

## FLOW ACTIVATION ENERGY OF DILUTE POLYMER SOLUTIONS RELATED TO MOLECULAR PARAMETERS

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An analysis has been made of the variation of the flow activation energy of polymer solutions at low concentrations and of its dependence on molecular parameters (molecular weight and rigidity of the polymer chain) and on the thermodynamic quality of the solvent. The activation energy values for poly(vinyl acetate), poly(methyl methacrylate), polystyrene and cellulose nitrate calculated from our own and other authors' data for the temperature dependence of intrinsic viscosity were correlated with those obtained by direct measurements.

An important factor characterizing the temperature dependence of the viscosity of polymer solutions is the flow activation energy of solution defined by

$$E = \partial \ln \eta / \partial (1/RT), \quad (1)$$

where  $\eta$  is absolute viscosity,  $T$  is temperature and  $R$  is the gas constant. It represents the minimum energy needed for overcoming the resistance of intermolecular forces during the flow of the liquid. In the temperature range close to the glass transition temperature  $T_g$  the flow activation energy is temperature-dependent; at temperatures remote from  $T_g$  it usually is constant. The difference between the flow activation energies of solution and solvent,  $E - E_s = \Delta E$ , for more concentrated solutions (c. above 10%) increases with increasing polymer concentration<sup>1-9</sup>. The steepness of the increase is said to depend on the character of the polymer and on the thermodynamic quality of the solvent.

Moore and coworkers<sup>10-15</sup> measured the flow activation energies of dilute polymer solutions and found that  $\Delta E$  of solutions of poly(vinyl acetate) and poly(methyl methacrylate) in thermodynamically poor solvents decreased with increasing concentration, the steeper the poorer the quality of the solvent used. For solutions of cellulose derivatives (cellulose triacetate and nitrate with 12.1% nitrogen)  $\Delta E$  of both dilute and concentrated solutions only increased with increasing concentration in all solvents used. Budtov<sup>16,17</sup> carried out a detailed analysis of the flow activation energy of dilute solutions in the surroundings of the  $\Theta$ -temperature and derived the function  $\Delta E$  vs  $c$  with a minimum; the function very adequately described

experimental results obtained for polystyrene in decalin. He also predicted that solutions in good solvents will exhibit a less pronounced dependence.

It has been our objective to carry out a more general analysis of the flow activation energy within the broadest possible range of the thermodynamic quality of solvent with respect to the statistical rigidity of the polymer chain. It appears that one has to bear in mind also changes in the solvent density and polymer concentration which under some circumstances, particularly at low concentrations and in good solvents-can have a decisive influence upon the magnitude of the flow activation energy.

## EXPERIMENTAL

*Polymers.* Linear polystyrene (Research Laboratories, Kaučuk, Kralupy n. Vlt.) was reprecipitated from benzene solution with methanol and dried *in vacuo* over phosphorus pentoxide at 60°C; its molecular weight ( $1.6 \cdot 10^5$ ) was calculated from intrinsic viscosity (measurements in benzene solutions at 25°C) using Meyerhoff's equation<sup>18</sup>,  $[\eta] = 1.23 \cdot 10^{-4} M_{\eta}^{0.72}$ . A sample of lacquer cellulose nitrate (Research Institute of Synthetic Resins and Lacquers, Pardubice) was dried to constant weight over phosphorus pentoxide at room temperature prior to weighing, nitrogen content was determined volumetrically by Dumas's micromethod modified by Večeřa<sup>19</sup> (11.88 to 12.13%, corresponds roughly to dinitrate), molecular weight ( $2.19 \cdot 10^4$ ) was estimated from intrinsic viscosity (cyclohexanone solutions at 25°C) from a relationship suggested by Moore and Edge<sup>11</sup>,  $[\eta] = 2.24 \cdot 10^{-4} M_{\eta}^{0.81}$  (although they used fractions determined osmotically in order to find the above dependence of molecular weights, this procedure proved to be the only possible one for an estimate of the viscosity average basing on intrinsic viscosity, as no other calibration for cellulose nitrate with c. 12% of nitrogen is known).

