Glass Transition Phenomenon in Vinylidene Chloride–Acrylonitrile Copolymers

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Synopsis

Investigations of glass transition phenomena were carried out on vinylidene chloride–acrylonitrile copolymers, purified commercial samples of known composition. With a view to analyzing this effect, the following physical parameters were investigated: specific volume $V_{s,25}$, T_g, and volume expansion coefficients α_L, α_g, and $\Delta\alpha$. The experimental results were analyzed on the basis of semiempirical and theoretical equations describing transitions to the glassy state. It was found that T_g dependence on weight fraction C_2 of acrylonitrile may be described by Wood's equation, with $k = 5.88$. Applying Gibb's and Kanig's theories as well as relations given by Hirai and Small, the energies associated with intermolecular interactions (A^*_{AB}, E_0, E_h, CED), and intramolecular interactions (stiffness energy ϵ) were calculated for copolymers of different composition. The copolymer T_g was found, above all, to depend on the stiffness energy ϵ, which increases with increasing acrylonitrile content in the copolymer.

INTRODUCTION

The glass transition temperature, T_g, is a characteristic property of polymers, defining a change in the state of a macromolecular system. It is connected with a change in the packing of molecules brought about by freezing the rotations of chain segments. Thus, it depends on the chemical structure of the mers and on parameters related to the inter- and intramolecular interaction energy. In copolymers, T_g is related in a complex fashion to the composition of the copolymer. Many authors such as Gordon and Taylor,[1] Wood,[2] Fox,[3] and Mandelkern[4] have derived semiempirical equations relating T_g to the weight fraction of comonomers. Others such as Gibbs,[5] Gibbs and Di-Marzio,[6] and Kanig[7] have treated this dependence more exactingly and with a better theoretical interpretation.

Many publications have been devoted to the T_g of copolymers of vinylidene chloride with various comonomers.[8-12] However, glass transition phenomena in vinylidene chloride–acrylonitrile copolymers have received little attention. Because of the interesting properties of this polymer, work was undertaken in this field with the aim of determining the effect of acrylonitrile content on the T_g of this copolymer and of explaining the observed facts.

EXPERIMENTAL

The vinylidene chloride–acrylonitrile copolymers were commercial products (Dow Chemical Co.) in the form of white, fine-grained powders. They contained the following percentage weights of acrylonitrile found by elemental analysis: 9%, 20%, 25%, and 50%. For comparison, polyacrylonitrile (PAN) and polyvinylidene (PCVD) chloride were also studied.

The T_g values and the volume expansion coefficients α_L and α_g above and below T_g were measured dilatometrically, using a Bekkedahl-type dilatometer[13] of length 35 cm, bulb volume ca. 8 cm^3, and with a calibrated capillary. About 0.3 g of the polymer sample was introduced into the dilatometer, which was then carefully degassed for 24 hr before being filled with mercury. The pressure in the vacuum system did not exceed 10^{-3} mm Hg during operations. Having been filled with mercury, the dilatometer was then transferred to a thermostat whose temperature was some 50°C above the anticipated T_g. After heating the sample for 2 hr, the thermostat temperature was lowered at a rate of 3°/min, the mercury level being read off at specific temperatures known to 0.05°C. Further readings were recorded at temperature intervals of from 5° to 7°, with the sample remaining at the given temperature for 15 min. The specific volumes at the given temperature T were calculated from the following equation:

$$V_S = V_{S,25} + \alpha \cdot \Delta T \qquad (1)$$

where $\alpha = \dfrac{\Delta V_S}{\Delta T} = \alpha_s \cdot V_{S,25} + \dfrac{S}{m} \cdot \dfrac{\Delta h}{\Delta T} - \dfrac{V_{Hg}}{m}(\alpha_{Hg} - \alpha_s)$, $V_{S,25}$ = sample specific volume at 25°C (298°K) found independently using a picnometer, ΔT = temperature difference $(T - 298°K)$, α_s = volume expansion coefficient of the dilatometer glass, α_{Hg} = volume expansion coefficient of mercury, V_{Hg} = volume of mercury, m = mass of mercury, S = capillary cross section, and Δh = change in mercury level in the capillary with temperature change ΔT.

