

On the Factors Governing the Pressure Dependence of the Viscosity of Moderately Concentrated Polymer Solutions*

H. GEERISSEN, J. R. SCHMIDT, and B. A. WOLF, *Institut für Physikalische Chemie der Universität Mainz, D-6500 Mainz, Germany, and Sonderforschungsbereich 41, Chemie und Physik der Makromoleküle, Mainz, Germany*

Synopsis

Viscosity measurements were carried out as a function of pressure and temperature with solutions of polystyrene in eight (endothermal) θ -solvents at the respective critical composition by means of a Searle-type apparatus. A rolling-ball viscometer was used for the investigation of the pure solvents. In all cases the viscosity coefficient increases in a more or less exponential manner when the pressure is raised. For θ -conditions, the volumes of activation of the solutions exceed that of the pure solvent by typically 10–15%. The exact amount of this extra effect stemming from the presence of the polymer and its variation with temperature can be qualitatively correlated with the heats of mixing. The ratio of the viscosity of the solution at 1000 and 1 bar, respectively, can be varied for a given solvent power (θ -temperature) by the choice of the solvent from ca. 2 (cyclopentane) to 4 (*trans*-decalin). Within a given system, the maximum effects that can be realized by a change of the solvent power via the variation of temperature ranges from ca. 3 to 6 (*tert*-butylacetate).

INTRODUCTION

Pressure influences on the viscosity of polymer-containing liquids play an important role in practice (polymer additives to motor oils, mineral oil recovery, etc.) and one would like to know in advance how much the viscosity increases for a particular system when the pressure is raised. The present report therefore deals with the following questions: To what extent are the pressure effects already fixed by the choice of the solvent, within which margins can they be altered by varying the temperature and what are the effects of the molecular weight of the polymer?

The influence of temperature has already been reported in a preceding article.¹ It had turned out that the temperature mainly influences the pressure effects via the thermodynamic interactions: the better the solvent, the less the viscosity rises with pressure. In order to filter out the influences which are a direct result of the chemical and geometric nature of the solvent, comparisons therefore must be carried out at identical thermodynamic conditions. There are two natural choices: θ or athermal conditions. Since the pressure effects are greater for the former and since they are in general easier to realize, the following experiments were all carried out in the region of endothermal θ -conditions. Three groups of θ -solvents were selected: alicyclic hydrocarbons, substituted *n*-alkanes, and carboxylic esters.

Data concerning the pressure influence on the viscosity of the pure solvents,

* Part of theses of H. G. and J. R. S.

which are needed for the discussion of the above questions, were taken from the literature whenever available. For the majority of the solvents, however, our own measurements were necessary.

EXPERIMENTAL

Materials

The measurements were performed with three polystyrene (PS) samples obtained from Pressure Chemical Company. The molecular weights and nonuniformities, $U = (M_w/M_n) - 1$, of the samples, as given by the producer, are: PS 600,000, Lot. No. 60914, $U \leq 0.10$; PS 390,000, Lot. No. 3b, $U \leq 0.10$; PS 100,000, Lot. No. 70111, $U \leq 0.06$.

A list of the solvents is given in Table I.

Apparatus and Procedures

Before starting the viscosity measurements, cloud point curves were taken for all systems by slowly ($0.1^\circ\text{C}/\text{min}$) cooling glass tubes containing the solution samples. The temperature at which the scale on the backside of the tubes could no longer be read was regarded as cloud point.

Viscosities of the polymer solutions were measured by means of a Searle-type Haake viscometer, described in more detail elsewhere.² The viscosity coefficients η stem from automatically recorded flow curves. The data for the solvents were obtained by means of a self-constructed rolling-ball viscometer. Details of this apparatus will be reported soon.³

RESULTS

Cloud Point Curves at Atmospheric Pressure

In order to ensure comparable thermodynamic conditions, all viscosity measurements had to be performed with solutions of approximately critical com-

TABLE I
List of Solvents

Solvent	Abbreviation	Producer/purity
1-Chlorododecane	1-ClC ₁₂	Fluka, puriss $\geq 99\%$
1-Chlorodecane	1-ClC ₁₀	Merck-Schuchardt, for synthesis $\geq 95\%$ (rectified over silver-mantle column)
1-Phenyldecane	1-PhC ₁₀	Merck-Schuchardt, for synthesis $\geq 97\%$
Cyclohexane	CH	Merck, p.a. $\geq 99.5\%$
Cyclopentane	CP	Fluka, purum $\geq 99\%$
<i>trans</i> -Decalin	TD	Merck-Schuchardt, for synthesis $\geq 96\%$
<i>tert</i> -Butylacetate	TBA	Merck-Schuchardt, for synthesis $\geq 99\%$ (rectified over silver-mantle column)
Diethyl malonate	DEM	Fluka, puriss. $\geq 99\%$

position. Since there were no critical data available for the present systems, the critical weight fraction of the polymer, w_{2c} , and the critical temperature T_c were determined from cloud point curves. The shape of all curves was as expected for polymers with narrow-molecular-weight distribution, i.e., there is no depression indicating a shift of the critical point out of the maximum of the cloud point curve. In fact, for polystyrene with $U \leq 0.1$, the critical point usually coincides with the maximum of the cloud point curve.⁴ The thus obtained critical data and θ -temperatures are summarized in Table II.

