

Improvement of polymer solubility: Influence of shear and of pressure

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Abstract: Polymer solutions and liquid polymer mixtures are in their phase-separation very sensitive to shear, in contrast to low molecular weight systems. Shear-induced changes of the demixing temperature up to 100 °C can be observed. The reason for this behavior lies in the ability of macromolecules to store energy in the stationary state while the system flows. Measurements with polymer solutions and with polymer blends reveal a multitude of phenomena. All experimental results can be rationalized at least semi-quantitatively on the basis of a theoretical approach using a generalized Gibbs energy of mixing containing the stored energy.

Pressure induced changes in the demixing conditions for polymer solutions turn out to be rather different for systems which phase separate upon cooling or upon heating. In the former case (UCSTs) the effects are small (typically $\pm 1\text{--}2$ K/100 bar), vary in sign and are hard to predict theoretically. In the latter case pressure practically always enhances miscibility and the effects are considerably larger (typically $+ 100\text{--}200$ K/100 bar). Theories based on the corresponding states principle yield reasonable forecasts for the behavior of such solutions.

INTRODUCTION

Solubility phenomena are in most cases studied in the quiescent state and at atmospheric pressure. The former practice results from the fact that the system must be at rest if one is interested in equilibrium properties, the latter is primarily due to the experimental difficulties associated with elevated pressures. There exist, however, numerous instances where it turns out mandatory to study the influences of shear and of pressure. For instance: Since the solubility of macromolecules is very responsive to flow, a change in the desirable phase state (during polymerization or processing) might cause considerable technical problems and the application of pressure is almost inevitable as one wants to produce polymers from gaseous monomers.

Shear influences

Experimental observations concerning the influences of shear on the phase separation of polymer-containing fluids already date back more than 40 years^{1,2}. Numerous investigations have dealt with this subject since then; a detailed list of references is given in the literature^{3–6}. Meanwhile systems exhibiting rather spectacular effects have been found. With solutions of incompatible polymers in a common solvent shear can enlarge the homogeneous region⁶ by 100 °C, there exist indications of shear induced islands of immiscibility in the case of polymer blends⁷ and an inversion in the sign of the effects upon a variation of shear rate was detected⁸ for polymer solutions in a single solvent. It is obvious that such a multitude of phenomena asks for theoretical understanding with the final goal of making the phase separation of flowing mixtures predictable.

One of the approaches⁹ that have turned out to be particularly useful introduces $\overline{\overline{\Delta G_\gamma}}$, the (segment molar, indicated by double bars) generalized Gibbs energy of mixing defined as

$$\overline{\overline{\Delta G_\gamma}} = \overline{\overline{\Delta G_z}} + \overline{\overline{\Delta E_s}} \quad (1)$$

$\overline{\overline{\Delta G_z}}$ is the equilibrium Gibbs energy of mixing (zero shear) and the second term accounts for the fact that polymer-containing systems can store significant amounts of energy during stationary flow, in contrast to mixtures of low molecular weight liquids. $\overline{\overline{\Delta E_s}}$ is calculated from $\overline{\overline{E_{s,i}}}$, the energies stored by the pure components and $\overline{\overline{E_s}}$, the energy stored in the mixture, as formulated below for a binary system; ϕ_i signifies volume (segment) fractions.

$$\overline{\overline{\Delta E_s}} = \overline{\overline{E_s}} - (\phi_1 \overline{\overline{E_{s,1}}} + \phi_2 \overline{\overline{E_{s,2}}}) \quad (2)$$

For quantitative calculations $\overline{\overline{\Delta G_z}}$ is - as usual - expressed in terms of the Flory-Huggins relation reading for two components

$$\frac{\overline{\overline{\Delta G_z}}}{RT} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + g \phi_1 \phi_2 \quad (3)$$

A realistic modeling makes it necessary to account for the concentration dependence of the interaction parameters g . The stored energy is accessible from the following relation^{9,6}

$$\overline{\overline{E_s}} = V_{\text{seg}} \frac{\tau_0}{\eta_0} (\eta \dot{\gamma})^2 \quad (4)$$

V_{seg} is the molar volume of a segment, η and τ are the viscosity and the characteristic viscometric relaxation time, respectively, $\dot{\gamma}$ is the shear rate and the index zero indicates linear viscoelastic behavior.

