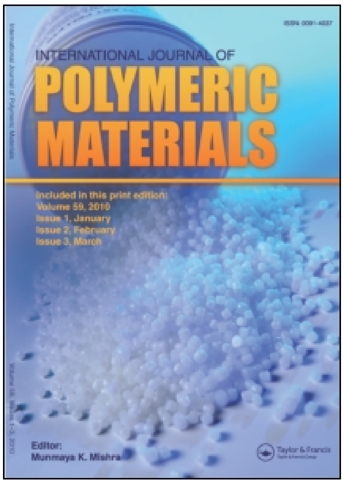

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The Influence of Chemical Structure on the Thermal Characteristics of Polymers

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The effects of chemical structure on the thermal characteristics of polymers are reviewed.

KEY WORDS Chemical structure, glass transition temperature, melting point, decomposition

Among the thermal characteristics of polymers the most important are glass transition temperature (T_g), melting point (T_m), thermal coefficient of volume expansion in glassy (L_g) and rubbery (L_L) states and the temperature of initial intensive thermal degradation (T_d). The characteristics T_g, T_m and $L_g(L_L)$ are generally accepted and do not require additional explanation. The T_d value can be determined from the crossing point of the tangents of the two branches of the TGA curve. The scheme of such a determination is shown on Figure 1. The investigations show that the rate constant of the process of thermal degradation increases very sharply within a narrow temperature interval. Figure 2 demonstrates the temperature dependence of the rate constant in the process of thermal degradation for a number of polyesters.

It can be concluded that for each polymer the rate constant sharply increases at a definite temperature interval. Consequently, intensive thermal degradation appears within a very narrow interval of temperatures and the T_d value falls within this interval. The T_d value depends to a small extent on the rate of heating and on the environment; therefore all the data correspond to a standard rate of heating (5°/min) in an inert environment.

All the characteristics given above can be calculated on the basis of the chemical structure of the repeating unit of the polymer, using the approach which has already been formulated.[1-11] This approach is based on examining a repeating unit of polymer in the form of a set of anharmonic oscillators. Each oscillator is constructed from a pair of atoms which possess the capacity for some kind of interaction. When estimating such properties as glass transition temperature, melting point and the thermal coefficient of volume expansion, the intermolecular interactions are used, both weak interactions (dispersion interactions) and strong interactions which arise from polar groups (dipole-dipole interactions, hydrogen bonds). The critical temperature of such an oscillator is regarded as the glass transition temperature or melting point.

When we estimate the temperature of the initial thermal degradation of a pol-

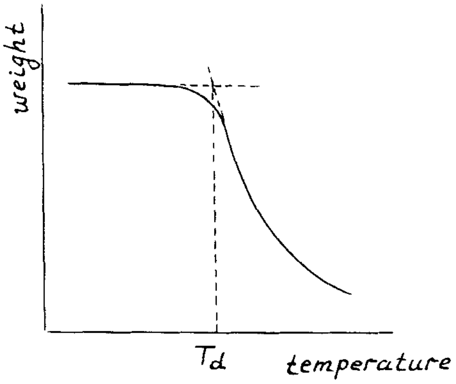


FIGURE 1 Typical TGA Curve.

ymer, the chemical interactions are examined; the critical temperature of such an anharmonic oscillator is regarded as the temperature of the start of intense degradation T_d.

As a result, it is possible to calculate a number of thermal characteristics, such as T_g, T_m, T_d, L_g and other properties (density, refractive undex, solubility parameter, etc.) taking into consideration the chemical structure of the repeating unit of polymer.

Let us examine the equations for calculations of these physical characteristics.

DENSITY

The density of polymers can be calculated as[1,2]:

$$\rho = \frac{K_{\text{av}} M_0}{N_A \sum_i \Delta V_i} \tag{1}$$

where M_0 is the molecular weight of the repeating unit of polymer, N_a is Avogadro number, $\Sigma_i \Delta V_i$ is the Van-der-Waals' volume of the repeating unit; ΔV_i is the Van-der-Waals' volume of i-atom included into repeating unit; K_{av} is the average coefficient of molecular packing which is equal to 0.681 for bulky specimens and 0.695 for films. The increments of Van-der-Waals' volume ΔV_i of different atoms in various surroundings, i.e., linked to different atoms, have been estimated. The increments are listed in References 1 and 2.