Due to the small curvature of the cloud-point curves in the critical region, w_{2c} can be determined with low accuracy only (ca. ± 0.5 wt-%).

TABLE II
Critical Data and θ -Temperatures of the Systems

System	θ , °C	w_{2c} , wt % PS	T_c , °C
1-ClC ₁₂ /PS 600,000	58.6 ⁵	6.0	44.7
/PS 390,000		8.0	41.1
/PS 100,000		14.0	27.8
1-ClC ₁₀ /PS 600,000	6.6 ⁵	5.5	0.9
1-PhC ₁₀ /PS 600,000	28.0 ⁶	6.0	22.3
CH/PS 600,000	34.0 ⁷	6.0	28.3
CP/PS 600,000	20.0	5.0	16.1
TD/PS 600,000	22.5	5.5	15.8
DEM/PS 600,000	31.0 ⁷	4.5	20.8

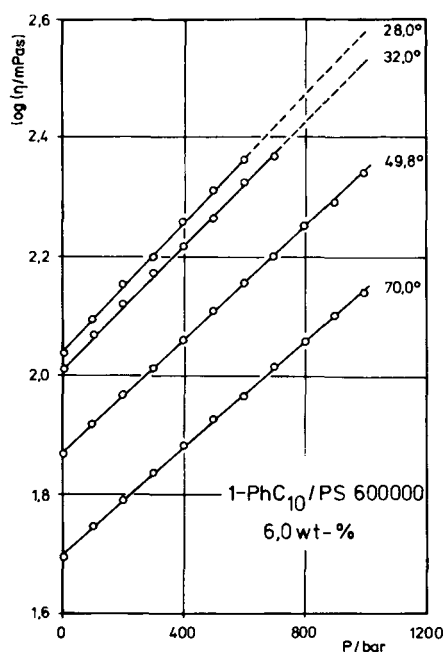


Fig. 1. Pressure dependence of the viscosity coefficient η for the 1-PhC₁₀/PS 600,000 system (critical concentration) and temperature (°C).

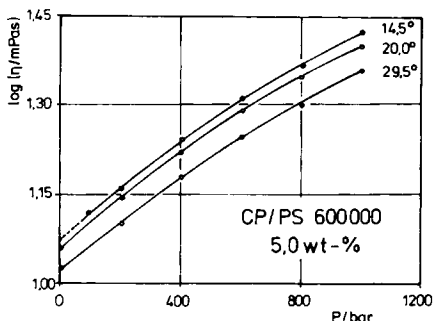


Fig. 2. Pressure dependence of the viscosity coefficient η for the CP/PS 600,000 system (critical concentration) and temperature ($^{\circ}\text{C}$).

Viscosity Measurements

Polymer Solutions

For all systems, linear relations between shear rate (max. 600 s^{-1}) and shear stress were observed, i.e., all solutions behave Newtonian. Figure 1 gives an example for the typical linear dependence of $\log \eta$ on pressure. Figure 2 shows the results for the only exception among the present systems (CP/PS).

The apparent volume of activation for the viscous flow, V^{\ddagger} , can be determined according to Bondi⁸ by means of

$$\left(\frac{\partial \ln \eta}{\partial P}\right)_{T,c} = \frac{V^{\ddagger}}{RT} \quad (1)$$

For practical use, the coefficient $f_{1000} = \eta_{1000 \text{ bar}}/\eta_{1 \text{ bar}}$ is sometimes advantageous. The characteristic parameters of the pressure dependence of the viscosity are summarized in Table III. Furthermore, the factor f_{1000} is graphically shown as a function of the distance to the θ -temperature ($T - \theta$) in Figure 3.

According to de Guzman,⁹ the apparent energy of activation for the viscous flow, E^{\ddagger} , can be obtained from plots of $\ln \eta$ vs. $1/T$:

$$\left(\frac{\partial \ln \eta}{\partial(1/T)}\right)_{P,c} = \frac{E^{\ddagger}}{R} \quad (2)$$

The activation energies were calculated for pressures of 1, 400, and 1000 bar. As can be seen from Table IV, E^{\ddagger} is raised by increasing pressure. Comparing the pressure dependence of E^{\ddagger} and the temperature dependence of V^{\ddagger} offers an opportunity to check the consistency of the measurements as long as η is a variable of state.

