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Combined Effects of Pressure and Shear on the Phase Separation of Polymer Solutions

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ABSTRACT: Experimental information available in the literature on the phase separation behavior of the system *trans*-decalin/polystyrene as a function of pressure and shear rate for different molar masses M of the polymer was used to check to which extent the effects of these two variables can be predicted theoretically. The Sanchez−Lacombe theory served as a basis for the description of the solutions at rest. To account for the nonequilibrium condition, the energy stored by the sheared mixtures while flowing was added to the Gibbs energy of mixing. The phase diagrams measured at rest and under atmospheric pressure can well be described by one parameter ($\Delta\epsilon^*$, measuring the interaction energy between unlike mers); $\Delta\epsilon^*$ is found to vary linearly with $M^{-0.5}$. The pressure dependencies of the cloud points (constant M and constant composition) are also modeled appropriately, if $\Delta\epsilon^*$ is allowed to decrease linearly with rising pressure. The predictions concerning the influence of shear are only qualitatively correct: In accord with the experimental findings, the phase separation conditions are practically identical for the stagnant and for the flowing solutions at low pressures; the homogeneous region is, however, increasingly extended by shear as pressure becomes larger.

Introduction

The question how a cooperative action of pressure and shear changes the phase separation behavior of polymer solutions is not only of scientific interest but also of practical relevance for the technical synthesis of polymers from gaseous monomers where the reacting mixtures are usually stirred.

The starting point of the present work is an early experimental observation[1] with solutions of polystyrene (PS) in *trans*-decalin (TD): At atmospheric pressure the phase separation temperatures of the sheared solutions are within the experimental error for the comparatively low molar mass PS, identical with that of the stagnant system. However, as pressure is increased at constant shear rate, the homogeneous region becomes markedly larger for the flowing mixtures than at rest. There are two main reasons why we decided to perform a more detailed analysis of our experimental observations of 1979: (i) to test whether the Sanchez−Lacombe lattice fluid theory[2−4] can describe the equilibrium behavior better than other theories that require three adjustable parameters[5] and (ii) to see to what extent the above-described effects of shear at higher pressures can be predicted by an approach[6] that generalizes the Gibbs energy of mixing. This approach has so far been quite successfully used for the modeling of shear effects in other systems.[7]

Theoretical Background

Gibbs Energy of Mixing for Stagnant Systems. Within the framework of the Sanchez−Lacombe theory[2,4] the following equations hold true for the Gibbs energy and for the thermal equation of state of the pure components and of the binary mixtures:

$$\bar{\bar{G}}_i = \frac{G_i}{r_i^0 N_i} = \epsilon_{ii}^*\left\{-\tilde{\rho}_i + \tilde{P}_i\tilde{v}_i + \tilde{T}_i\left[(\tilde{v}_i - 1)\ln(1 - \tilde{\rho}_i) + \frac{1}{r_i^0}\ln\left(\frac{\tilde{\rho}_i}{\omega_i^0}\right)\right]\right\} \quad (1)$$

$$\tilde{\rho}_i^{\,2} + \tilde{P}_i + \tilde{T}_i\left[\ln(1 - \tilde{\rho}_i) + \left(1 - \frac{1}{r_i^0}\right)\tilde{\rho}_i\right] = 0 \quad (2)$$

$$\bar{\bar{G}}_\mathrm{M} = \frac{G_\mathrm{M}}{rN} = \epsilon^*\left\{-\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} + \frac{\phi_1}{r_1}\ln\frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{\omega_2}\right]\right\} \quad (3)$$

