1192 *Macromolecules* **1982**, *15*, 1192-1195

Pressure Dependence of Intrinsic Viscosities and Huggins Constants for Polystyrene in *tert*-Butyl Acetate

Jürgen R. Schmidt and B. A. Wolf*

Institut für Physikalische Chemie der Universität Mainz and Sonderforschungsbereich 41, D-6500 Mainz, West Germany. *Received February 19, 1982*

ABSTRACT: The viscosity of dilute solutions of polystyrene in *tert*-butyl acetate was measured at temperatures ranging from 1.6 to 130 °C and pressures up to 4000 bar by means of a rolling-ball viscometer. From information concerning the second osmotic virial coefficient, A_2, it is known that the present system exhibits an endothermal Θ temperature at 15.5 °C, becomes athermal at 45 °C, and reaches an exothermal Θ point at 109.5 °C at atmospheric pressure. The present viscosity measurements show that the intrinsic viscosity $[\eta]$ assumes maximum values for variable pressure as well as for variable temperature. Huggins constants and $[\eta]$ change in opposite directions; different relations between these two quantities are, however, observed for pressures below and above the maximum in $[\eta](p)$. The highest pressure influence on $[\eta]$ is observed at 130 °C, where the increase is 75% on going from 1 to 3500 bar. For atmospheric pressure a one-to-one correspondence between $[\eta]$ and A_2 is discernible; $[\eta]$ assumes its maximum value when the solution becomes athermal; this maximum is shifted by +6 K/100 bar on the application of pressure. From the coil expansion factor α_η ($\alpha_\eta^3 = [\eta]/[\eta]_\Theta$) it is possible to estimate A_2 theoretically. To this end one can either set $\alpha_\eta = \alpha_s$ (α_s is the expansion factor of the radius of gyration) or $\alpha_\eta^3 = \alpha_s^{2.43}$. The A_2 values obtained under the first assumption are closer to the measured $A_2(T;$ 1 bar) than those resulting from the second.

Introduction

In context with our investigations of the pressure influences on the thermodynamic and rheological properties of polymer solutions, measurements of the viscosity of dilute solutions seemed of special interest. These measurements yield direct information on the effect of thermodynamics on rheological properties, since the intrinsic viscosity (a measure for the size of the isolated molecules) and the Huggins constant (a measure for their mutual interaction) are both influenced by changes of the solvent power. Besides this theoretical interest such measurements are also important for technical reasons (polymer additives in motor oils, oil recovery, etc.).

The pressure dependence of the intrinsic viscosity has already been studied with two systems, poly(dimethylsiloxane)/cyclohexyl bromide[1] and polystyrene/*trans*-decalin,[2] in a narrow range of temperature and pressure around the endothermal Θ point. It was the goal of the present work to extend such investigations over a greater range of p and T. We have chosen the system polystyrene/*tert*-butyl acetate, since the endo- and the exothermal Θ temperatures lie comparatively close together ($\Theta_+ = 15.5$ °C, $\Theta_- = 109.5$ °C).[3] Thus a large spectrum of thermodynamic conditions, including the athermal case, is accessible with this system.

Experimental Section

The polystyrene sample was obtained from Pressure Chemical Co. (lot 4b, $M_w = 110000$, $U = (M_w/M_n) - 1 < 0.06$). *tert*-Butyl acetate (Merck-Schuchardt, for synthesis) was dried over anhydrous Na_2SO_4 and distilled over a silver mantle column (bp 97-98 °C, $n^{25}_D = 1.3839$).

The viscosity measurements were performed by means of a rolling-ball viscometer constructed in this laboratory. The block diagram of the apparatus is shown in Figure 1. A steel autoclave contains the measuring cell, consisting of a precision glass tube (KPG tube, 16-mm i.d., Schott-Glaswerke) and a glass ball (15.81-mm diameter, Fa. Hauser, 6336 Solms). The viscosity is determined from the time the ball needs to traverse the distance (100 mm) between two light barriers. The rolling time can be read with an accuracy of ±0.01 s. In order to investigate a possible shear rate dependence of the viscosity, measurements were performed at several fixed angles of inclination, ranging from about 10° to about 80°. The viscometer was located in a bath regulated within ±0.1 °C. The measureing temperatures ranged from 1.6 to 130 °C. The pressure is read by means of a DMS pressure transducer (Fa. Burster) with an accuracy of ±5 bar. The maximum pressure was 4000 bar.