On the basis of eqs. (1) and (2), one arrives at

$$\begin{aligned} \left(\frac{\partial E^{\ddagger}}{\partial P}\right)_{T,c} &= -RT^2 \left[\frac{\partial}{\partial P} \left(\frac{\partial \ln \eta}{\partial T} \right)_{P,c} \right]_{T,c} = -RT^2 \left[\frac{\partial}{\partial T} \left(\frac{\partial \ln \eta}{\partial P} \right)_{T,c} \right]_{P,c} \\ &= -T^2 \left[\frac{\partial}{\partial P} \left(\frac{V^{\ddagger}}{T} \right) \right]_{P,c} \\ &= V^{\ddagger} - T \left(\frac{\partial V^{\ddagger}}{\partial T} \right)_{P,c} \end{aligned} \quad (3)$$

TABLE III
Volume of Activation V^\ddagger for the Viscous Flow and Coefficient f_{1000} at Different Temperatures

System	T, °C	f_{1000}	V^\ddagger , cm ³ /mol
1-ClC ₁₂ /PS 600,000	48.0	2.97	29.1
	58.4	2.83	28.7
	73.2	2.66	28.2
	89.9	2.47	27.2
1-ClC ₁₂ /PS 390,000	48.2	2.95	28.9
	58.1	2.78	28.2
	73.3	2.60	27.5
1-ClC ₁₂ /PS 100,000	48.3	3.05	29.8
	58.2	2.75	27.9
	72.8	2.54	26.8
1-ClC ₁₀ /PS 600,000	6.6	3.07	26.2
	29.5	2.81	26.0
	48.0	2.60	25.7
	58.6	2.54	25.5
1-PhC ₁₀ /PS 600,000	28.0	3.44	31.0
	32.0	3.31	30.4
	49.9	2.99	29.3
	70.0	2.82	29.6 ^a
	29.05	4.20 ^b	36.0
CH/PS 600,000	34.0	3.80	34.1
	43.6	3.40	32.3
	14.5	2.23	19.2
CP/PS 600,000	20.0	2.20	19.2
	29.5	2.16	19.3
	18.0	4.37	35.7
TD/PS 600,000	22.4	3.97	33.7
	34.7	3.32	30.7
	49.7	2.90	28.6
	23.2	2.75	24.9
	31.2	2.59	24.1
DEM/PS 600,000	41.0	2.49	23.8

^a The reincrease of V^\ddagger in this case can probably be explained by the approach to the exothermal θ -temperature⁶ by analogy with a previous observation.¹

^b The pressure range accessible in this system is limited by the high and strongly pressure-dependent melting point of CH. The indicated values of f_{1000} were obtained by an extrapolation of the $\log \eta$ vs. p curves measured up to 500 bar.

For substances showing no or only small changes of V^\ddagger with temperature, the activation volume becomes identical with the pressure dependence of the activation energy.

Figure 4 shows the dependence of E^\ddagger on p for TD/PS 600,000, and Figure 5 the corresponding dependence of V^\ddagger on T . The quantities necessary for the examination of eq. (3), are collected below:
(test of consistency, for TD/PS 600,000)

T, K	$\left(\frac{\partial V^\ddagger}{\partial T}\right)_{P,c}, m^3/mol \cdot K$	$\left(\frac{\partial E}{\partial P}\right)_{T,c}, m^3/mol$	$V^\ddagger - T \left(\frac{\partial V^\ddagger}{\partial T}\right)_{P,c}, m^3/mol$
295.5 ₅ = θ	-3.7×10^{-5}	9.0×10^{-5}	14.3×10^{-5}

Taking into account that there are six steps (among which are four differentiations) necessary for the evaluation according to eq. (3) and in view of the experimental errors, the agreement seems quite satisfactory.

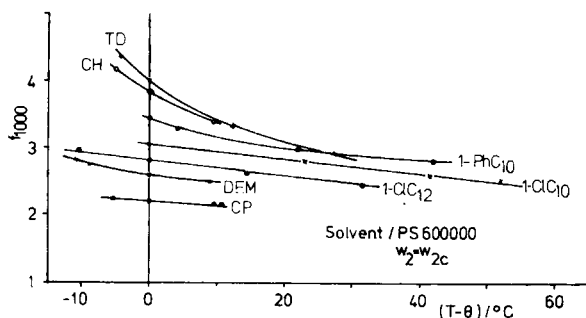


Fig. 3. Plot of $f_{1000} = \eta_{1000 \text{ bar}} / \eta_{1 \text{ bar}}$ vs. $(T - \theta)$ for the indicated systems.

The influence of chain length was studied for the system 1-ClC₁₂/PS by means of three molecular weights. The results are also summarized in Table III and are graphically shown in Figure 6.

Solvents

Table V contains the values for f_{1000} and V_0^\ddagger obtained from measurements in the rolling ball viscometer. For CH and TD, the corresponding literature data are listed. For each solvent, the θ -temperature of the respective polymer solution was chosen as one measuring temperature in view of the comparison of the different solutions. In order to enable a direct comparison of the pure solvents, too, 30°C was chosen as a second common temperature. In Figures 7 and 8, the results are plotted as $\log \eta$ vs. p .