GLASS TRANSITION TEMPERATURE

Glass transition temperature T_g can be calculated as[1-3]:

$$T_g = 0.455 \frac{Z(D_0)}{R} \tag{2}$$

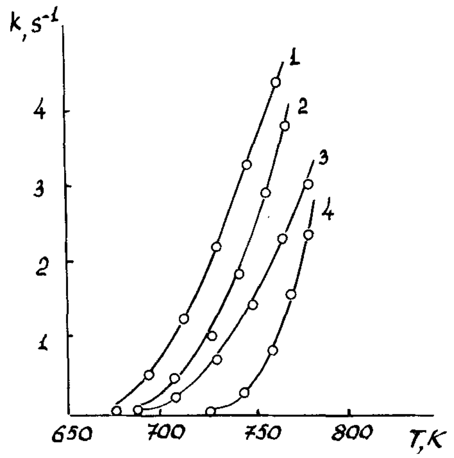


FIGURE 2 The temperature dependence of the rate constant in the process of thermal degradation for the polyesters on the basis of terephthalic acid and phenolphthalein, and for polysulfons on the basis of bisphenol A (2), phenolphthalein (3) and phenolfluorene.

where

$$D_0 = \frac{\sum_i \Delta V_i}{\sum_i 1/(D_{0,i}\Delta V_i)} \tag{3}$$

$D_{0,i}$ is the total energy of interaction between the i-th atom and the neighbouring atoms, Z is the coordination number of i-th atoms, R = universal gas constant. For practical purposes Equation (3) can be written as:

$$T_g = \frac{\sum_i \Delta V_i}{\sum_i a_i \Delta V_i + \sum_j b_j} \tag{4}$$

where a_i are increments which are related to the energies of dispersion of intermolecular interactions; the presence of polar groups resulting in significant intermolecular interaction is accounted for by specific increments b_j (dipole-dipole interaction, hydrogen bonds).

The a_i and b_j values for different atoms and any types of interactions are presented in References 1 and 2.

COEFFICIENT OF THERMAL EXPANSION

Coefficient of thermal expansion in glassy state L_g can be calculated as[1-3]:

$$L_g = \frac{\sum_i L_i \Delta V_i + \sum_j \beta_j}{\sum_i \Delta V_i} \tag{5}$$

where $L_i = a_i(K_o/K_g - 1)$, $\beta_j = b_j(K_o/K_g - 1)$; K_o and K_g are coefficients of molecular packing at a temperature close to 0°K and T_g. It has been shown[1-3] that coefficients K_o and K_g are constant for all the polymers: $K_o = 0.731$ and $K_g = 0.667$.

The coefficient of thermal expansion L_L in a rubbery state can be calculated from Equation Simha-Boyer

$$(L_L - L_g)T_g = 0.115 \tag{6}$$

but the accuracy of such a calculation is not good.

TEMPERATURE OF INITIAL THERMAL DEGRADATION

This temperature, T_d, can be determined from the crossing point of the tangents of the TGA curve determined under the following conditions: inert environment and low rate of heating (see Figure 1). The T_d value can be determined from the equation[1,2,4]:

$$T_d = \frac{\sum\limits_i \Delta V_i}{\sum\limits_i K_i \Delta V_i} \tag{7}$$

where

$$K_i = \frac{63}{2} \cdot \frac{R}{(ad_0E)_i}$$

a is the parameter of Morse potential, d_0 is the equilibrium distance between the chemically linked atoms, E = the energy of the link dissociation. The K_i values for the atoms differ for the same type of atoms depending on the participation of the atoms in specific interactions (dipole-dipole, hydrogen bonds). The K_i values are listed in the tables of References 1 and 2.