*Solvents.* Butyl acetate, cyclohexanone, decalin (mixture of isomers), butyl propionate, methyl ethyl ketone and tetralin, all analytical purity grade, were redistilled. Methyl benzoate, dimethyl phthalate and butylcellosolve were purified by column distillation.

*Viscometry.* Viscosities of dilute and concentrated solutions (solutions having a higher concentration were prepared in conical flasks by stirring with steel balls while rotating the flasks on an inclined plane; all solutions were filtered under pressure through fritted glasses S2) were measured in capillary viscometers of the Ubbelohde type (shear stress c.  $10 \text{ dyn cm}^{-2}$ ); corrections for losses of kinetic energy, the end effect and drainage effect were neglected because of high flow times. Intrinsic viscosity and the Huggins constant were obtained by extrapolation according to Heller's method<sup>20</sup>. Absolute viscosities were determined by direct calculation from the flow time using a relationship determined from viscosity measurements in a series of sucrose calibration solutions. The solution densities were determined pycnometrically (5 ml in vol.). Measurements carried out with a Weissenberger rheogoniometer confirmed that the dependence of viscosity on shear stress under experimental conditions in capillary viscometers was negligibly small for all systems under investigation, so that the viscosities thus obtained could be regarded as values determined at zero shear stress.

## RESULTS AND DISCUSSION

The dependence of viscosity on concentration for dilute polymer solutions can very adequately be described by Staudinger's equation<sup>21</sup>

$$\ln \eta_r = [\eta] c + (k - 0.5) [\eta]^2 c^2 + \dots; \quad (2)$$

$\eta_r$  is relative viscosity given by the ratio of the viscosities of solution and solvent  $\eta_s$ ,  $[\eta]$  is intrinsic viscosity,  $k$  is the Huggins interaction constant and  $c$  is concentration expressed in  $g$  of the polymer per 100 ml of solvent. From Eq. (2) we have for the contribution of the polymer to the flow activation energy

$$\begin{aligned} \Delta E &= E - E_s = -RT^2(\partial \ln \eta_r / \partial T) = \\ &= -RT^2\{c[\eta] [(\partial \ln [\eta] / \partial T) + (\partial \ln c / \partial T)] + c^2[\eta]^2 [(\partial k / \partial T) + \\ &\quad + 2(k - 0.5) (\partial \ln [\eta] / \partial T) + 2(k - 0.5) (\partial \ln c / \partial T)]\}. \end{aligned} \quad (3)$$

The initial slope of the  $\Delta E$  vs  $c$  dependence at zero concentration is given by

$$s = (\partial \Delta E / \partial c)_{c=0} = -RT^2[\eta] [(\partial \ln [\eta] / \partial T) + (\partial \ln \rho_s / \partial T)], \quad (4)$$

where  $\rho_s$  is the solvent density. It can be seen that the sign of the slope  $s$  is exclusively determined by the temperature dependence of intrinsic viscosity and solvent density.

Let us now examine under what circumstances the addition of the polymer component to the solvent will reduce the resistance of the intermolecular forces, *i.e.* when  $s$  is negative. According to Eq. (4), the inequality

$$(\partial \ln [\eta] / \partial T) + (\partial \ln \rho_s / \partial T) > 0 \quad (5)$$

or

$$(\partial \ln [\eta] / \partial T) > (\partial \ln \bar{v}_1 / \partial T) \quad (6)$$

should be fulfilled, where  $\bar{v}_1$  is the specific volume of the solvent. This means that some increase in temperature must cause a larger expansion of the volume of the solution limited by the polymer coil than of the volume of the same weight amount of solvent without polymer. In other words, the degree of expansion of the volume of the system due to a change in the temperature will increase if the polymer component is added to the solvent.