Due to a new approach in the calculation of phase diagrams (direct minimization of the Gibbs energy¹⁰ avoiding derivatives) it has become comparatively simple to extend the present treatment of flowing systems formulated above for two components to practically any number of species.

Equation 1 allows an easy rationalization of the experimental finding that the application of shear increases the homogeneous region in some cases but the heterogeneous region in others. This is demonstrated in the scheme given below. In this graph $\overline{\overline{E_s}}$ is shown instead of $\overline{\overline{\Delta E_s}}$ for the sake of clarity; this can be done without committing an error since the addition or subtraction of a term that depends linearly on concentration to the Gibbs energy of mixing does not change the composition of the coexisting phases. The situation depicted left in Fig. 3 is typical for low shear rates and components with pronouncedly different ability to store energy; a more than linear increase with rising content of B can undo the hump in $\overline{\overline{\Delta G_z}}$, leading to phase separation in the stagnant system. Conversely, for higher shear rates where mixtures rich in the higher molecular weight component B exhibit non-Newtonian flow behavior, the situation shown on the right hand side of this scheme is characteristic. In this case the increase in $\overline{\overline{E_s}}$ levels off with increasing ϕ_B and the stored energy can thus produce a hump in the generalized Gibbs energy of mixing.

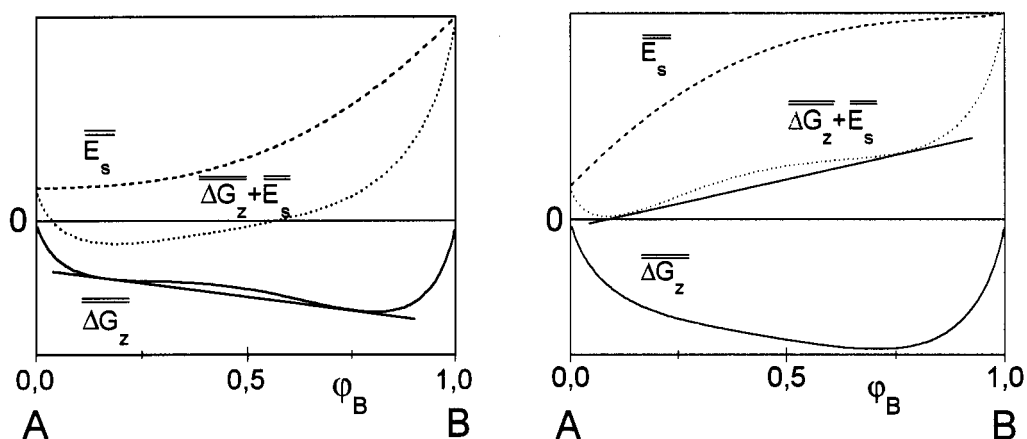


Fig. 1: Scheme (based on eq 1) demonstrating the effect of the stored energy on the phase behavior of flowing systems. The situation in the case of shear induced homogenization is shown on the left hand side and that for shear induced phase separation on the right hand side. The double tangents fix the compositions of the coexisting phases

Model calculations on the basis of the above equations using realistic values for Flory-Huggins interaction parameters and stored energies as a function of temperature and composition allow a more detailed analysis of shear effects. They yield the features¹¹ depicted in Fig. 2 for systems with upper and lower critical solutions temperatures, respectively. This schematic representation shows all possible effects, some of them are, however, not general but bound to particular conditions. Typically the one-phase region becomes larger up to a characteristic maximum extent as the shear rate is increased starting from zero. Upon a further augmentation of shear one observes a reduction and an inversion of the effect, i.e. an enlargement of the two-phase region, again up to a characteristic maximum value. Finally, at very high shear rates, the deviations from equilibrium decrease and vanish asymptotically. Furthermore, different types of shear induced islands of immiscibility are observed.