A plot of specific volume V_S against T gives the T_g of the samples from the intersection of the two linear sections. A typical graph for a vinylidene chloride–acrylonitrile copolymer with 20% acrylonitrile is shown in Figure 1. Slopes of the linear function $V_S = f(T)$ give the volume expansion coefficients α_L, α_g, above and below T_g in units of cm^3/g deg. Thus,

$$\alpha_g = \frac{\Delta V_S}{\Delta T} \qquad T < T_g$$

$$\alpha_L = \frac{\Delta V_S}{\Delta T} \qquad T > T_g$$

RESULTS AND DISCUSSION

Results of the work on copolymers, polyacrylonitrile, and poly(vinylidene chloride) enabled the relationships between specific volumes $V_{S,25}$, T_g, and

volume expansion coefficients α_L, α_g, and $\Delta\alpha = \alpha_L - \alpha_g$ on copolymer composition to be determined. The free volumes defined by Simha and Boyer as being equal to $\Delta\alpha \times T_g$ and $\alpha_L \times T_g$ were also calculated, as was $\varphi^*_{f_1} = \Delta\alpha/\alpha_L$, the characteristic parameter of Kanig's theory, equal to the
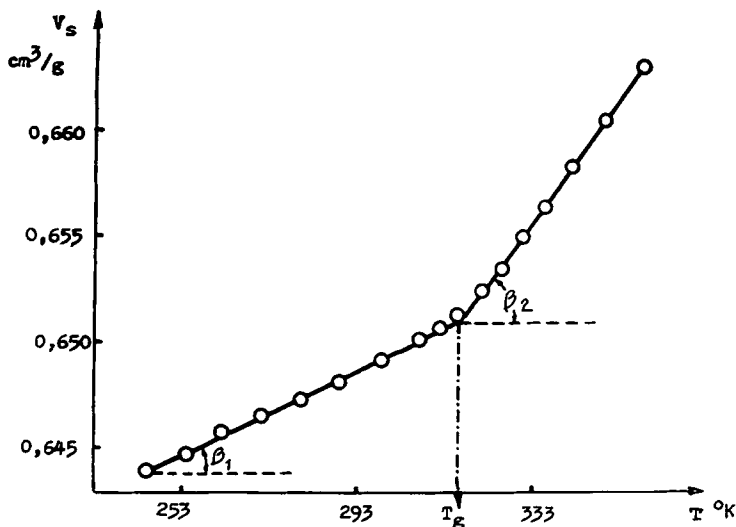

Fig. 1. Dependence of specific volume on T for a copolymer of 20% weight fraction acrylonitrile.

ratio of hole volume to total free volume at T_g. The effect of the inter- and intramolecular interaction energies on copolymer T_g was also discussed.

Dependences of Specific Volumes $V_{S,25}, T_g$, Volume Expansion Coefficients α_L, α_g, and $\Delta\alpha$, and Other Related Parameters on Copolymer Composition

A plot of specific volumes against weight and mole fractions of acrylonitrile is shown in Figure 2. Marked deviations from linearity indicate that the specific volumes of the comonomers are not additive. Figure 3 shows the dependence of T_g on weight fraction C_2 and mole fraction n_2 of acrylonitrile. As can be seen, the line joining the T_g's of both homopolymers has a definite positive deviation. The equation linking T_g with copolymer composition was first given by Gordon and Taylor:[1]