THE RATIO T_g/T_m

The relation T_g/T_m (T_m = the melting point) can be described as[1,2,5]:

$$\frac{T_g}{T_m} = \frac{1}{\dfrac{\sum\limits_i \Delta V_i}{\sum\limits_i (\delta_i \Delta V_i + \gamma_j)} - A} \tag{8}$$

where

$$\delta = \frac{1}{K_i}(K_o - K_g), \qquad \gamma_j = \beta_j(K_o - K_g)$$

K_i is the partial coefficient of molecular packing of i-th atom, β_j accounts for the contribution of specific intermolecular interactions (dipole-dipole, hydrogen bonds, etc.) to the total molar volume of polymer. The value

$$A = K_g/(K_o - K_g) = 10.418$$

The δ_i and γ_j values are listed in the tables of References 1 and 2.

REFRACTIVE INDEX

The refractive index n can be calculated using the equation[6]:

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{N_A \sum_i \Delta V_i}{K_{av}} = R \tag{9}$$

where R is the molar refraction, $\Sigma_i \Delta V_i$ = Van-der-Waals' volume of the repeating unit of the polymer, $K_{av} = 0.681$ for bulk polymers, and $K_{av} = 0.695$ for films. Molar refraction values R_i for various atoms are listed in the tables of References 1 and 2.

SPECIFIC COHESION ENERGY (SOLUBILITY PARAMETER OR HILDEBRANDT PARAMETER)

This value δ can be calculated as[1,2,7]:

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \tag{10}$$

where $\Sigma_i \Delta E_i^*$ represents the cohesion energy of the solvent or polymer decreased by a number characterizing the ratio of the solvent or polymer molar volume to the Van-der-Waals' volume. ΔE_i^* is the contribution of the i-th atom or i-th type of intermolecular interaction into ΔE^*. All the calculations are developed for the solvent molecule or for repeating unit of the polymer. The increments ΔE_i^* are listed in the tables of References 1 and 2.

STRESS-OPTICAL COEFFICIENT

The value C_σ is the coefficient of proportionality between the mechanical stress σ and birefringence Δn resulting from stress. The stress-optical coefficient can be calculated as[1,2,6]:

$$C = \frac{\sum_i C_i}{N_A \sum_i \Delta V_i} + \Pi \tag{11}$$

where C_i is the increment specifying the contribution of the i-th atom and i-th type of intermolecular interaction into the C_σ value, Π is the universal parameter having a value of $0.3544 \times 10^{-3}\ (\text{MPa})^{-1}$. C_i values are listed in the tables of References 1 and 2.

SURFACE TENSION

Surface tension γ_p of the polymers can be calculated as[8]:

$$\gamma_p = C_j \frac{\sum_i \Delta E_i^*}{\left(\sum_i \Delta V_i\right)^{2/3} m^{1/3}} \tag{12}$$

where m is the number of atoms in the polymers repeating unit, C_j values are constants and vary depending on the type of the polymer. For nonpolar polymers of the I-st group (hydrocarbons, perfluorocompounds, polyethers) $C_{1,n} = 0.128$; for polar polymers of the I-st group (polyesters, polyamides, for polymers including nitro group, etc.) $C_{1,p} = 0.0751$; for polymers including hydroxyl and carboxyl groups $C_{2,p} = 0.0476$; for polymers including nitrile groups $C_{3,p} = 0.060$.

The values γ_s and γ_p are useful for the prediction of solubility parameters in organic solvents. In order to predict the solubility of amorphous polymers the next relation can be used[9]:

$$M \le 1.374\phi(\sigma - \sqrt{\phi^2 - 1 + a}) \tag{13}$$

where $M = \delta_p^2/\delta_s^2$, δ_p and δ_s are the Hildebrandt solubility parameters for the polymer and solvent respectively; $a = \gamma_{sp}/\gamma_s$, where γ_{sp} is the interface tension value calculated in accordance to the following equation:

