and ΔV_i are known^{2,3} practically for all atoms and atom groups included in polymers with different structures, the proposed method can be used for calculation of δ for practically any polymer. The determination of δ is known to be of great importance in the evaluation of polymer solubility and polymer compatibility, both with plasticizers and with one another.

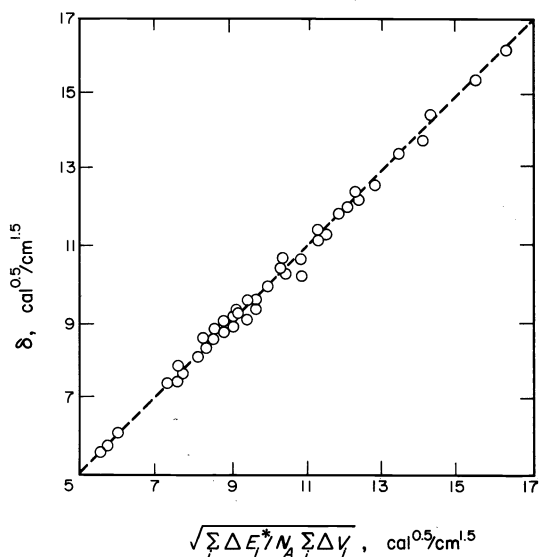


Fig. 6. Dependence of δ on the ratio $\sum_i \Delta E_i^*/N_A \sum_i \Delta V_i$ for low-molecular weight liquids.

REFERENCES

1. A. I. Kitaigorodskii, Organic crystallography, *Izdat. AN SSSR* (1955).
2. G. L. Slonimskii, A. A. Askadskii and A. I. Kitaigorodskii,

- Vasokomolek. soyedin.* **11A**, 494 (1969); **16A**, 424 (1974).
- ³A. A. Askadskii, Deformation of polymers, *Izdat. "Khimia"*, M. (1973).
- ⁴J. E. Lennard-Jones, *Proc. Roy. Soc.* **A106**, 441 (1924).
- ⁵V. T. Dashevskii, Conformation of organic molecules, *Izdat. "Khimia"*, M. (1974).
- ⁶A. I. Kitaigorodskii, Molecular crystals, *Izdat. "Nauka"*, M. (1971).
- ⁷R. G. Beaman, *J. Polymer Sci.* **9**, 472 (1953).
- ⁸W. A. Lee and G. J. Knight, *Brit. Polymer J.* **2**, 1-2 (1970).
- ⁹P. A. Small, *J. Appl. Chem.* **3**, 71 (1953).
- ¹⁰J. D. Crowley, G. S. Teague, Jr. and J. W. L., Jr., *J. Paint Tech.* **38** (496), 269 (1966).
- ¹¹C. M. Hansen, *J. Paint Tech.* **39** (505), 104 (1967).
- ¹²J. L. Gardon, *J. Paint Tech.* **38** (492) (1966).
- ¹³J. L. Gardon, Cohesive energy density, in: *Encyclopedia of Polymer Science and Technology*. H. Mark *et al.*