$$A_1 C_1 (T_g - T_{g1}) + A_2 C_2 (T_g - T_{g2}) = 0 \qquad (2)$$

where T_g, T_{g1}, and T_{g2} are the glass transition temperatures of a copolymer (of weight fraction C_1 of one comonomer), homopolymer 1, and homopolymer 2, respectively; $C_2 = 1 - C_1$; A_1, A_2 are constants for a given copolymer and equal to $\Delta\alpha_1$ and $\Delta\alpha_2$, respectively, where $\Delta\alpha_1$ and $\Delta\alpha_2$ are the differences in the volume expansion coefficients above and below T_g of the homo-
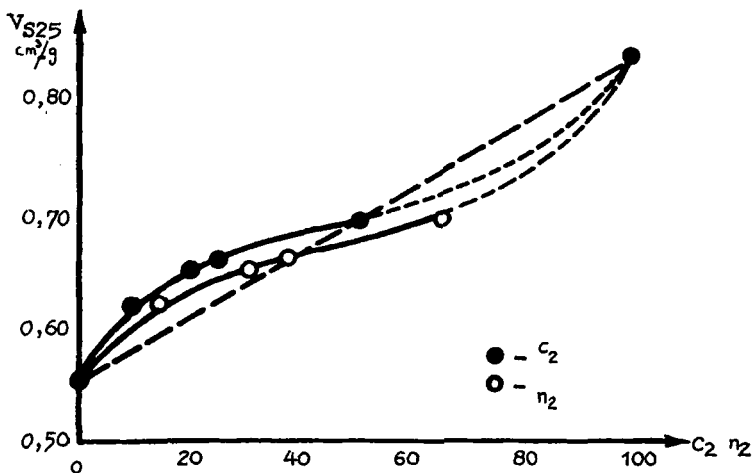
Fig. 2. Dependence of specific volume $V_{S,25}$ on weight fraction C_2 and mole fraction n_2 of acrylonitrile in copolymer at 25°C.
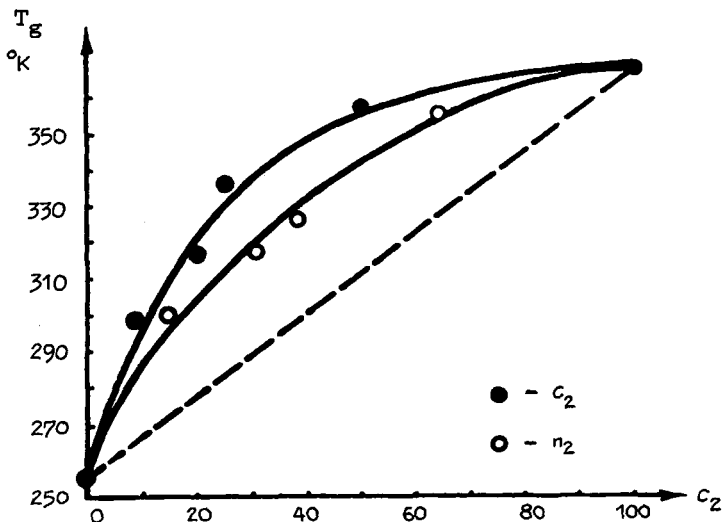

Fig. 3. Tg dependence on weight fraction C_2 and mole fraction n_2 of acrylonitrile.

polymers. Substituting $A_2/A_1 = k$ and $C_1 = 1 - C_2$ into eq. (2) and rearranging gives

$$T_g = \frac{T_{g_1} + (kT_{g_2} - T_{g_1})C_2}{1 - (1 - k)C_2}.$$ (3)

At $A_1 = A_2$ $(k = 1)$, T_g is a linear function of weight fraction C_2. For the investigated vinylidene chloride–acrylonitrile copolymers $k \neq 1$.

For eq. (3) to be satisfied, k should equal the following:

$$k = \frac{\Delta\alpha_2}{\Delta\alpha_1} = \frac{\Delta\alpha_{2,\text{PAN}}}{\Delta\alpha_{1,\text{PCVD}}} = 18.3.$$