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \quad (4)$$

$\bar{\bar{G}}_\mathrm{M}$ is the Gibbs energy per mer of the mixture and $\bar{\bar{G}}_i$ that for the pure component i ($i = 1$ or 2); r_i and r_i^0 are the number of lattice sites occupied by a molecule of component i in the fluid mixtures and in the pure fluid, respectively. These quantities are related to r, the average number of mers per molecule of the mixture, to the number of molecules N, and to ϕ_i, the close-packed volume fractions of the components, by

$$rN = r_1N_1 + r_2N_2 = r_1^0N_1 + r_2^0N_2 \quad (5)$$

$$N = N_1 + N_2 \quad (6)$$

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \quad (7)$$

ϵ_{ii}^* represents the interaction energy per mer of the pure component i; ϵ^*, the interaction energy per mer of the binary mixture, is given by

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$$\epsilon^* = \phi_1{}^2\epsilon_{11}^* + 2\phi_1\phi_2\epsilon_{12}^* + \phi_2{}^2\epsilon_{22}^* \tag{8}$$

where ϵ_{12}^* stands for the interaction energy of a mer belonging to component *1* when it is surrounded by z mers belonging to component 2.

$\tilde{\rho}$, $\tilde{P}$, $\tilde{v}$, $\tilde{T}$ and $\tilde{\rho}_i$, $\tilde{P}_i$, $\tilde{v}_i$, $\tilde{T}_i$ are the reduced densities, pressures, volumes, and temperatures for the mixtures and for the pure component i, respectively. They are defined as

$$\tilde{P}_i = P/P_i^* \qquad \tilde{P} = P/P^* \tag{9}$$

$$\tilde{T}_i = T/T_i^* \qquad \tilde{T} = T/T^* \tag{10}$$

$$\tilde{v}_i = V_i/V_i^* \qquad \tilde{v} = V/V^* \tag{11}$$

$$\tilde{\rho}_i = 1/\tilde{v}_i \qquad \tilde{\rho} = 1/\tilde{v} \tag{12}$$

with

$$V_i^* = r_i^0 N_i v_i^* \qquad V^* = (r_1N_1 + r_2N_2)v^* \tag{13}$$

P^*, T^*, and P_i^*, T_i^* are the scaling pressures and temperatures for the mixture and for the pure component i; these reduction parameters are accessible according to the following relations

$$P_i^* = \epsilon_{ii}^*/v_i^* \qquad P^* = \epsilon^*/v^* \tag{14}$$

$$T_i^* = \epsilon_{ii}^*/k \qquad T^* = \epsilon^*/k \tag{15}$$

where k is the Boltzmann constant. The volumes of a mer in the mixture, v^*, and in the pure component v_i^*, are related by

$$r_iv^* = r_i^0v_i^* \qquad \frac{1}{v^*}\frac{\phi_1}{v_1^*} + \frac{\phi_2}{v_2^*} \tag{16}$$

ω_i and ω_i^0 designate the number of configurations that are available to the r_i-mer and to the r_i^0-mer in the close-packed state;[3,8] they are calculated from δ_i and δ_i^0, the flexibility parameters of the r_i-mer and r_i^0-mer, and from σ_i and σ_i^0, the symmetry numbers of the r_i-mer and r_i^0-mer, by

$$\omega_i = \delta_ir_i/\sigma_i\mathrm{e}^{r_i-1} \qquad \omega_i^0 = \delta_i^0\, r_i^0/\sigma_i^0\mathrm{e}^{r_i^0-1} \tag{17}$$

The following expressions for the parameters of eq 17 were chosen for the present calculations: $\sigma_i = \sigma_i^0 = 1$, $\delta_i^0 = \delta_{i,\max}^0 = z(z-1)^{r_i{}^{0}-2}$, and $\delta_i = \delta_{i,\max} = z(z-1)^{r_i{}^{0}-2}$, where z, the coordination number of the lattice, was taken[17] to be 12. The exact values of σ are of inconsequential importance.[3] The starting point of calculations for equilibrium conditions (zero shear rate) is $\Delta\bar{\bar{G}}_\mathrm{M}$, the Gibbs energy of mixing per mer

$$\Delta\bar{\bar{G}}_\mathrm{M} = \bar{\bar{G}}_\mathrm{M} - (\phi_1\bar{\bar{G}}_1 + \phi_2\bar{\bar{G}}_2) \tag{18}$$