DISCUSSION

Influence of Solvent and Molecular Weight of the Polymer

As already mentioned (Figs. 1 and 2), the viscosities of the polymer solutions increase with pressure in a nearly exponential manner. The f_{1000} and V^\ddagger values contained in Table III show how the effects vary from solvent to solvent and how they change with temperature. In order to lay the specific influences of the solvents bare, the same thermodynamic conditions must prevail in all systems. The measurements were therefore performed with solutions of critical compo-

TABLE IV
Energy of Activation E^\ddagger for Viscous Flow at Different Pressures

System	E^\ddagger , kJ/mol		
	1 bar	400 bar	1000 bar
1-ClC ₁₂ /PS 600,000	19.2	20.8	23.0
1-ClC ₁₀ /PS 600,000	11.7	13.1	14.6
1-PhC ₁₀ /PS 600,000	16.0	17.6	20.1
CH/PS 600,000	14.1	18.2	—
		(350 bar)	
CP/PS 600,000	5.5	6.9	7.3
TD/PS 600,000	11.9	15.8	21.0
DEM/PS 600,000	12.5	14.1	16.7

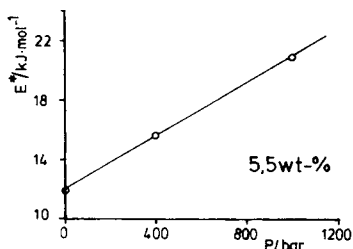


Fig. 4. Pressure dependence of activation energy E^\ddagger for *trans*-decalin/polystyrene 600,000.

sitions and in the region of the θ -temperature at $p = 1$ bar. Even if $T = \theta_1$ bar in all cases, strict equivalence is normally lost, however, as the pressure is raised. Figure 9 shows f_{1000} for all solutions of PS 600,000 at their corresponding θ -temperature under atmospheric pressure. In addition, this graph contains the results for the system TBA/PS 110,000 ($w_2 = 15$ wt %) which have been reported elsewhere.¹

The following features concerning the influence of the solvents can be seen from this scheme:

(a) Long-chain hydrocarbons: In this group, the f_{1000} values of the systems 1-ClC₁₂/PS and 1-ClC₁₀/PS are equal within the limits of error ($\pm 5\%$), whereas the exchange of the halogen against the larger phenyl group increases f_{1000} by about 15%.

(b) Alicyclic hydrocarbons: Two facts seem noteworthy with these systems—the comparable f_{1000} values of the CH/PS and TD/PS systems and the much smaller f_{1000} of the CP/PS system.

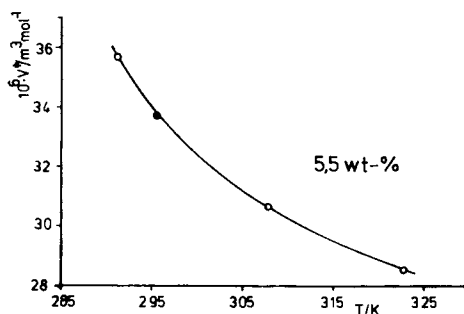


Fig. 5. Temperature dependence of activation volume V^\ddagger for *trans*-decalin/polystyrene 600,000.

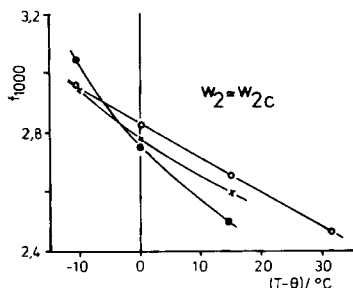


Fig. 6. Plot of $f_{1000} = \eta_{1000 \text{ bar}} / \eta_{1 \text{ bar}}$ vs. $(T - \theta)$ for 1-chlorododecane/polystyrene and different molecular weights: 600,000 (O); 390,000 (X); 100,000 (●).

TABLE V
Volume of Activation for Viscous flow V_0^\ddagger and Coefficient f_{1000} as Function of Temperature for Pure Solvents

Solvents	$T, ^\circ\text{C}$	f_{1000}	$V_0^\ddagger, \text{cm}^3/\text{mol}$
1-ClC ₁₀	6.6	2.85	24.4
	30.0	2.56	21.7
	60.0	2.36	23.8
1-PhC ₁₀	28.0	2.95	27.1
	30.0	2.93	27.1
CP	20.0	2.10	18.1
	30.0	2.10	18.7
CH	30.0	3.19 ^{10a}	29.2
	34.0	3.09 ¹⁰	28.8
	30.0	2.96 ¹¹	27.4
TD	25.0	3.15 ¹²	28.4
	30.0	2.91 ¹³	28.9
	22.5	3.29 ^b	29.3
TBA	1.6	2.89	24.2
	27.1	2.59	23.8
	54.3	2.44	24.3
	80.2	2.45	26.3

^a See footnote Table III.

^b Calculated from viscosity data for 25 and 30°C.

(c) Carboxylic esters: The difference between DEM/PS and TBA/PS is comparable to the difference between CH/PS and CP/PS. TBA/PS shows an f_{1000} value which is about 40% higher than that of DEM/PS.