Experimentally, k was determined from Wood's eq. (2), i.e.,

$$T_g = - \frac{1}{k} (T_g - T_{g1}) \frac{1 - C_2}{C_2} + T_{g2}. \qquad (4)$$

A plot of T_g versus $X = (T_g - T_{g1})(1 - C_2)/C_2$, using experimental values, gave k equal to 5.88 (from the slope of the graph in Fig. 4). This value differs from the one calculated from the Gordon-Taylor equation, and thus this equation does not hold in the case of this copolymer. Using the k value
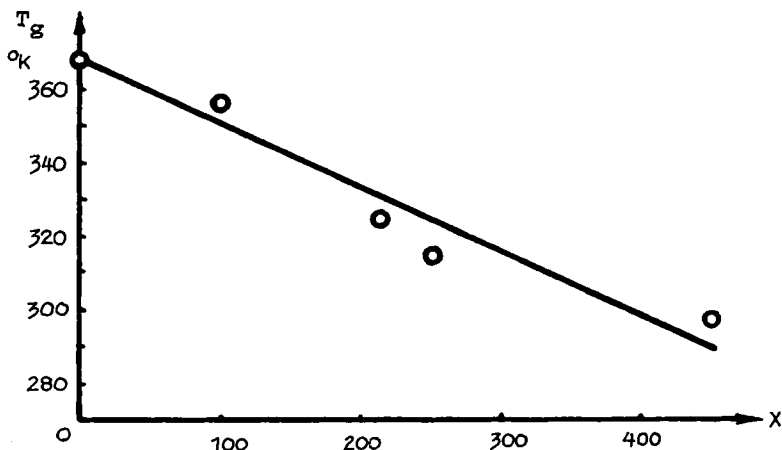

Fig. 4. Copolymer Tg dependence on $X = T_g - T_{g1} \, 1 - C_2/C_2$, where T_g is the glass transition temperature of polyvinylidene chloride and C_2 is the weight fraction of acrylonitrile.
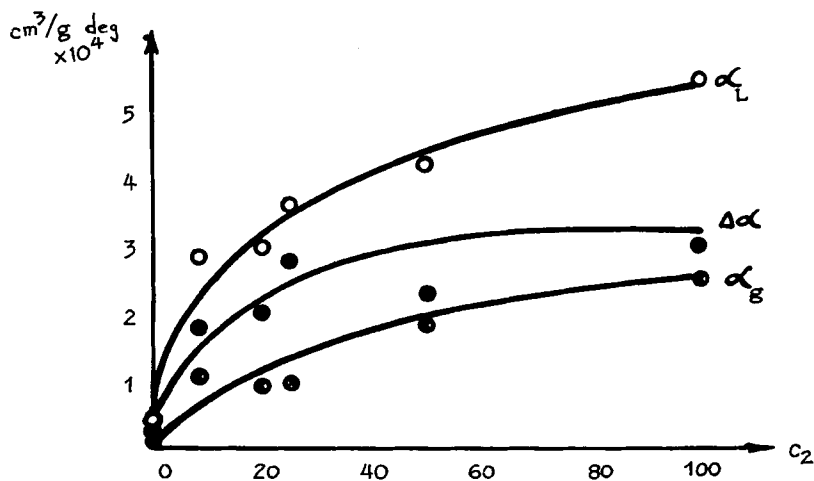