The interaction between unlike mers is expressed in terms of $\Delta\epsilon^*$, its deviation from the arithmetic mean of the interaction between like ones

$$\Delta\epsilon^* = \epsilon_{12}^* - \frac{\epsilon_{11}^* + \epsilon_{22}^*}{2} \tag{19}$$

ϵ^* can thus be expressed as

$$\epsilon^* + \phi_1\epsilon_{11}^* + \phi_2\epsilon_{22}^* + 2\phi_1\phi_2\Delta\epsilon^* \tag{20}$$

Gibbs Energy for Sheared Systems

$\bar{\bar{G}}_{\dot{\gamma}}$, the Gibbs energy per mol of segments, generalized for flowing systems, can be expressed as[9]

$$\bar{\bar{G}}_{\dot{\gamma}} = \bar{\bar{G}}_\mathrm{z} + \bar{\bar{E}}_\mathrm{s} \tag{21}$$

where $\bar{\bar{G}}_\mathrm{z}$ is the Gibbs energy for zero shear (equilibrium conditions, $\bar{\bar{G}}_\mathrm{M}$ of eq 3) and $\bar{\bar{E}}_\mathrm{s}$ denotes the energy that is stored in the flowing system[10] per mole of segments. Strictly speaking, the equation of state should be different for the flowing system and that at rest. However, due to the fact that the stored energy is typically less than 10^{-3} of the Gibbs energy of mixing, the differences remain so minute that they need not be considered in the present calculations.

For the present considerations, which exclusively refer to Newtonian fluids, the following simple relation holds true for the stored energy

$$\bar{\bar{E}}_\mathrm{s} = \tilde{v}v^*\eta_0\tau_0\dot{\gamma}^2 \tag{22}$$

η_0 is the zero shear viscosity and τ_0 is the characteristic viscometric relaxation time.[11] For the present calculations τ_0 is taken to be proportional to the Rouse[12] relaxation time:

$$\tau_\mathrm{R} = \frac{6}{\pi^2}[(\eta_0 - \eta_\mathrm{S})M_2/(c_2RT)] \tag{23}$$

η_S is the viscosity of solvent, and c_2 is the polymer concentration (mass/volume). Since experimental data demonstrate[13,14] that viscometric relaxation times and Rouse relaxation times are often not identical but only proportional to each other, the following relation was used for the subsequent calculations

$$\tau_0 = k_\tau\tau_\mathrm{R} \tag{24}$$

where k_τ is a proportionality constant.

The spinodal and binodal curves were computed on an ordinary PC (486 DX2-66 MHz) by means of a method not requiring the derivatives of the Gibbs energy.[15,16] The scaling parameters ϵ_{ii}^*, v_i^*, and r_i^0 (or T_i^*, P_i^*, and ρ_i^*) stem from experimental *PVT* data of the pure components, where the following relation

$$r_i^0 = M_iP_i^*/kT_i^*\rho_i^* \tag{25}$$

was used to obtain r_i^0 from the molecular weight M_i and the close-packed density ρ_i^*.

Comparison between Experiment and Theory

Phase Separation of the Stagnant Solutions. The scaling parameters of the pure substances used for the calculations and the characteristic data of the polymers (molecular weights and polydispersity indices) for which the experiments have been carried out are collected in Table 1.