Concerning the influence of molecular weight, when comparing f_{1000} for the three representatives of the systems 1-ClC₁₂/PS (600,000; 390,000; and 100,000)

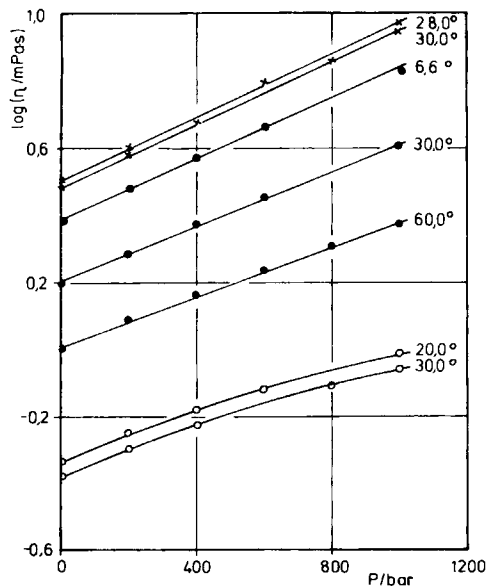


Fig. 7. Pressure dependence of the viscosity coefficient η for the pure solvents cyclopentane (O), 1-chlorododecane (●), and 1-phenyldecane (×) at the indicated temperatures ($^\circ\text{C}$).

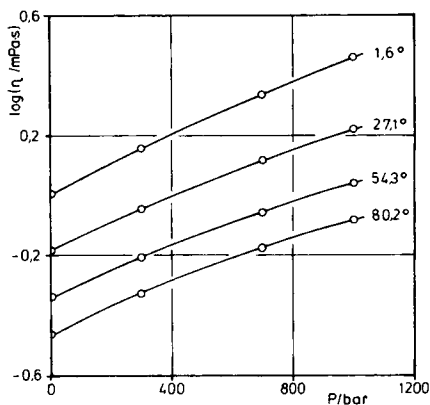


Fig. 8. Pressure dependence of the viscosity coefficient η of the pure solvent *tert*-butyl acetate at the indicated temperatures ($^{\circ}\text{C}$).

at $T = \theta \approx 58^{\circ}\text{C}$ and at the respective critical composition, it becomes obvious that the influence of the polymer chain length is, at least in this case, of only minor importance. If, however, one compares the pressure influence at a given constant concentration, significant differences show up. In Figure 10, the ratio $(V^{\ddagger}/V_0^{\ddagger})_{\theta}$ is shown as a function of the weight fraction w_2 of the polymer, assuming that this ratio increases linearly with polymer concentration. From this figure one obtains the following values for f_{1000} for example at $w_2 = 6$ wt % PS (dotted line in Fig. 10): 2.52, 2.67, and 2.83. Furthermore, it should be noted (Fig. 6, Table III) that the temperature dependence of V^{\ddagger} or f_{1000} is slightly increased when the molecular weight is lowered. The same observation was made with TBA/PS 110,000 and 670,000.

Analogous to the behavior of polymer solutions, the viscosity of the solvents increases with pressure in an almost exponential manner. Comparing the f_{1000} values at 30°C leads to the following results (cf. Table V): The value of 1-PhC₁₀ is about 15% higher than that of 1-C₁₀; CH and TD do not differ appreciably, and CP shows the smallest value of f_{1000} , much smaller than that of CH.

Investigations of Kuss¹¹ have shown that f_{1000} is nearly independent of chain length within a homologous series when the lowest-molecular-weight members are excluded. On the other hand, the pressure dependence is increased by the build-in of bulky groups. This explains the larger f_{1000} value for 1-PhC₁₀ as compared with 1-C₁₀ and 1-C₁₂.

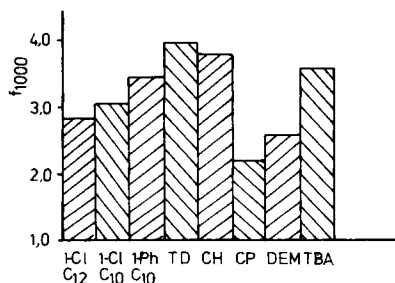


Fig. 9. Plot of $f_{1000} = \eta_{1000 \text{ bar}}/\eta_{1 \text{ bar}}$ for the indicated solvent/polystyrene 600,000 systems at $T = \theta$ and $w_2 = w_{2c}$. In the case of *tert*-butyl acetate/polystyrene, the molecular weight is 110,000, $\theta = 15.5^{\circ}\text{C}$ and $w_2 = 15.5$ wt %.

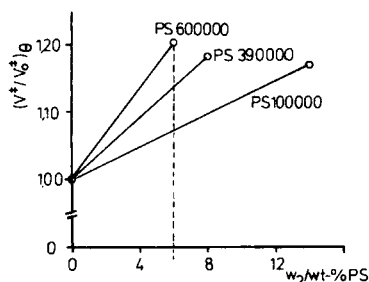


Fig. 10. Reduced volume of activation normalized to the solvent, $V^{\ddagger}/V_0^{\ddagger}$ (index 0 = solvent) as function of polymer concentration for the 1-chlorododecane/polystyrene system and the molecular weights 600,000; 390,000; and 100,000 at $T = \theta$.

The large difference in the f_{1000} values of the six-membered and the five-membered monocyclic compounds is not restricted to hydrocarbons. The same can be observed with the corresponding ketones and alcohols.¹¹ Generally, substances with six C atoms in a ring show a higher pressure dependence of viscosity than those with five atoms. An explanation for this finding is probably offered by the shape of the molecules. Near room temperature, CH exists almost exclusively in the stiff chair configuration; the C atoms are alternatingly arranged in two parallel planes (distance about 0.5 Å). CP, however, exists in an almost flat structure. According to Pitzer,¹⁴ the atoms are arranged in such a way that only one sticks out of the plane of the four other atoms by ca. 0.2 Å; this configuration is not fixed but rather fluctuating, so that alternatingly each C atom will get into this position.