Fig. 5. Dependence of α_L, α_g, and $\Delta\alpha$ on weight fraction C_2 of acrylonitrile.
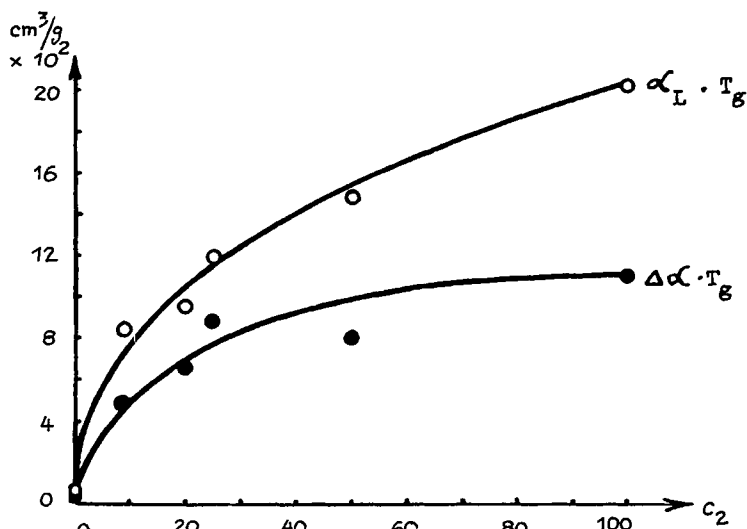
Fig. 6. Dependence of $\Delta\alpha \cdot T_g$ and $\alpha_L \cdot T_g$ on weight fraction C_2 of acrylonitrile.
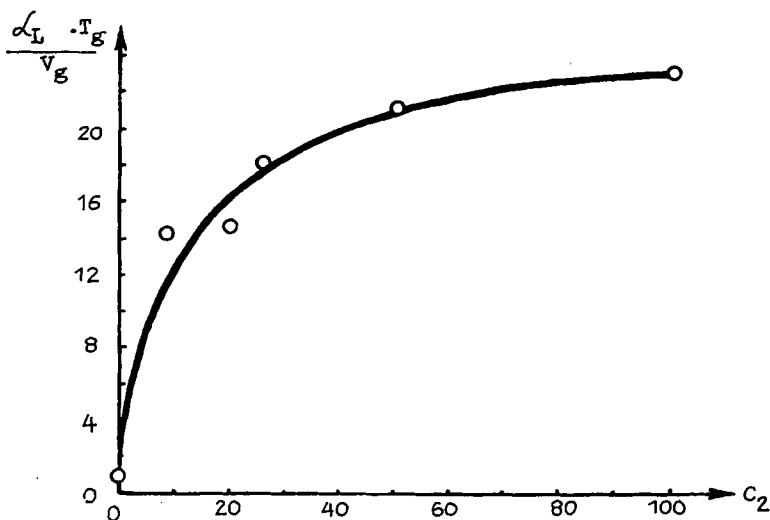

Fig. 7. Dependence of $\dfrac{\alpha_L \cdot T_g}{V_g}$ on weight fraction C_2 of acrylonitrile, where V_g is the specific volume at T_g.

from Figure 4, the dependence of T_g on C_2 may be given by eq. (4) which reduces to

$$T_g = \frac{502C_2 - 18}{1 + 4.47C_2}.$$

Similarly, the Fox equation, which may also be transformed to the Gordon-Taylor equation with $k = T_{g_1}/T_{g_2} = 0.69$, does not hold for the investi-

gated copolymer systems. The coefficient k can also be calculated from the Gibbs-Di-Marzio theory in the following way:

$$k = \frac{A_2}{A_1} = \frac{\alpha_B W_A}{\alpha_A W_B} = 1.83$$

where W_A and W_B are the molecular weights of vinylidene chloride and acrylonitrile mers, respectively, and $\alpha_A = \alpha_B = 2$ is the number of flexible rotatable bonds (estimated by Gibbs)[5]. The value of k calculated in this way is three times smaller than the k value obtained experimentally from Figure 4. Figure 5 shows the relationship between volume expansion coefficients and weight fraction of acrylonitrile. The values of these coefficients markedly increase with increasing acrylonitrile content, in a nonlinear way. The largest changes in these values are observed at the beginning of the curves (low C_2 values corresponding to the addition of small amounts of acrylonitrile to polyvinylidene chloride). The Simha-Boyer[14,21] constants $K_1 = (\Delta\alpha \cdot T_g)$ and $(K_2 = \alpha_L \cdot T_g)$, defined as the free volumes at T_g, vary in a similar way with increasing acrylonitrile content (Fig. 6). Thus, their values change from 0.0041 to 0.1097 and from 0.0057 to 0.2017, values which deviate considerably from the values of 0.113 and 0.164 anticipated by Simha and Boyer. In Figure 7, the ratio $\alpha_L \cdot T_g / V_g$ (free volume on specific volume at T_g) is plotted against weight fraction C_2 of acrylonitrile in copolymer. The rapid increase in $\alpha_L \cdot T_g / V_g$ at the beginning of the curve and the slowing down when C_2 exceeds 30% indicate that a change in packing takes place when a certain weight fraction of acrylonitrile is exceeded.