(a) Atmospheric Pressure. To model quantitatively the experimental phase diagrams of the system *trans*-decalin/polystyrene for different molecular weights M (here M_w in kg/mol), a generalization[17] of the original Sanchez–Lacombe theory requiring an additional pa-

Table 1. Characteristics of the Components and of the System[a]

	M_w/kg mol^{-1}	M_w/M_n	r_i^0
PS 110	110	≤1.06	7164.0
PS 390	390	≤1.10	25400.0
PS 2500	2500	≈1.30	162818.0
	T_i^*/K	P_i^*/K	ρ_i^*/g cm^{-3}
TD	621	3110	0.935
PS	635	3816	1.1245
$\Delta\epsilon_\infty^* k^{-1}$/K eq 24	k_M/K kg$^{1/2}$ mol$^{1/2}$ eq 24		$\Delta V N_A$/cm^3 mol^{-1} eq 25
12.7	2.68		0.033

[a] The scaling parameters for TD were taken from the literature;[3] those of PS stem from the evaluation of *PVT* data extrapolated from measurements at higher temperatures[22] into the *T*-region of present interest (0−105 °C).

rameter is not requested. However, to model the experimental findings appropriately, it turned out to be necessary to introduce a molecular weight dependence of $\Delta\epsilon^*$. For that purpose eq 26 was formulated by analogy to the scaling relation given by de Gennes[18] for the molecular weight dependence of the Flory−Huggins interaction parameter as follows:

$$\Delta\epsilon^*/k = \Delta\epsilon_\infty^*/k + k_M M^{-1/2} \tag{26}$$

In this relation for $\Delta\epsilon_\infty^*/k$, the value of $\Delta\epsilon^*$ for infinite molecular weight results to be −12.7 K and k_M, accounting for the effects of end groups, to be 2.68 K kg$^{1/2}$ mol$^{1/2}$.

It is shown in Figure 1 how well the calculated binodal curves and critical points agree with the cloud point curves and critical points measured earlier[5] for atmospheric pressure. It appears noteworthy in this context that the critical volume fraction of the polymer calculated for infinite *M* is different from zero; this behavior indicates[19] that the second term in the series expansion of the Flory−Huggins interaction parameter as a function of the volume fraction of the polymer is larger than $^1/_3$.

(b) Pressure Influence. According to the present results $\Delta\epsilon^*$ not only depends on *M* but also varies with pressure. The experimental findings can be described best by means of the following relation

$$\Delta\epsilon^* = \Delta\epsilon_{P=P_0}^* - (P - P_0)\Delta V \tag{27}$$

formulated by analogy to the well-known relations of phenomenological thermodynamics. For the present system the corresponding evaluation yields $\Delta V N_A$ = 0.033 cm^3/mol, where N_A is the Avogadro number. The agreement between measured and calculated cloud points is shown in Figure 2.

The present calculations yield a slight minimum in the pressure dependence of the cloud point curves, which corresponds to a pressure of optimum miscibility. Previous measurements[20] with the system cyclohexane/polystyrene, which is very similar to the present one, have demonstrated that such minima can indeed exist. According to the present calculations, the pressure at which the solvent power becomes the largest increases as the chain length of the polymer is raised.

Phase Separation of the Sheared Solutions. So far we have only dealt with the demixing of the quiescent polymer solutions. How the application of shear changes the phase separation behavior will now be calculated for one molar mass of the polymer (PS 110). For that purpose the stored energy is needed, i.e. (cf. eq 22), an analytical expression for the viscosity of the system as a function of composition, temperature, and pressure within the homogeneous region close to the phase separation conditions.

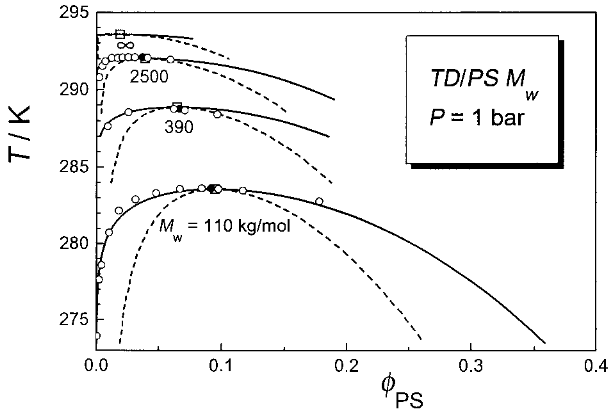

Figure 1. Measured cloud points (open circles) and calculated binodals (solid lines) plus spinodals (broken lines) as a function of composition for solutions of polystyrene of the indicated molar masses in *trans*-decalin; no distinction is made[23] between volume fractions and close-packed volume fractions. Measured (full circles) and calculated critical points (open squares) are also shown.