The explanation for the great similarity of the f_{1000} values of CH and TD is, however, less obvious. If one looks at the molecular structure of the two substances, the change from CH to TD could be compared to a chain prolongation in the case of the aliphatic hydrocarbons. Naturally, this consideration does not hold true for the cis-isomer of decalin. Indeed, the f_{1000} value¹⁵ for cis-decalin is about 25% higher than that of the trans isomer as a result of the increased bulkiness. A similar situation is found with the cis-trans isomers of octahydroindene.¹⁵ Generally spoken, it seems that bulkier molecules show a higher pressure dependence of viscosity than less bulky molecules.

Hogenboom, Webb and Dixon¹⁵ tried to use the critical compressibility factor $Z_c = p_c V_c / RT_c$ as a measure of the "bulkiness" or "rigidity" of bicyclic compounds. Hirschfelder, Curtiss, and Bird¹⁶ could show that Z_c is indeed a rough measure for the symmetry and rigidity of a molecule. Usually Z_c decreases with increasing complexity of the structure. Hogenboom and co-workers tried to obtain a correlation between Z_c and the pressure dependence of the viscosity. They found that cis isomers have lower Z_c values and higher pressure dependences as compared to the trans isomers. This concept is, however, inapplicable to the monocyclic compounds CP and CH: both compounds have the same critical compressibility factor Z_c (0.276), although they differ widely in f_{1000} .

Within the limits of error, the same f_{1000} values were obtained for 1-ClC₁₀/PS and 1-ClC₁₂/PS; this also holds true for the pure solvents. An increase in f_{1000} by 15% due to the substitution of the chlorine atom by the phenyl group is observed with the pure solvent as well as with the solution. A comparable behavior of CH and TD is found with the polymer solutions as well as with the solvents.

The lowest f_{1000} values of all systems are observed for CP/PS; the same holds true for the pure solvents, among which CP shows the least pressure dependence.

For the above two groups of solvents, the solutions well reflect the behavior of the pure solvents, which in turn is, at least partly, determined by the molecular structure. A comparison of the molecular structures of the two esters DEM (dicarboxylic compound) and TBA (monocarboxylic compound) is not that easy. The higher pressure influence for the system TBA/PS is in accord with the experience that the introduction of bulky groups (*tert*-butyl group) increases the pressure influence.

Finally, it will briefly be discussed whether the pressure dependence of the viscosity of solutions can be forecast from the data of the pure solvents. For this purpose, the f_{1000} values for polymer solutions and solvents (index 0) at $T = \theta$ and the quotients $f_{1000}/(f_{1000})_0$ are summarized in Table VI. The data in column 4 show that the f_{1000} values of the polymer solutions are generally about 10–20% higher than those of the solvents. If the pressure dependence of the viscosity of the solvent is known, the behavior of the polymer solution can therefore probably be predicted within $\pm 10\%$.

Thermodynamic Influences

The results for constant thermodynamic conditions (w_{2c}, θ) demonstrate that f_{1000} values ranging from 2 (CP/PS) to 4 (CH/PS, TD/PS) can be obtained by variation of the solvent. Now we examine how the systems respond to the changes in solvent power induced by a variation of temperature. As can be seen from Figures 3 and 11, the dependence of f_{1000} and V^\ddagger upon temperature is very different for the different systems: for CP/PS it is extremely low, whereas the systems CH/PS and TD/PS show a high temperature dependence.

Earlier measurements for TBA/PS 110,000 have already demonstrated that V^\ddagger passes a minimum at the temperature at which the solution becomes athermal.¹ Therefore the ratio $V^\ddagger/V_{\text{ath}}$ or $(f_{1000})_\theta/(f_{1000})_{\text{ath}}$ can be considered as a measure of the maximum thermodynamic effects that can be realized within a given system by variation of temperature. For the two systems TBA/PS 110,000 and 1-PhC₁₀/PS 600,000, T_{ath} is known at least approximately so that the cor-

TABLE VI
Comparison of the f_{1000} -values for polymer solutions (PS 600,000) and solvents at $T = \theta$.

Solvent	f_{1000}	$(f_{1000})_0$	$f_{1000}/(f_{1000})_0$
1-ClC ₁₀ /PS	3.07	2.85	1.08
1-ClC ₁₂ /PS	2.83 ^a	2.36	1.20
1-PhC ₁₀ /PS	3.44	2.95	1.17
CH/PS	3.80	3.09	1.23
CP/PS	2.20	2.10	1.05
TD/PS	3.97	3.29	1.21

^a f_{1000} of 1-ClC₁₀ at the θ -temperature of 1-ClC₁₂.