Effect of Inter- and Intramolecular Interactions on the T_g of Vinylidene Chloride–Acrylonitrile Copolymers

The effect of intermolecular interactions on polymer and copolymer T_g has been considered by many authors.[7,15,16,17] From this aspect, the effect of copolymer composition on T_g has also been discussed.[7] Kanig, for example, treats copolymers as a statistical mixture of both mers A and B and holes and derives the molar enthalpy of mixing for this mixture which at T_g (hole saturation) equals zero. The equation describing T_g in terms of modified comonomer B content Φ_{fB} has the following form:

$$\frac{T_{gA} - T_g}{\Phi_{fB}} = \frac{\varphi^*_{f2}(2A^*_{AB} - A^*_{AA} - A^*_{BB})}{R(\ln \varphi^*_{f1} + \varphi^*_{f2})} \Phi_{fB} - \frac{\varphi^*_{f2} 2(A^*_{BB} - A^*_{AB})}{R(\ln \varphi^*_{f1} + \varphi^*_{f2})}$$

$$(5)$$

where

$$\Phi_{fB} = \frac{m_B}{m_B + m_A \dfrac{\Delta\alpha_A}{\Delta\alpha_B}}$$

m_A and m_B are the weight fraction of components A and B in the copolymer (A = vinylidene chloride, B = acrylonitrile), and $\Delta\alpha_A$ and $\Delta\alpha_B$ are the dif-

ferences in the volume expansion coefficients above and below T_g for homo-polymers A and B; φ^*_{f1} and φ^*_{f2} are constants, characteristic of Kaning's eq. (5) and are defined as follows:

$$\varphi^*_{f1} = \frac{\text{hole volume}}{\text{free volume}} = \frac{T_g(\alpha_L - \alpha_g)}{T_g \cdot \alpha_L} = \frac{\Delta\alpha}{\alpha_L} = 0.64$$

$$\varphi^*_{f2} = \frac{\text{vibration volume}}{\text{free volume}} = \frac{T_g \cdot \alpha_g}{T_g \cdot \alpha_L} = \frac{\alpha_g}{\alpha_L} = 0.36$$

A^*_{AA} and A^*_{BB} are the energies needed to produce 1 mole of holes in hole-free polymer melt composed of pure components A and B. They can be obtained from the equation

$$A^*_{MM} = 0.664 \, R \, T_g$$

where R is the gas constant.
A^*_{AB} is associated with the energy needed to produce 1 mole of holes on separating the structural units A and B. Its value can be found from the slope of the function

$$\frac{T_{gA} - T_g}{\Phi_{fB}} = f(\Phi_{fB}),$$

knowing φ^*_{f1}, φ^*_{f2}, A^*_{AA} and A^*_{BB}. The above parameters were found to have the following values: $\varphi^*_{f1} = 0.69 \pm 0.04$, $\varphi^*_{f2} = 0.31 \pm 0.04$ (average values for copolymers and homopolymers), $A^*_{AA} = 339$ cal/mole, $A^*_{BB} = 495$ cal/mole $A^*_{AB} = 310$ cal/mole A^*_{AA}, A^*_{AB}, and A^*_{BB} according to Kanig's theory are intermolecular interaction parameters and their values indicate that T_g depends exclusively on intermolecular forces.
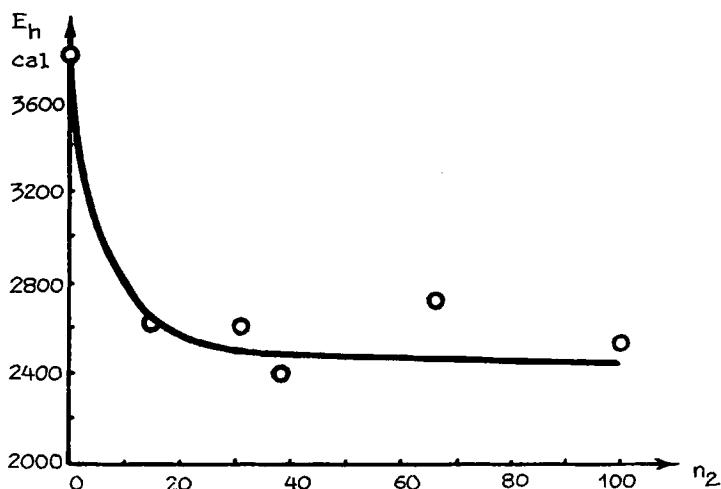