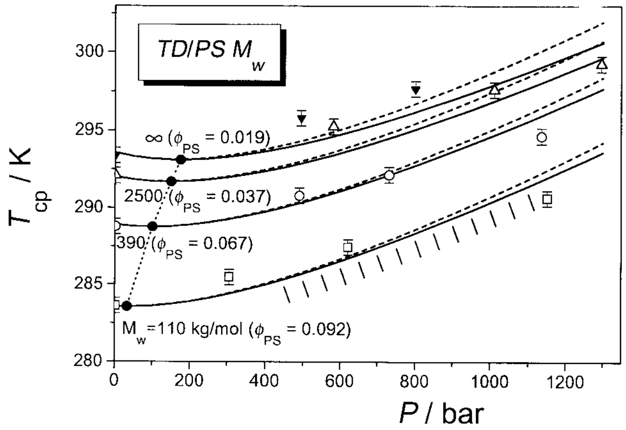

Figure 2. Cloud points for solutions of polystyrene of different molar masses in *trans*-decalin as a function of pressure: (open symbols) measurements,[1] (full triangles) extrapolation to infinite molar mass; (full lines) calculated isopleths; (broken lines) calculated critical curves. The volume fractions of the polymer are the critical ones at atmospheric pressure. Since the critical composition changes with pressure according to theory, the calculated critical curves (broken lines) differ from the isopleths (full lines). The pressures of optimum solvent quality are indicated by full circles. The two-phase area is indicated by hatching.

(a) Stored Energy. Measured viscosities[1,21] can be well represented mathematically by the following equation for the weight fraction of the polymer, w_2, ranging from 0 to 0.12

$$\ln \eta_0(T,P,w_2) = A(T_0,P_0,w_2) + \frac{B(w_2)}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{C(T,w_2)}{RT}(P - P_0) \tag{28}$$

where *R* is the gas constant and *A*, *B*, and *C* are fitting

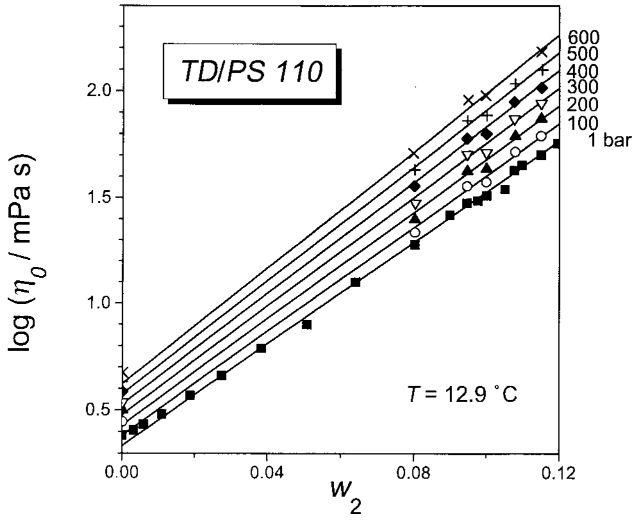

Figure 3. Zero shear viscosity of solutions of PS 110 in *trans*-decalin as a function of the weight fraction w_2 of the polymer at the indicated pressures. The lines are calculated according to eq 28 by means of the parameters given in Table 2.