The viscosity coefficients η were calculated according to

$$\eta = K(\rho_b - \rho_f)t \tag{1}$$

where t is the rolling time and ρ_b and ρ_f are the densities of the ball and the fluid, respectively; the constant K is determined from viscosities measured in an Ubbelohde viscometer. The results for *trans*-decalin, for which the viscosities under elevated pressure are known,[4] showed that K is independent of p and T.

The densities of the fluids were measured in a Kratky apparatus (Fa. Paar, Graz, Austria) for pressures up to 400 bar. The values thus obtained were extrapolated to high pressures by means of the Tait equation:

$$\rho = \frac{\rho_0}{1 - A \ln [1 + (p - p_0)/B]} \tag{2}$$

where ρ and ρ_0 are the densities at pressures p and p_0, respectively, and A and B are constants for a given concentration and temperature. Because of the much smaller compressibility of glass as compared to that of the fluids, the pressure dependence of ρ_b was neglected in eq 1.

Results and Discussion

The rolling times ranged from 25 to 9850 s, and were reproducible to within 0.3% over the whole range.

In order to examine whether the viscosities of the solutions and the resulting intrinsic viscosities depend on the shear rate D, measurements were performed at several angles of inclination. Since the solvent surely shows Newtonian behavior, a shear rate dependence of the viscosity of the solutions will lead to different values for η_{rel} at different angles, i.e., different shear rates. Therefore we examined whether t_{rel} ($t_{solution}/t_{solvent} \sim \eta_{rel}$) depends on the inverse of the rolling time for the solution, t^{-1}, which, according to experiments recorded in the literature,[5] is proportional to the mean value of D. Figure 2 shows an example: For all pressures, t_{rel} turned out to be independent of t^{-1}, i.e., independent of D. The approximate range for the shear rate is indicated below the t^{-1} scale. These values were estimated from data reported in the literature[5] and should only be regarded as an approximate measure of D.

Figure 3 gives an example of the results in terms of log η vs. p for different temperatures. For 27.2 °C one finds the usually observed[6] linear dependence of log η on p, at least for higher pressures. As the temperature is raised, the plots become increasingly curved. At 1.6 °C the curve

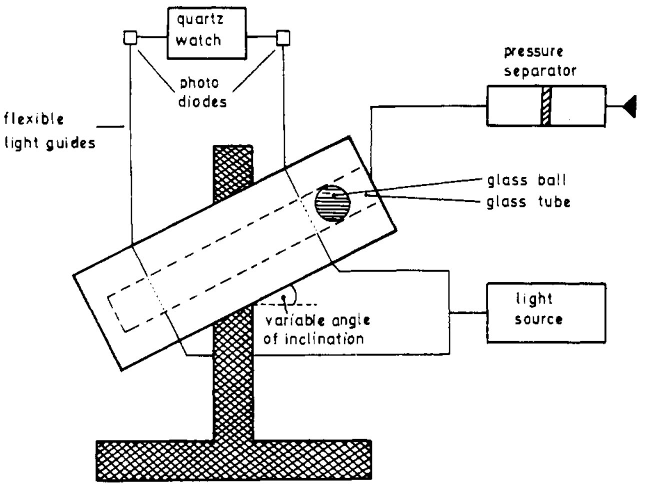

Figure 1. Block diagram of the rolling-ball viscometer.

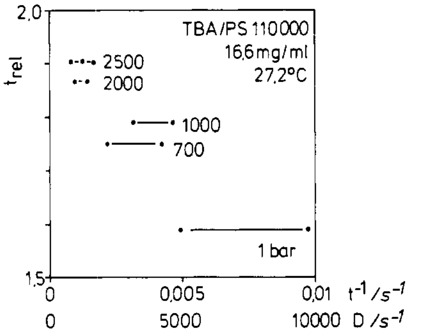

Figure 2. Check of Newtonian behavior: t_{rel} = (rolling time in solution)/(rolling time in solvent) vs. inverse of rolling time in solution (t^{-1}) and approximate mean shear rate (D), respectively.