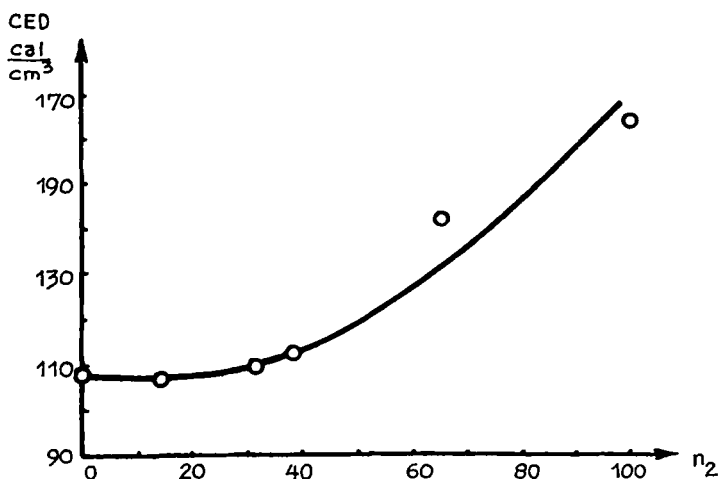Fig. 8. Dependence of energy E_h on mole fraction n_2 of acrylonitrile.

Fig. 9. Dependence of the cohesion energy density (CED) on mole fraction n_2 of acrylonitrile.
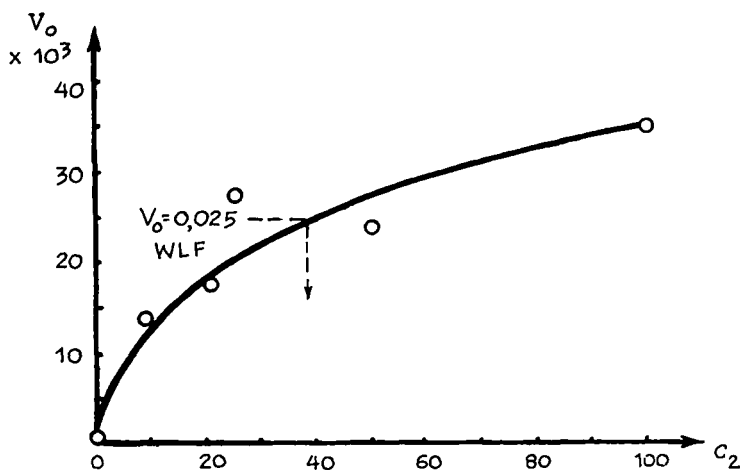

Fig. 10. Dependence of free volume V_0 at T_g on weight fraction C_2 of acrylonitrile.

Hirai and Eyring[15] correlate $\Delta\alpha$ and T_g with E_h, the energy needed to produce holes in the polymer. Its value can be found from the equation

$$\Delta\alpha \cdot T_g = \frac{E_h}{RT_g} \exp\left[- \frac{E_h}{RT_g} \right].$$ (7)