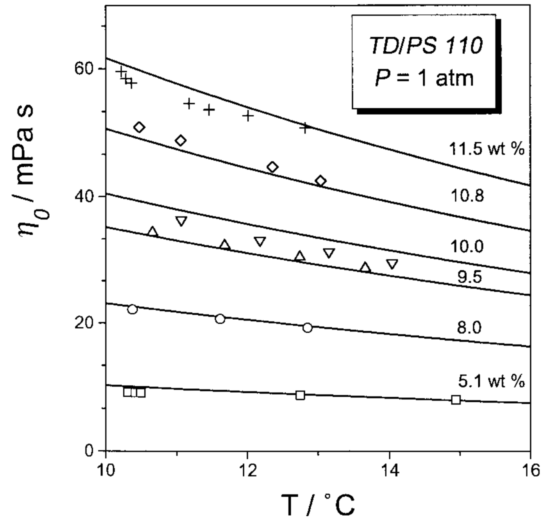

Figure 4. Zero shear viscosity of solutions of PS 110 in *trans*-decalin as a function of temperature for the indicated polymer concentrations. The lines are calculated according to eq 28 by means of the parameters given in Table 2.

parameters defined as

$$A(T_0,P_0,w_2) = A_0 + k_1 w_2 \tag{29}$$

$$B(w_2) = B_0 + k_2 w_2 \tag{30}$$

$$C(T,w_2) = (C_0 + k_3 w_2)T \tag{31}$$

Equations 28–31 were fitted by means of a nonlinear least-squares optimization procedure to the experimental data,[1,21] which are in part shown in Figures 3–5. These graphs also demonstrate the quality of the mathematical description. The values of the different parameters assumed for the present system are given in Table 2.

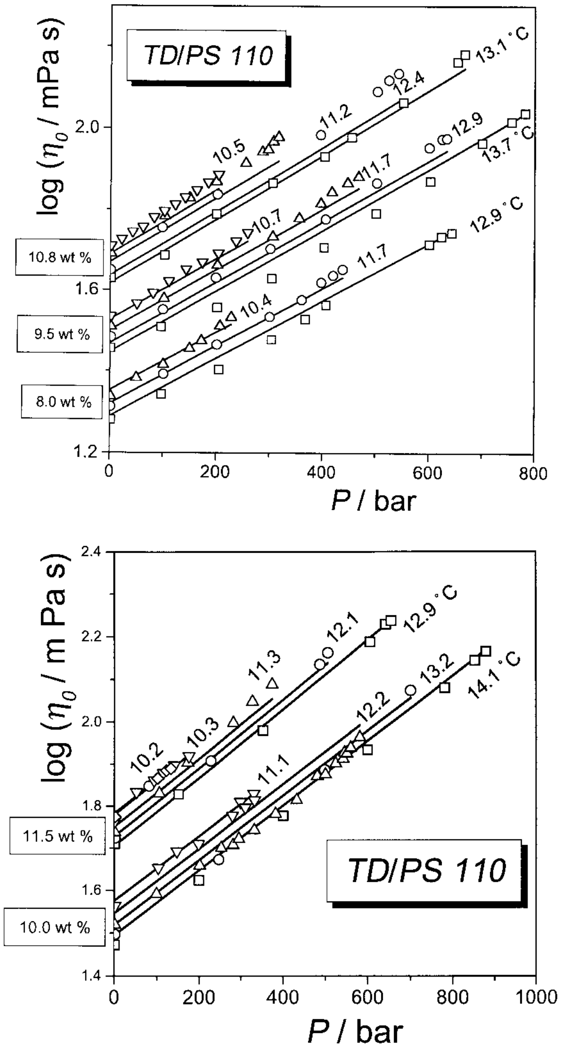

Figure 5. (a and b) Zero shear viscosity of solutions of PS 110 in *trans*-decalin as a function of pressure for the indicated polymer concentrations and temperatures. The lines are calculated according to eq 28 by means of the parameters given in Table 2.