$$\gamma_{sp} = \gamma_p + \gamma_s - 2\phi(\gamma_p\gamma_s)^{1/2} \tag{14}$$

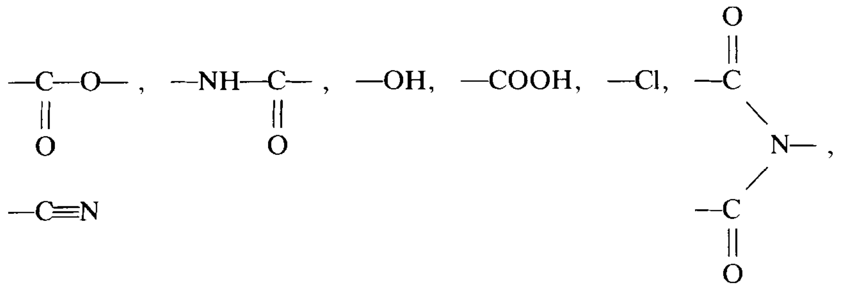
where γ_p and γ_s are the surface tensions of the polymer and solvent respectively.

$$\phi = \frac{4(V_s V_p)^{1/3}}{(V_s^{1/3} + V_p^{1/3})^2} \tag{15}$$

where V_s and V_p are the molar volumes of the solvent and of the polymer's repeating unit.

For developing the molecular design of polymers, the computer program has been created to solve direct and reverse problems, consisting of: 1) determination of polymer properties from the given repeating unit structure; 2) development of a computer simulation of polymers with predetermined physical properties (the search for such repeating units which would impart the given physical properties to a polymer).

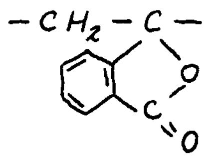
Let us examine the influence of the chemical structure of polymers on the temperature of initial thermal degradation, T_d, in detail. It should be noted that the repeating unit of a polymer very often contains the polar groups. For example these groups are as follows:



$-\underset{\underset{O}{\|}}{C}-O-$, $-NH-\underset{\underset{O}{\|}}{C}-$, $-OH$, $-COOH$, $-Cl$, $-C\equiv N$

and so on.

The contribution from atoms which were introduced into these groups differs from the contribution from the same atoms which form the non-polar groups and possess only weak dispersion interactions. This special feature was taken into consideration in Reference 4. As a result, the situation arises when the polar groups on the one hand lead to an increasing of the glass transition temperature and melting point, but on the other hand promote a decrease in the temperature of initial thermal degradation. For many polymers the T_d value is higher than the T_g and T_m values, but often thermal degradation appears before the glass transition temperature is attained. For example, the glass transition temperature T_g for the polymer[12]



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is equal to 390°, but the temperature of initial thermal degradation $T_d = 260°$ (the value T_g has been determined by extrapolation of the plot T_g versus the molar part of the structure I containing copolymers with styrene or methyl methacrylate).[13]

In connection with the specific influence of different atoms and groups on the thermal characteristics of polymers it is very interesting to analyze the dependences between different thermal characteristics. The dependences can be analyzed using