The temperature dependence of the specific volume of the solvent is positive for usual solvents and  $\partial \ln \bar{v}_1 / \partial T$  varies with a scatter of several tens of per cent around  $1 \cdot 10^{-3}$ . The temperature dependence of intrinsic viscosity can vary. We expressed it by deriving Flory's expression<sup>22</sup>

$$[\eta] = \Phi(\bar{r}_0^2/M)^{3/2} M^{1/2} \alpha^3 \quad (7)$$

with respect to temperature as

$$(\partial \ln [\eta]/\partial T) = (\partial \ln \Phi/\partial T) + \frac{3}{2}(\partial \ln \bar{r}_0^2/\partial T) + (\partial \ln \alpha^3/\partial T); \quad (8)$$

$(\bar{r}_0^2)^{1/2}$  is the root mean square end-to-end distance of an unperturbed macromolecular coil and  $\alpha^3$  is the expansion factor).  $\Phi$  is Flory's parameter; it is constant for polymers of the vinyl type where the polymer coil is practically impermeable to the solvent.

According to Flory's theory the dependence of the expansion factor on the thermodynamic quality of the solvent is given by

$$\alpha^5 - \alpha^3 = K(\bar{v}^2/v_1)(\bar{r}_0^2/M)^{-3/2} \psi(1 - \Theta/T) M^{1/2} \quad (9)$$

( $K = 2.86 \cdot 10^{-24}$ ,  $\bar{v}$  is the partial specific volume of the polymer,  $v_1$  is the molar volume of the solvent,  $\psi$  is the entropic interaction parameter of the polymer-solvent system, and  $\Theta$  is the Flory temperature). By using Eqs (6), (8) and (9) and assuming a constant  $\Phi$  one can calculate the temperature dependence of intrinsic viscosity and determine the condition for the negative slope ( $s$ ) as

$$\begin{aligned} & \frac{3}{2}(\partial \ln \bar{r}_0^2/\partial T) + [3(\alpha^5 - \alpha^3)/(5\alpha^5 - 3\alpha^3)] [2(\partial \ln \bar{v}/\partial T) - \\ & - (\partial \ln v_1/\partial T) - \frac{3}{2}(\partial \ln \bar{r}_0^2/\partial T)] - 1/T + \\ & + (3/T) \{K\bar{v}^2\psi M^{1/2}/[(5\alpha^5 - 3\alpha^3)(\bar{r}_0^2/M)^{3/2} v_1]\} > \\ & > (\partial \ln \bar{v}_1/\partial T). \end{aligned} \quad (10)$$

Under the  $\Theta$ -conditions the second term is zero and the relationship is reduced to the condition

$$\frac{3}{2}(\partial \ln \bar{r}_0^2/\partial T) + 3/\Theta \{K\bar{v}^2\psi M^{1/2}/2(\bar{r}_0^2/M)^{3/2} v_1\} > (\partial \ln \bar{v}_1/\partial T). \quad (11)$$

The coefficient of the temperature dependence of unperturbed dimensions depends individually on the polymer structure<sup>2,3</sup>. For  $\partial \ln \bar{r}_0^2/\partial T$  both positive (polystyrene, polybutene, poly(dimethyl siloxane), rubber) and negative (poly(2-methylpropene), polymethylene) values are given lying in an interval  $c. \pm 1 \cdot 10^{-3}$ . Table I gives a comparison of the values of the first term  $A = (3/2)(\partial \ln \bar{r}_0^2/\partial T)$ , of the second term  $B = (3/\Theta) K\bar{v}^2\psi M^{1/2}/2(\bar{r}_0^2/M)^{3/2} v_1$  and of the third term  $C = \partial \ln \bar{v}_1/\partial T$  for poly(2-methylpropene), polystyrene and poly(dimethylsiloxane), mol.wt.  $10^4$  (approximately the lower limit of molecular weights where Flory's theory can still be applied and where the characteristic ratio  $\bar{r}_0^2/M$  is independent of molecular weight) in the  $\Theta$ -solvent. The interaction constants have been taken from the literature<sup>2,4,25</sup>. The sum  $A + B$  clearly prevails over the term  $C$ , even though the term  $A$  is negative so that inequality (11) is always fulfilled and the initial slope of the dependence of  $\Delta E$  on polymer concentration for all the systems mentioned above is negative.