Table 2. Values of the Fitting Parameters in Eq 28[a]

A_0	B_0, kJ/mol	C_0, cm^3/mol	k_1	k_2, kJ/mol	k_3, cm^3/mol
0.773	29.1	9.19×10^{-3}	27.464	131.70	5.51×10^{-2}

[a] Reference temperature $T_0 = 286.05$ K and reference pressure $P_0 = 1$ bar.

The calculation of the stored energy according to eq 22 also requires information on the viscometric relaxation time τ_0, which was not determined experimentally since the solutions are Newtonian fluids in the interesting range of shear rates. As mentioned above, τ_0 can be set to be proportional to the Rouse relaxation time[12] (see eq 24). This approximation has already been successfully applied for the modeling of shear influence in the case of solutions of incompatible polymers in a common solvent.[7]

(b) Combined Effects of Shear and Pressure. The experimental observations concerning the effect of shear on the phase separation of a 10.8 wt % solution of PS 110 in TD at different pressures and temperatures are compared with the predictions of the model with the generalized Gibbs energy.

The calculation of $\bar{\bar{G}}_z$ is based on the parameters resulting from the evaluation of data for all polymer samples of different molar mass; this is the reason for the comparatively large discrepancy between the calculated cloud point curve and the experimental points shown in Figure 6 for a solution of PS 110 in TD at its critical composition under atmospheric conditions; the

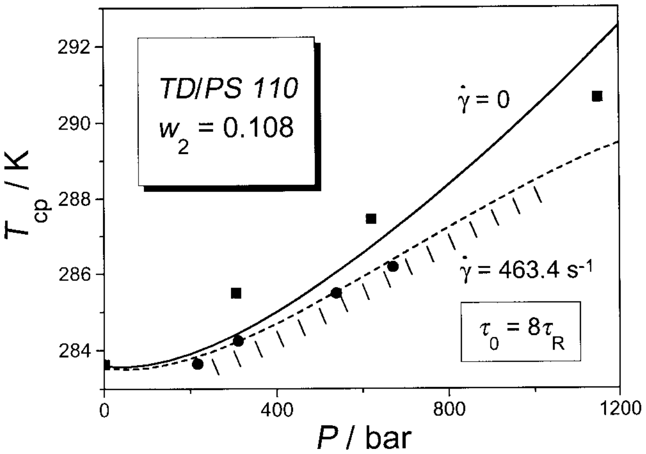

Figure 6. Measured pressure dependence of the cloud point temperature for a 10.8 wt % solution of PS 110 in TD at rest (squares) and at a shear rate of 463.4 s^{-1} (circles). The corresponding curves (full line for the stagnant system and broken line for the flowing system) were calculated theoretically by means of eqs 21 and 22 where the zero shear viscosity was expressed by eq 28 and the characteristic viscometric relaxation time was taken to be 8-fold the Rouse relaxation time. The two-phase area is indicated by hatching.

stored energy $\bar{\bar{E}}_s$ was computed from measured rheological data by means of eqs 28, 23, and 24, setting $k_\tau = 8$, a value in agreement with rheological information.[14] The phase separation conditions calculated from the generalized Gibbs energy are represented by a broken line in this graph.

The central feature of the so far only experimental observation concerning the combined influences of shear and pressure is well reproduced by the present outcome: Only at higher pressures where the viscosity of the solutions (and, therefore, their ability to store energy) is large does shear change notably the conditions for phase separation. Without the introduction of at least one additional parameter or direct experimental determination of τ_0, it is, however, impossible to reach quantitative agreement between experiment and theory. On the theoretical side, the introduction of a dependence of k_τ on η_0, as suggested by measurements,[14] would be a possibility.

In conclusion it can be stated that the present approach appears to be promising for the theoretical description of the cooperative action of pressure and shear on the phase separation of polymer solutions. It is evident that its applicability must be checked by means of additional experiments and that it will most likely require some refinements with the modeling of the stored energy.

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