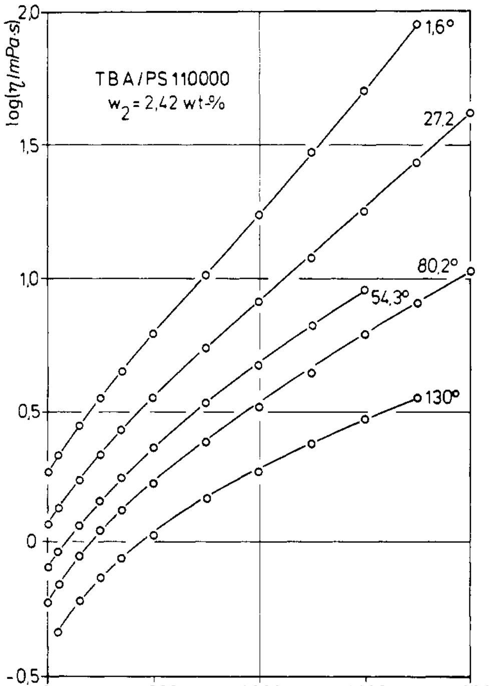

Figure 3. Pressure dependence of log η for the indicated weight fraction w_2 of the polymer and the indicated temperatures.

displays a point of inflection, which may be due to the approach to the solid state.[7]

Intrinsic viscosities $[\eta]$ and Huggins constants k_H were determined according to the Huggins equation[8]

$$\eta_{red} = [\eta] + k_H[\eta]^2c \tag{3}$$

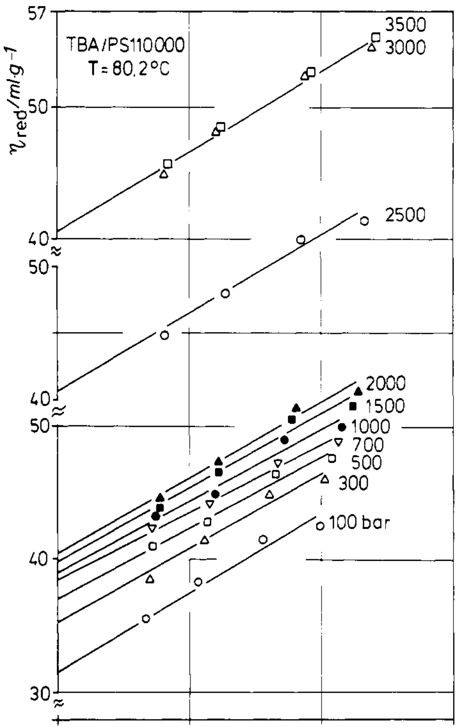

Figure 4. Huggins plots (reduced viscosity η_{red} vs. polymer concentration c) for 80.2 °C and the indicated pressures.

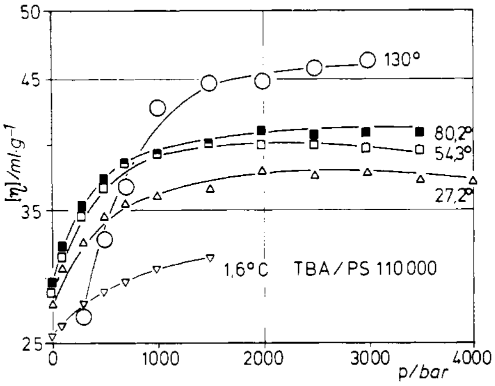

Figure 5. Pressure dependence of the intrinsic viscosity $[\eta]$ at the indicated temperatures.

where $\eta_{red} = 1/c(\eta_{rel} - 1)$ is the reduced viscosity and c is the polymer concentration.