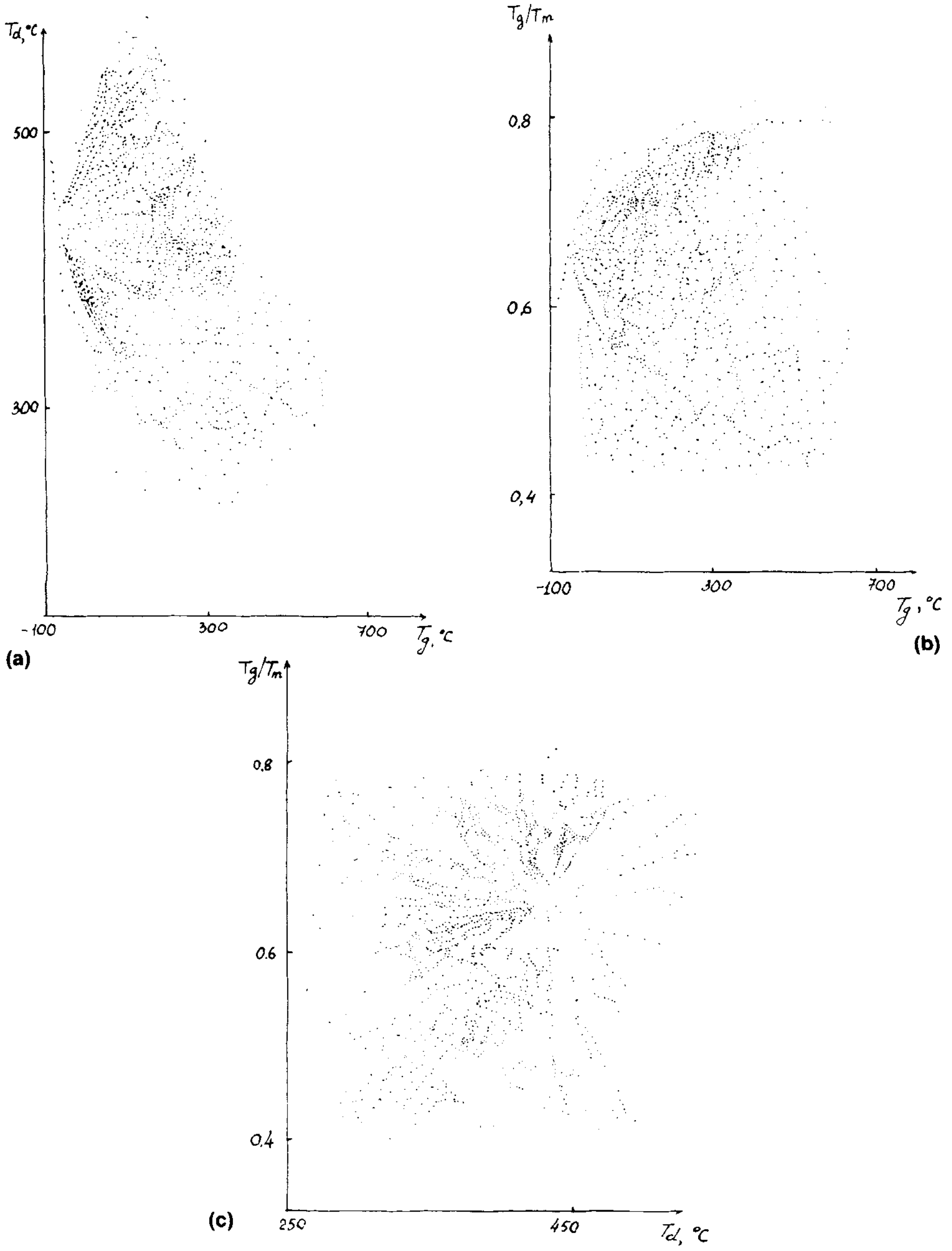


FIGURE 3 The diagrams of combination (a) T_g and T_d, (b) T_g and T_m, (c) T_m and T_d.

the diagrams of a combination of different properties of polymers. The X-axis characterizes any physical characteristic (for example, T_g) of the polymer, the Y-axis characterizes another physical or chemical characteristic (for example, T_d) for the same polymer. If the same procedure has been done for many polymers a region of points is formed which characterizes the region of combination for two properties chosen. The polymers which possess two chosen characteristics fit inside this region. The coexistence of two characteristics outside this region is impossible.

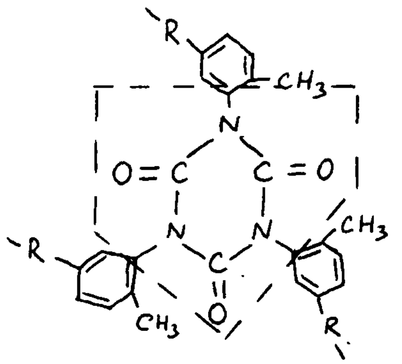
Figure 3 shows the diagrams of combination T_g and T_d, T_g and T_m, T_m and T_d. These diagrams have been created as a result of the computer synthesis of polymers using Equations (4), (7) and (8). It can be seen that total dependence between T_g and T_d, T_g and T_m, T_d and T_m is absent but inside of each region can be traced individual dependences which characterize the behavior of different types of polymers. These diagrams permit us to solve a key question concerning the possibility of the preparation of polymers, which simultaneously possess some predetermined properties. Using the diagrams one can find ultimate thermal characteristics for organic polymers.