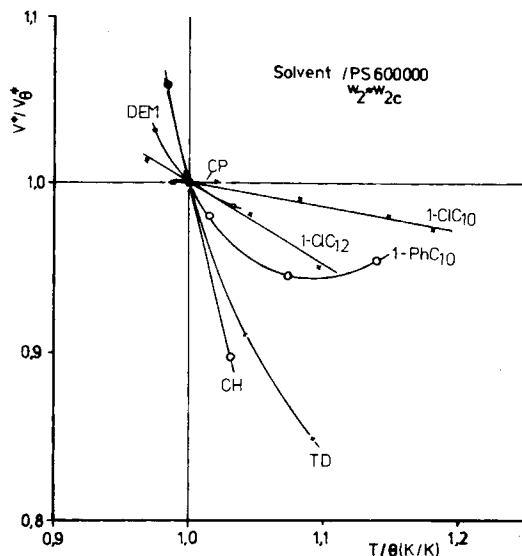


Fig. 11. Reduced volume of activation normalized to its value at the θ -temperature $V^{\ddagger}/V_{\theta}^{\ddagger}$ as function of T/θ (K/K) for the indicated systems.

responding information can be supplied:

System	θ , °C	T_{ath} , °C	$(f_{1000})_{\theta}/(f_{1000})_{\text{ath}}$	$V_{\theta}^{\ddagger}/V_{\text{ath}}^{\ddagger}$
1-PhC ₁₀ /PS 600,000	28.0	≈60	1.2	1.05
TBA/PS 110,000	15.5	41	1.3	1.2

The observed thermodynamic influences on V^{\ddagger} can be explained¹ by the fact that an increase in solvent power leads to a reduction in the number of intersegmental contacts, i.e., to a reduction of the "pull-along" effect that a given segment exerts on other segments. This reduces the size of the flow unit and consequently the activation volume which normally constitutes a certain percentage of it.

That the decrease in the pressure influences on the viscosity of the solution, which results from an increase in temperature, really stems from the change of the thermodynamic interaction and does not merely reflect the pressure dependence of the viscosity of the pure solvent can be seen from Figures 12 and 13. Here, the effects are compared in terms of the f_{1000} values, which are preferable

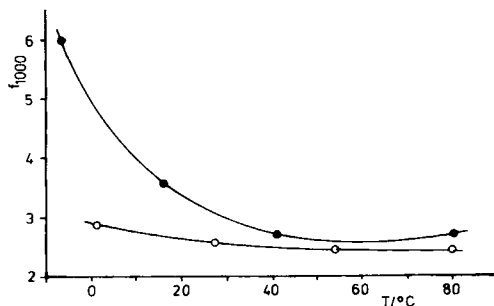


Fig. 12. Plot of $f_{1000} = \eta_{1000 \text{ bar}}/\eta_{1 \text{ bar}}$ as function of T (°C) for the system *tert*-butylacetate/polystyrene 110,000¹) (●) and for the pure solvent *tert*-butyl acetate (○).

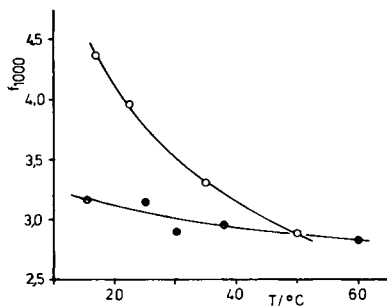


Fig. 13. Plot of $f_{1000} = \eta_{1000 \text{ bar}}/\eta_1 \text{ bar}$ as function of T ($^{\circ}\text{C}$) for the system *trans*-decalin/polystyrene 600,000 (O) and for the pure solvent *trans*-decalin (●,^{12,13} ●¹⁵).

for practical purposes. The theoretically more relevant temperature dependence of the activation volume of the solution in excess to that of the solvent ($V^{\ddagger} - V_0^{\ddagger}$) can be seen from Figure 14 for two systems.

In the light of the above, the hypothesis is near at hand that the extent of the “pull-along” effect for polymer solutions in different solvents but at the same Gibbs’ energy of mixing is correlated to the heats of mixing. If this were true, the excess volume of activation at the θ -temperature and its temperature dependence should increase in the same proportion as the heat of mixing when one goes from one θ -solvent to another.

The data necessary for an inspection of this idea are collected in Table VII. Unfortunately, the information concerning the Flory–Huggins parameter and

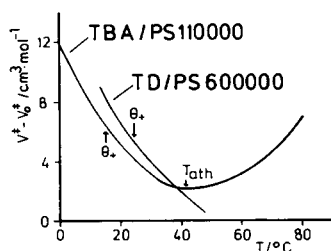


Fig. 14. Excess volume of activation ($V^{\ddagger} - V_0^{\ddagger}$) (index 0 = solvent) as function of T ($^{\circ}\text{C}$) for the indicated systems; T_{ath} is the temperature at which the system TBA/PS 110,000 becomes athermal.