An example of this evaluation is shown in Figure 4 for one temperature and various pressures. The intercepts, corresponding to the intrinsic viscosities, increase with increasing pressure. The pressure dependence of $[\eta]$ however, damps out at higher pressures, and the values for the highest pressures become practically identical. These results can be seen more clearly from Figure 5, where $[\eta]$ is plotted vs. pressure p. Initially $[\eta]$ increases markedly as the pressure is raised. This is in accordance with the already known fact[9] that the solvent power increases with increasing pressure for this system. At pressures above approximately 2000 bar the curves for the higher temperatures (80.2 and 130 °C) flatten. The curves for the lower temperatures (54.3 and 27.2 °C) even assume a maximum at approximately 2000 bar, an indication for a decrease in solvent power at sufficiently high pressures. Indeed, measurements of the pressure dependence of the second osmotic virial coefficient A_2 with the same system point to the occurrence of such a maximum in solvent power.[10]

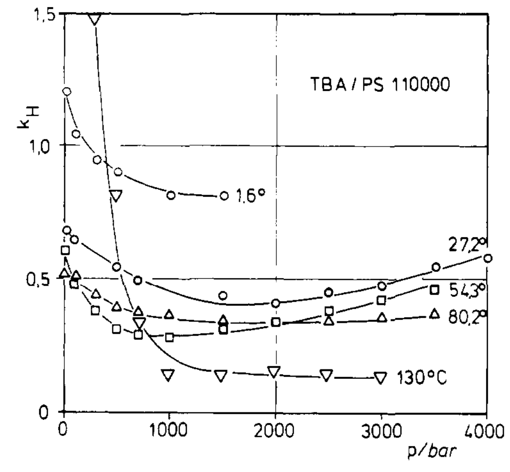

Figure 6. Pressure dependence of the Huggins constant k_H at the indicated temperatures.

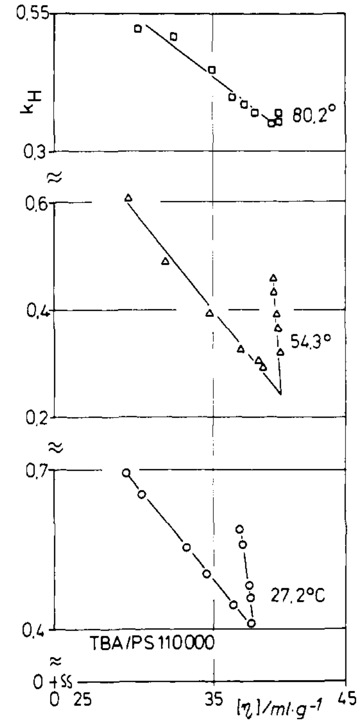

Figure 7. Plot of the Huggins constant k_H vs. the intrinsic viscosity $[\eta]$ for the indicated temperatures.

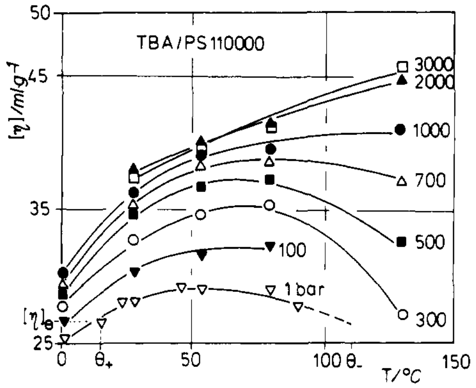

Figure 8. Temperature dependence of the intrinsic viscosity $[\eta]$ at the indicated pressures (Θ_+ = endothermal Θ temperature and Θ_- = exothermal Θ temperature as obtained by light scattering[3]).

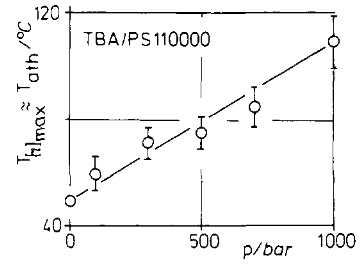

Figure 9. Plot of the maxima of the $[\eta](T)$ curves (Figure 8) vs. pressure p.