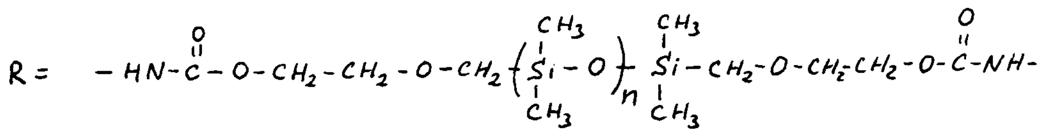
Now let us examine the thermal characteristics for polymer networks. In the case of networks, the equation for glass transition temperature is written in the form:

$$T_g = \frac{\sum_i \Delta V_i}{\left(\sum_i a_i \Delta V_i + b_i\right)_l + \left(\sum_i K_i \Delta V_i\right)_{c.p.}} \tag{16}$$

where $\Sigma_i\ \Delta V_i$ is the repeating fragment of the network; $(\Sigma_i\ a_i \Delta V_i + b_i)_l$ is the set of increments for the linear fragments and $(\Sigma_i\ K_i \Delta V_i)_{c.p.}$ is the set of increments for the crosslinked points. The structure of the crosslinked point must be presented in the form of a group of atoms which includes an atom from which chain branching occurs and neighbouring atoms chemically bind with it and the nearest substituents.

In the case of highly crosslinked networks in which the distance between points amounts to a few repeating units or even less than one unit the role of the crosslinked point is very important. Let us examine experimental data for recently obtained crosslinked polymers possessing unusual properties.[14,15] For example, crosslinked polyisocyanurates of the following chemical structure have been synthesized as actual structures:





$$R = -HN-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-CH_2\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n\underset{CH_3}{\overset{CH_3}{Si}}-CH_2-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-NH-$$

The role of a crosslinked point here is played by the trifunctional isocyanurate ring with adjacent benzene ring carbon atoms, while the role of linear fragments is played by organosilicon chains with different magnitudes of n, connected to points by the spacers. The structure of the crosslinked point is enclosed by a dashed line.

For the crosslinked structure shown above an expression was obtained which connects the T_g-value with the number of dimethylsiloxane units n in a linear fragment:

$$T_g(K) = \frac{750g + 108.15n}{2450 + 721.5n} \times 10^3 \tag{17}$$

Calculations by means of Equation (17) are given in Table I. This table contains also the calculated and experimental values of the equilibrium elastic moduli E_∞ (estimates of the equilibrium modulus were carried out by the method in Reference 16).

The analysis of all the data indicates that in References 14 and 15 transparent materials were obtained which in mechanical properties possess a number of features distinguishing them from glassy and rubbery polymeric substances. The main feature is that the presence of bulky rigid cross-linked points of non-uniform chemical structure and the presence of flexible organosilicon chains connecting these points lead to a situation where we have two transition temperatures with very steady changes in the elastic modulus between them. This temperature region is very extensive (~180°) and is the working region in which two given polymers behave like glassy polymers but possess a considerably lower and more controllable elastic modulus compared with polymer glasses. The elastic modulus changes as a function of distance between the neighbouring crosslinked points and varies from 3×10^3 MPa to 3 MPa. This provides new opportunities for using polymeric materials in the fields of engineering where a combination of creep compliance and elasticity is needed.

TABLE I

Values of calculated glass transition temperature T_g and equilibrium elastic modulus E_∞ of cured macrodiisocyanates as a function of number of dimethylsiloxane units n

n	T_g, C	$E_{\text{calc.}}$, MPa	$E_{\text{exp.}}$, MPa
0	33	—	—
1	−2	884	866
2	−25	249	283
3	−41	123	149
6	−67	40	43
9	−80	22	24
19	−99	8	7
43	−112	3	3
∞	−123	—	—

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