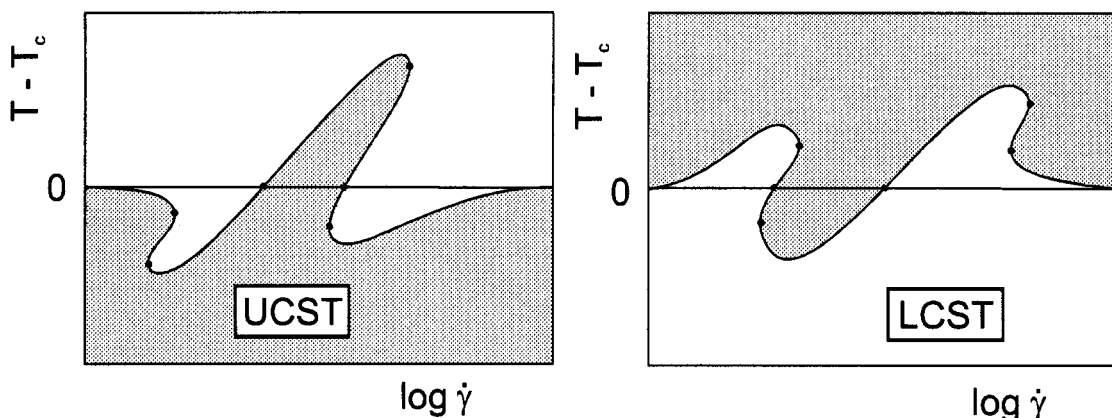


Fig. 2: Difference between the phase separation temperature of sheared mixtures of critical composition and the critical temperature of the stagnant system as a function of shear rate (logarithmic scale).

The shear effects shown in the above graphs approach zero for very low and very high values of $\dot{\gamma}$; the former fact is trivial and the latter due to an increasingly linear variation of the stored

energy with composition. All experimentally observed features are well reproduced: The inversion of the effects as well as the occurrence of shear induced closed loops of immiscibility on the two-phase side of T_c (inner islands) and on the one phase side (outer islands). The latter peculiarity implies that a system with an UCST may in the sheared state phase separate upon heating and conversely, one with a LCST upon cooling. A more detailed discussion is given in reference 11. It appears worthwhile to mention that the calculated complex behavior is indeed helpful for the understanding of unexpected and intriguing experimental findings⁵.

Pressure influences

Studies concerning the effects of hydrostatic pressure on the solubility of polymers are even older (particularly in industry) than those on the effects of shear. During the past years solutions in condensed gases have become of particular interest¹², not only because of enhanced solubility but also because of the high molecular mobility of the polymers in such mixtures. The present discussion starts with the comparison of typical features for systems with UCSTs and LCSTs, respectively. For simplicity the author uses results obtained in his own group; additional literature is given in the references of the papers (CP/PS¹³, 1-PhC₁₀/PS¹³, CH/PS¹³, n-C₅/PIB¹⁴, DEE/PS¹⁵, IO/PDMA¹⁶, the abbreviations are explained in the legend) from which the data shown in Fig. 3 are taken.