Concerning the Huggins constant, it is well-known from measurements at normal pressure that k_H varies oppositely to the intrinsic viscosity when the temperature (solvent power) is changed. Figure 6 shows that this holds true for changes in solvent power due to changes in pressure as well. The increase of k_H at higher pressures, however, is much more distinct than the corresponding decrease of $[\eta]$. This result becomes obvious from Figure 7, which shows plots of k_H vs. $[\eta]$ for three temperatures. For isothermal conditions one observes two practically linear relations between k_H and $[\eta]$ for lower and higher pressures, respectively. Their intersection coincides with the maximum in the $[\eta](p)$ curves. The corresponding plots for isobaric conditions (not given in this paper) show only small differences between the points for higher and lower temperatures not exceeding the limits of error. This result seems to indicate that the Huggins constant, which is a measure for the mutual interaction of the coils at high dilution, is not exclusively determined by the solvent power; additional hydrodynamic effects seem to play an important role. This is, of course, in accordance with various theories[11] for k_H, which all allow for thermodynamic as well as rheological influences on k_H. One can imagine that these hydrodynamic effects will be different for high and low pressures, because of the change of fluid structure with increase of pressure. Further investigations will be made of this topic, which might reveal more about the not yet completely understood Huggins constant.

Figure 8 shows the temperature dependence of $[\eta]$ for various pressures. These curves have been obtained from isobaric cuts through the isotherms $[\eta](p)$ in Figure 5. Assuming $[\eta]_\Theta$ to be independent of p, it can be concluded from the dependences depicted in Figure 8 that the endothermal Θ temperature is moderately lowered and the exothermal Θ temperature markedly increased by pressure. Comparing the $[\eta](T)$ curve for 1 bar with the measured $A_2(T)$ curve (Figure 10) shows that $[\eta]$ changes analogously to A_2. The maximum in $[\eta](T)$ coincides with the maximum in $A_2(T)$, which is practically identical with athermal conditions (vanishing heat of dilution). As the pressure is raised, the maxima of the $[\eta](T)$ curves are shifted toward higher temperatures. At pressures above 1000 bar no maximum can be observed in the temperature range under investigation. Figure 9 shows a plot of these maxima as a function of p. The pressure dependence of $T_{[\eta]_{\max}} \approx T_{\text{athermal}}$ is approximately 6 K/100 bar.

In the following section relations stemming from the Flory–Fox theory[12] and excluded volume theory[13,14] will be used for the calculation of A_2. The thus calculated values for p = 1 bar will be compared to the measured $A_2(T)$ curve. Division of $[\eta]$ by $[\eta]_\Theta$, the intrinsic viscosity at the Θ temperatures (1 bar), yields the coil expansion coefficient α_η^3.

$$\alpha_\eta^3 = [\eta]/[\eta]_\Theta \qquad (4)$$

As was shown by light scattering,[3] the unperturbed dimensions are equal at the two Θ temperatures. Therefore $[\eta]_\Theta$ can be regarded as independent of T in the temperature range under investigation. From the linear expansion

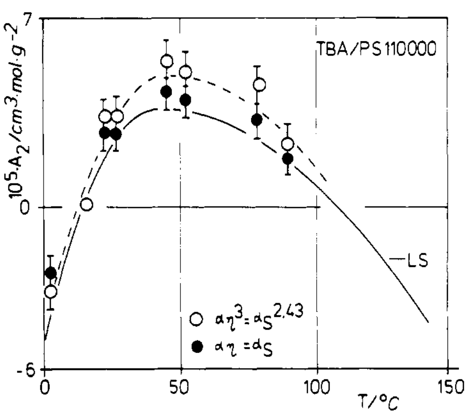

Figure 10. Comparison of the second osmotic virial coefficient A_2 calculated from the measured intrinsic viscosities via eq 5-9 with the directly measured $A_2(T)$ curve[3].