The second term  $B$  increases with increasing molecular weight and the prevalence of the left side increases. This explains the initial decrease in  $\Delta E$  with concentration experimentally found for vinyl polymers in the  $\Theta$ -systems, as well as the dependence of the initial slope on molecular weight<sup>10-15</sup>.

The improvement of the thermodynamic quality of solvent or the increase in the expansion coefficient is reflected in expression (10) so that the second (negative) term increases while the third (positive) decreases. This will have as a consequence that the total value of the left side of the inequality will also decrease with increasing  $\alpha^3$ , the negative initial value of the slope will decrease and pass to positive values. Accordingly, the initial slope of thermodynamic dependences in thermodynamically good solvents is predominantly positive.

The smaller flexibility of the macromolecular chain will cause a higher permeability of the polymer coil for the solvent, which will be reflected in a change in  $\Phi$  or in its temperature dependence. According to Kirkwood and Riseman<sup>26</sup>, the parameter  $\Phi$  is determined by the permeability function  $X F(X)$  obeying the relationship

$$\Phi = (\pi/6)^{3/2} (N_A/100) X F(X) \quad (12)$$

( $N_A$  is the Avogadro number). As indicated by Marrian and Hermans<sup>27</sup> and Burchar<sup>28</sup>, the function  $X F(X)$  depends on the characteristic ratio of the coil ( $\bar{r}_0^2/M$ ) and on the molecular weight  $M$  according to

$$X F(X) = [X F(X)]_\infty m/(1 + m), \quad (13)$$

where  $m$  is proportional to  $(\bar{r}_0^2/M)^{-1/2} M^{1/2}$  and  $[X F(X)]_\infty$  is the limiting value of the permeability function for an impermeable coil. The differentiation of  $\Phi$  with respect to temperature

$$\partial \ln \Phi / \partial T = -[\frac{1}{2}(1 + m)] [\partial \ln \bar{r}_0^2 / \partial T], \quad (14)$$

TABLE I

Terms from Eq. (11) for Polymer with Molecular Weight  $M=10^4$

$$A = (3/2) (\partial \ln \bar{r}_0^2 / \partial T), \quad B = (3/\Theta) K \bar{v}^2 \psi M^{1/2} / 2(\bar{r}_0^2/M)^{3/2} \bar{v}_1, \quad C = \partial \ln \bar{v}_1 / \partial T.$$

| Polymer                | Solvent             | $A \cdot 10^3$ | $B \cdot 10^3$ | $C \cdot 10^3$ |
|------------------------|---------------------|----------------|----------------|----------------|
| Poly(2-methylpropane)  | benzene             | -0.42          | 8.2            | 1.25           |
| Polystyrene            | decalin             | 0.66           | 5.7            | 1.63           |
| Poly(dimethylsiloxane) | methyl ethyl ketone | 1.06           | 6.5            | 1.33           |

represents a term which should be added to the left side of inequality (10). For more rigid macromolecular chains, such as *e.g.* those of cellulose nitrate, measurements of the temperature dependence of the second virial coefficient gave a very small third term in Eq. (8), virtually negligible with respect to the first two<sup>29</sup>. The temperature dependence of intrinsic viscosity (Eq. (8)) is then described by a simple expression

$$\partial \ln [\eta] / \partial T = (\partial \ln \bar{r}_0^2 / \partial T) \left[ \frac{1}{2} - \frac{1}{2}(1 + m) \right]. \quad (15)$$