Figure 8 gives the dependence of E_h on mole fraction n_2. The large drop in E_h which occurs after introducing small amounts of acrylonitrile is almost certainly connected with the observed increase in free volume (Fig. 6). On the other hand, the cohesion energy density (CED), calculated according to Small,[18] increases only after the weight fraction of acrylonitrile has
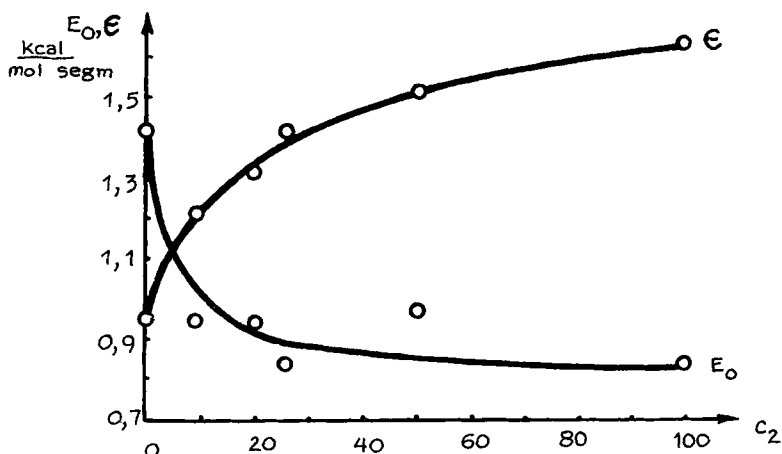
Fig. 11. Dependence of intermolecular interaction energy E_0 and stiffness energy ϵ on weight fraction C_2 of acrylonitrile.
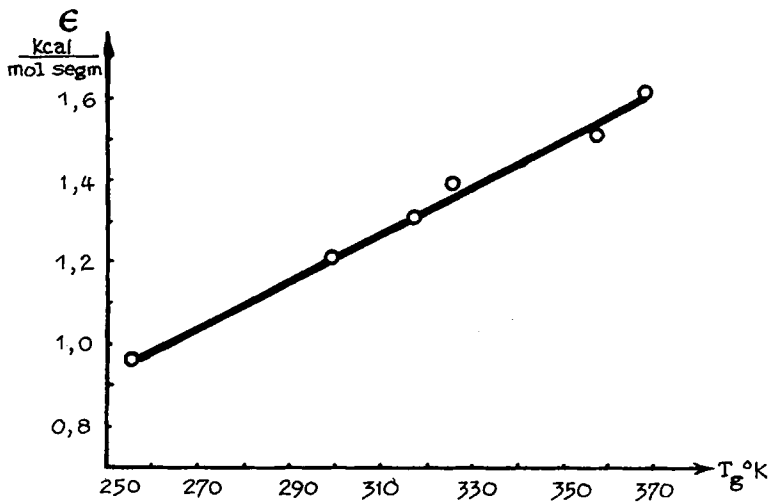

Fig. 12. T_g dependence on stiffness energy ϵ.

exceeded 40%. Thus, one can suppose that dipole–dipole interactions increase strongly only after a certain acrylonitrile content has been exceeded. This, in turn, brings about an increase in cohesion energy density (Fig. 9), and a lowering of specific volume (Fig. 2), and slows down the rate of free volume increase (Fig. 6). No correlation was found between the variations in E_h and CED for the investigated copolymers, on analysis of their dependences on n_2.

The Gibbs-Di-Marzio theory is of considerable importance among theories of polymer transitions to the glass state, taking into account the effect of inter- and intramolecular interactions on T_g. The theory also considers that the stiffness energy of the chain, ϵ, resulting from intramolecular interactions has a decisive effect on T_g. A value for this energy may be obtained

by first calculating the free volume V_0 and T_g, from Moacanin's and Simha's equations (this can be compared[6] with the constant free volume $V_{0,\text{WLF}}$ at T_g[20]). The intermolecular interaction energy E_0 and the intramolecular interaction energy ϵ, the stiffness energy, may then be calculated, assuming that the network coordination constant Z equals 4. The dependences of V_0, E_0, and ϵ on weight fraction of acrylonitrile C_2 are given in Figures 10 and 11. In Figure 10, the free volume $V_0 = 0.025$ is indicated as $V_{0,\text{WLF}}$. The increase in free volume V_0 is analogous to the increase in free volumes $\Delta\alpha \cdot T_g$ and $\alpha_L \cdot T_g$ (Fig. 6). while the energy E_0 decreases with increasing C_2, in exactly the same way as E_h. The stiffness energy ϵ, however, increases with increasing weight fraction of acrylonitrile, A plot of T_g versus ϵ (Fig. 12) shows the two variables to be directly proportional to each other and leads to the conclusion that the stiffness energy has an important effect on polymer and copolymer T_g's. The stiffness energy is, by definition, the difference in energy between the cis and trans conformations of a segment capable of rotation about the main chain axis. Stiffening the chain brought about, in part, by interaction of the polar group, —C≡N results in an increase in ϵ values with increasing acrylonitrile content (the calculated difference in stiffness energies of polyacrylonitrile and poly(vinylidene chloride) equals 0.68 kcal/mole segment).

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