TABLE VII
Collection of Data for the Discussion of the Influence of the Enthalpy of Mixing on the Rheological Behavior of Solutions of Polystyrene 600,000 in the Indicated Solvents^a

Solvent	$-A_{2,H}^{\theta} \times 10^4$, $\text{cm}^3/\text{g}^2\cdot\text{mol}$	$(V^{\ddagger} - V_0^{\ddagger})_{\theta}$, cm^3/mol	$-\left[\partial(V^{\ddagger}/V_{\theta}^{\ddagger})/\partial(T/\theta)\right]_{\theta}$	$(V_0^{\ddagger}/V_{\text{mol}})_{\theta}$
TBA	7.1 (PS 110000) ¹⁸	5.3	1.1	0.18
1-ClC ₁₀	7.4 (PS 406,000) ⁵	1.8	0.15	0.12
DEM	7.4 (PS 170,000) ⁵	—	0.8	—
1-PhC ₁₀	12.0 (PS 390,000) ⁶	3.9	1.5	0.11
TD	16.4 (PS 110,000) ¹⁷	4.4	2.3	0.18
CH	30.4 (PS 170,000) ⁷	5.3	3.3	0.26

^a In the case of TBA: polystyrene 110,000. The data in the last column are for the pure solvents.

its enthalpy part is not available for the present polymer concentrations, so that the second osmotic virial coefficient A_2 (zero at $T = \theta$) and its enthalpy part $A_{2,H}$ have to be used instead. A further difficulty lies in the fact that these enthalpy data have generally been obtained for lower-molecular-weight polystyrenes, so that a truly quantitative discussion is not possible. Nevertheless, the general tendency seems to be confirmed, as long as one compares solvents which are chemically and geometrically not too dissimilar.

Table VII also contains the ratios of activation volume and molar volume for the different pure solvents, and it is surprising to see that they also seem to correlate with $A_{2,H}$. A speculative explanation for this finding could be sought in the specific geometry of chemically similar solvent molecules: the bulkier the constitution, the higher the percentage of the molar volume that is needed as the activation volume for the motion of a solvent molecule past its neighbors in the pure state and the worse also the possibilities to interact with polymer segments in the solution, i.e., the higher the corresponding $|A_{2,H}|$ value.

CONCLUSIONS

The present results show that the pressure dependence of the viscosity of polymer solutions and the influence of temperature on it is already more or less fixed by the choice of the solvent.

If high f_{1000} values are required, bulky molecules (e.g., CH, TD) which themselves already show a high pressure dependence of viscosity must be used as solvents. Low f_{1000} values will be obtained if molecules with low bulkiness (e.g., the almost flat CP) are chosen. Long-chain solvent molecules (e.g., ClC₁₀, ClC₁₂) will give f_{1000} values that lie between these extremes. In the vicinity of the θ -temperature, f_{1000} normally is about 10–20% higher for the polymer solutions than for the corresponding pure solvent. In the case of endothermal solutions, f_{1000} decreases when the temperature is raised and athermal conditions are approached. The magnitude of f_{1000} and its variation with temperature depend on the enthalpy of mixing: highly endothermal systems (e.g., TD/PS, CH/PS) show the highest f_{1000} values and the highest temperature dependence of f_{1000} .

Note added in proof: The pressure dependence of the demixing of the present solutions was also studied viscometrically. The results are published in *Coll. Pol. Sci.*, **259**, 1214 (1981).

The authors gratefully acknowledge a stipend from the Max-Buchner-Stiftung.

References

1. J. R. Schmidt and B. A. Wolf, *Makromol. Chem.*, **180**, 517 (1979).
2. B. A. Wolf and R. Jend, *Macromolecules*, **12**, 732 (1979).
3. J. R. Schmidt and B. A. Wolf, in preparation.
4. B. A. Wolf and R. Jend, *Makromol. Chem.*, **178**, 1811 (1977).
5. T. A. Orofino, *J. Chem. Phys.*, **45**, 4310 (1966).
6. B. A. Wolf and H. Geerissen, *Makromol. Chem. Rapid Comm.*, to appear.
7. G. V. Schulz and H. Baumann, *Makromol. Chem.*, **60**, 120 (1963).
8. A. Bondi, *Ann. N.Y. Acad. Sci.*, **53**, 870 (1951).
9. J. de Guzman, *An. R. Soc. Esp. Fis. Quim.*, **11**, 353 (1913).
10. A. F. Collings and E. McLaughlin, *Trans. Farad. Soc.*, **67**, 340 (1971).
11. E. Kuss, *Z. Angew. Phys.*, **8**, 372 (1955).

12. E. Kuss and G. R. Schulze, in *Proceedings of World Petrol. Congr., 4th Rome, Proc. Sect. V*, 1955, p. 101.
13. J. M. Boelhouwer and L. H. Toneman, in *Proceedings of Conf. Lubrication and Wear, Inst. Mech. Eng.*, London, 1957, p. 214.
14. K. S. Pitzer, *Science*, **101**, 672 (1945); J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).
15. D. L. Hogenboom, W. Webb, and J. A. Dickson, *J. Chem. Phys.*, **46**, 2586 (1967).
16. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
17. M. Lechner and G. V. Schulz, *Eur. Polym. J.*, **6**, 945 (1970).
18. B. A. Wolf and H. J. Adam, *J. Chem. Phys.*, **75**, 4121 (1981).

Received June 8, 1981

Accepted August 25, 1981