The value of the second term in square brackets,  $1/2(1 + m)$ , varies depending on the molecular weight of the polymer from  $1/2$  (for  $M = 0$ ) to zero (for  $M = \infty$ ) and for sufficiently high molecular weight it can be neglected. Consequently, the temperature dependence of intrinsic viscosity is exclusively determined by the term  $\partial \ln \bar{r}_0^2 / \partial T$ , which is strongly negative<sup>29</sup>; therefore, the right side of inequality (6) is unambiguously greater and the slope  $s$  is markedly positive. This explains the step increase in  $\Delta E$  with concentration for cellulose derivatives, much greater than for vinyl polymers in thermodynamically good solvents.

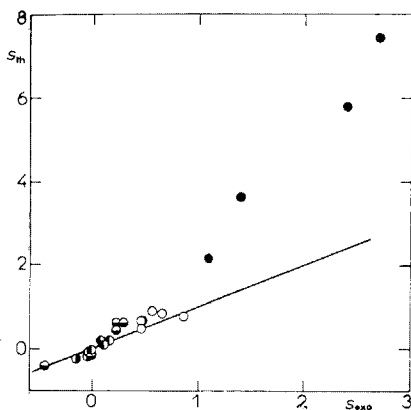


FIG. 1

Correlation of Experimental and Calculated Values of Initial Slopes of Concentration Dependence of Differences of Flow Activation Energies between Solution and Solvent

Measured data: ● polystyrene in decalin, dimethyl phthalate, cyclohexanone and tetralin; ○ cellulose nitrate in cyclohexanone, methyl ethyl ketone, butylcellosolve, butyl acetate, methyl benzoate and dimethyl phthalate; reported data: ● poly(vinyl acetate)<sup>12</sup> ( $M = 1.48 \cdot 10^5$ ) in methanol, toluene, acetone, dioxane, and chloroform; ● poly(methyl methacrylate)<sup>13</sup> ( $M = 1.22 \cdot 10^5$ ) in acetone, toluene, chloroform and benzene; ● cellulose nitrate<sup>11</sup> ( $M = 1 \cdot 10^5$ ) in acetone, methyl acetate, pentyl methyl ketone and butyl acetate (solvents are given in the order of increasing  $s_{\text{exp}}$ ) — theory (straight line with unit slope).

Fig. 1 shows the correlation of experimental values of the initial slope,  $s_{\text{exp}}$ , determined from the direct plot  $\Delta E$  vs  $c$ , and of the values of  $s_{\text{th}}$  calculated from relationship (4). Data for the vinyl polymers were taken from the literature for poly(methyl methacrylate) and poly(vinyl acetate)<sup>14</sup>; for polystyrene they were obtained by measurements. Both foreign<sup>11</sup> and our own results were used for cellulose nitrate. The dependence of both quantities in the positive and negative region is obvious. The corresponding values of  $s_{\text{exp}}$  and  $s_{\text{th}}$  are almost identical for the vinyl polymers and our sample of cellulose nitrate. The  $s_{\text{th}}$  values for cellulose nitrate calculated from data taken from the literature<sup>11</sup> are higher and the departure of the points from the  $s_{\text{exp}} = s_{\text{th}}$  increases with  $s_{\text{exp}}$ . The cause can be seen in an inadequate extrapolation of intrinsic viscosities from the region of too high concentrations.

It follows from experimental measurements that in those cases where the initial slope is positive (solutions of cellulose nitrate and vinyl polymers in good solvents) the experimental course of the dependence  $\Delta E$  vs  $c$  at low and higher concentrations of the polymer remains monotonically increasing. In poor quality solvents the effect of interaction terms of the series expansion (2) leads to a reverse dependence after a short decrease, and  $\Delta E$  also goes on increasing with polymer concentration. To obtain a universal theoretical function describing these courses would require as a basis a relationship expressing viscosity over a broad range of concentrations, solvent quality, and chain flexibility. Unfortunately, no such expression has been derived so far.

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