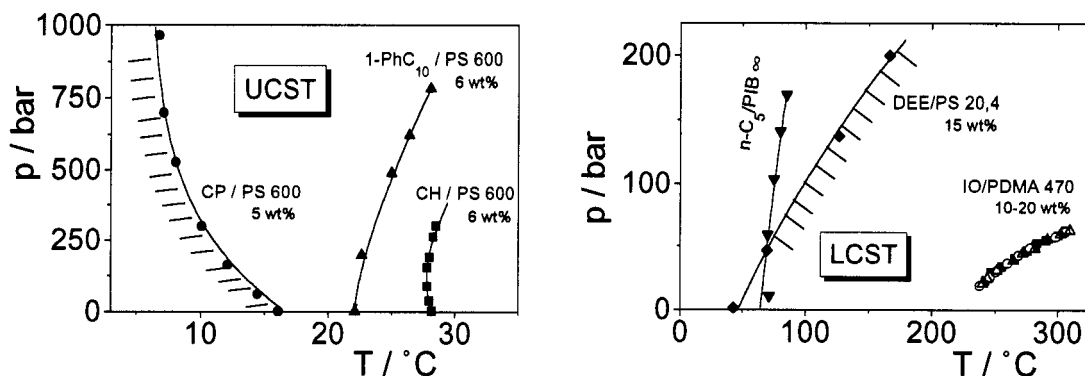


Fig. 3: Demixing pressures as a function of temperatures for polymer solutions exhibiting UCSTs (left) or LCSTs (right); the two-phase side of the curves is indicated by hatching. The abbreviations have the following meaning. PS: polystyrene, PIB: polyisobutylene, PDMA: poly(*n*-decylmethacrylate), CP: cyclopentane, 1-Ph-C₁₀: 1-phenyldecane, CH: cyclohexane, n-C₅: *n*-pentane, DEE: diethylether, IO: iso-octane. The figures after the abbreviation of the polymer indicate their molar mass in kg/mol; the polymer concentration in the mixtures is indicated in the graphs. The data for PIB refer to infinite molar mass and stem from light scattering measurements; the curve for PDMA ends at low temperatures on the vapor pressure curve of the solvent.

From the typical examples shown above it becomes immediately obvious that the changes in solubility resulting from an increase in pressure are much more pronounced for LCSTs than for UCSTs (please note the largely different scales). For systems which phase separate upon heating the homogeneous area of the phase diagrams expands in practically all cases; the changes are usually on the order of ca. 100 to 200 K per 100 bar. For systems which demix upon cooling the effects are smaller by a factor of approx. 100. Furthermore, the probabilities for an augmentation or a reduction in solubility are comparable; there even exist examples, as shown in Fig. 3 for the system CH/PS 600, where one observes a pressure of optimum miscibility.

From considerations based on phenomenological thermodynamic it is evident that a theory which should be capable of describing pressure influences must account for the volume changes upon mixing. Most approaches start from the corresponding states principle, i.e. use the same mathematical expression for the thermal equation of state of the components and of the mixture. Two relations are most widely used, that of Flory, Orwoll and Vrij¹⁷ and that of Sanchez and Lacombe¹⁸. In both cases one often uses two system specific parameters of enthalpic and entropic nature, respectively, and at least one and very often two of the many parameters have to be adjusted in order to describe reality.

With phase separation upon cooling neither of the two approaches is of great help, since not even the sign of pressure effects can be forecast reliably. In these cases, however, a simple rule of the thumb comes in handy. The distance of the upper critical temperature T_{uc} from the melting point of the solvent T_{mp} can serve for a qualitative prediction¹³: For $(T_{uc} - T_{mp})/T_{mp} (K/K) < 0.20$ the solubility of the polymer decreases with pressure; if this quantity exceeds 0.25, the solubility is enhanced. This finding can be rationalized in the following manner. Due to the dense packing of the solvent close to its solid state the introduction of the polymer will lead to a positive volume of mixing near T_{mp} and consequently to a reduction of miscibility by pressure; on the other hand, in those cases where the phase separation occurs at a larger distance from T_{mp} , a considerable fraction of the volume of the solvents is free of matter. Since these voids will at least be partially occupied by the polymer as it dissolves, the excess volume results negative and the solubility rises with pressure. It is obvious that the just described free volume effects become of particular importance in the case of LCSTs in agreement with the experimental observations.

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