coefficient α the second osmotic virial coefficient A_2 can be calculated by means of eq 5, where no distinction is

$$A_2 = \frac{\alpha^5 - \alpha^3}{2(0.4913)C_M M^{1/2}} \frac{1}{\rho_2{}^2 V_1} h(z) \qquad (5)$$

$$C_M = \frac{27(\langle R \rangle_\theta{}^2/M)^{-3/2}}{2^{5/2}\pi^{3/2}\rho_2{}^2 V_1} \qquad (6)$$

made between the expansion coefficient for the hydrodynamic radius α_η and that for the radius of gyration α_s.[12] In eq 5, $\langle R \rangle_\theta{}^2$ is the unperturbed mean-square radius of the polymer, M is the molecular weight, ρ_2 is the density of the polymer, and V_1 is the molar volume of the solvent. The first factor in eq 5 stems from the Flory-Fox theory[12] and is equal to $^1/_2 - \chi$, where χ is the Flory-Huggins interaction parameter. The entire eq 5 relates $^1/_2 - \chi$ and A_2. Orofino and Flory[13] have given the following expression for $h(z)$:

$$h(z) = \ln{(1 + C_1 z \alpha^{-3})}/C_1 z \alpha^{-3} \qquad (7)$$

with

$$z = (\alpha^5 - \alpha^3)/C_2 \qquad (8)$$

where $C_1 = 5.73$ and $C_2 = 1.28$ according to Stockmayer.[14]

In contrast to the original Flory theory ($\alpha_\eta = \alpha_s$), Yamakawa and Kurata[15] point out that the expansion factors for the hydrodynamic radius and the radius of gyration cannot be equal. According to their theory[15] the following approximate relation holds between α_η and α_s:

$$\alpha_\eta{}^3 \cong \alpha_s{}^{2.43} \qquad (9)$$

The calculation of A_2 was performed twice: (i) under the assumption of $\alpha_\eta = \alpha_s$ and (ii) by use of eq 9. In Figure 10 the results are compared with the already mentioned measured $A_2(T)$ curve:[3] the agreement is better for (i) than for (ii). This result is in contrast to other experimental findings[16] that support the Yamakawa-Kurata theory. It is, however, in accordance with a statistical evaluation[17] of published data, according to which the experimental results can be better described by assuming an identity of α_η and α_s than by eq 9. It should be kept in mind that the theories underlying eq 7-9 are only approximate.

Acknowledgment. We are grateful to Professor H. Lentz for help with the construction and production of the high-pressure cell.

References and Notes

(1) Kubota, K.; Ogino, K. *Macromolecules* **1979,** *12,* 74.
(2) Kubota, K.; Ogino, K. *Polymer* **1979,** *20,* 175.
(3) Wolf, B. A.; Adam, H.-J. *J. Chem. Phys.* **1981,** *75,* 4121.
(4) Boelhouwer, J. M. W.; Toneman, L. H. *Proc. Conf. Lubr. Wear* **1957,** 214.
(5) Falcke, F. J.; Schurz, J. *Gummi, Asbest, + Kunstst.* **1972,** *8,* 739.
(6) Schmidt, J. R.; Wolf, B. A. *Makromol. Chem.* **1979,** *180,* 157. Geerissen, H.; Schmidt, J. R.; Wolf, B. A. *J. Appl. Polym. Sci.* **1982,** *27,* 1277.
(7) Hogenboom, D. L.; Webb, W.; Dixon, J. A. *J. Chem. Phys.* **1967,** *46,* 2586 and literature cited therein.
(8) Huggins, M. L. *J. Am. Chem. Soc.* **1942,** *64,* 2716.
(9) Saeki, S.; Kuwahara, N.; Kaneko, M. *Macromolecules* **1976,** *9,* 101.
(10) Schuch, W., unpublished results.
(11) Yamakawa, H. *J. Chem. Phys.* **1961,** *34,* 1360. Muthukumar, M.; Freed, K. F. *Macromolecules* **1977,** *10,* 899. Sakai, T. *J. Polym. Sci., Part A-2* **1968,** *6,* 1535.
(12) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* **1951,** *73,* 1904.
(13) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957,** *26,* 1067.
(14) Stockmayer, W. H. *Makromol. Chem.* **1960,** *35,* 54.
(15) Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958,** *29,* 311.
(16) Schulz, G. V.; Kirste, R. *Z. Phys. Chem. (Frankfurt/Main)* **1961,** *30,* 171.
(17) Guaita, M.; Chiantore, O. *Makromol. Chem.* **1975,** *176,* 195. Chiantore, O.; Guaita, M. *Ibid.* **1979,** *180,* 2197.