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Phase diagrams calculated for flowing polymer solutions: spinodal and three phase conditions

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Summary

Spinodal lines and critical points (CPs) are calculated for flowing solutions of polystyrene in *trans*-decalin. Three types of CPs can be distinguished: The first consists of stable CPs (ordinary critical line) and originates from the CP of the quiescent system. The other two CPs are bound to shear. Additional stable CPs (extraordinary critical line) result for higher polymer concentrations and unstable CPs for intermediate concentrations. Ordinary and unstable critical line merge in a heterogeneous double CP. The coexistence of three phases in the flowing system (eulytic points) comes to an end as two of them merge upon an increase in shear rate at a critical end point.

Introduction

The question whether flowing polymer containing systems phase separate differently from the corresponding quiescent ones has already been posed many years ago (1). Theoretical calculations concerning that item were performed by introducing a generalized Gibbs energy of mixing by the addition of the energy the system stores while flowing (2). Under this assumption the tools of thermodynamics can be applied in the usual way. Alternative approaches to describe the influences of flow on the phase diagrams are compiled and discussed in a recently published review (3).

For a solution of polystyrene with a molar mass of 850.3 kg/mol (5000 segments in terms of the Flory-Huggins theory) in *trans*-decalin (TD / PS N=5000) some first information concerning the composition of the phases which coexist under given shear conditions at a constant temperature could be obtained by means of a graphical construction of double tangents (2). A comparison (4,5) with experimental data demonstrated the reliability of the present approach. Due to the rather laborious procedure only part of the information which interests could, however, be obtained at that time. For that reason we adopt a computer-based method (6,7) for the calculation of spinodal and additional critical points to answer the following questions for the above system: How do the spinodals look like, what is the shape of the critical lines and do there exist double critical points and/or critical end points? Since no new equations are used for the present calculations and in

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view of the limited space they are not repeated here; all information can be found in reference (2).

Results and Discussion

Phenomenological background. Figure 1 shows how the different regions of stability and coexistence of phases are determined from ΔG, the Gibbs energy of mixing per one mol of segments, as a function φ_2, the volume fraction (fraction of segments) of component 2. The rather complex looking shape of $\Delta G(\varphi_2)$ is characteristic for flowing polymer solutions where one can observe two two-phase regions separated by a composition range of miscibility. The scheme of Figure 1 shows two ranges of instability, situated between the left pair of open circles and between the right pair. There exist six double tangents in the present case, two are stable, one is metastable, and three are unstable tie lines.

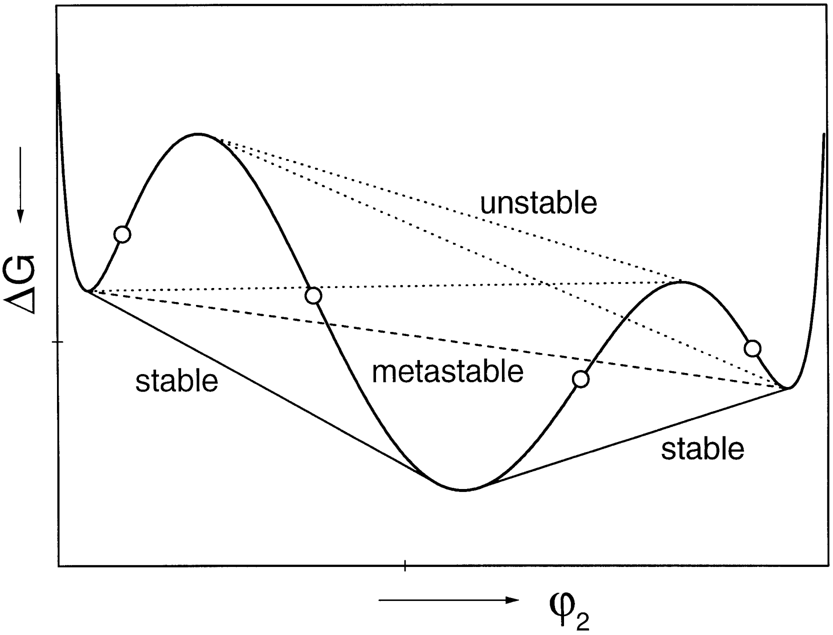

Figure 1. Scheme demonstrating the positions of the different kinds of double tangents to the Gibbs energy of mixing as a function of φ2, the volume fraction of component 2, leading to the equality of the chemical potential in the coexisting phases. Also indicated are the spinodal conditions (points of inflection, open symbols).

Spinodal lines and critical points. From Figure 2 it can be seen how the spinodal line changes as compared with that for the stagnant system upon an increase of shear rate $\dot{\gamma}$. For the flowing systems there exist two kinds of stable critical points (CPs); one, subsequently called ordinary CP, develops from that for the stagnant solution (full squares) and is always situated below the equilibrium critical temperature and composition. The second type of CP (open squares) , named extraordinary, originates at very low shear rates outside the composition range within which the present model can be applied. Both types of CPs move towards lower polymer concentration as $\dot{\gamma}$ is raised. The third kind of CPs (full circles) is unstable. For the highest shear rate of Figure 2 the spinodal exhibits a shoulder, i.e. a point of inflection with a horizontal tangent. This point is a double critical point (DCP).

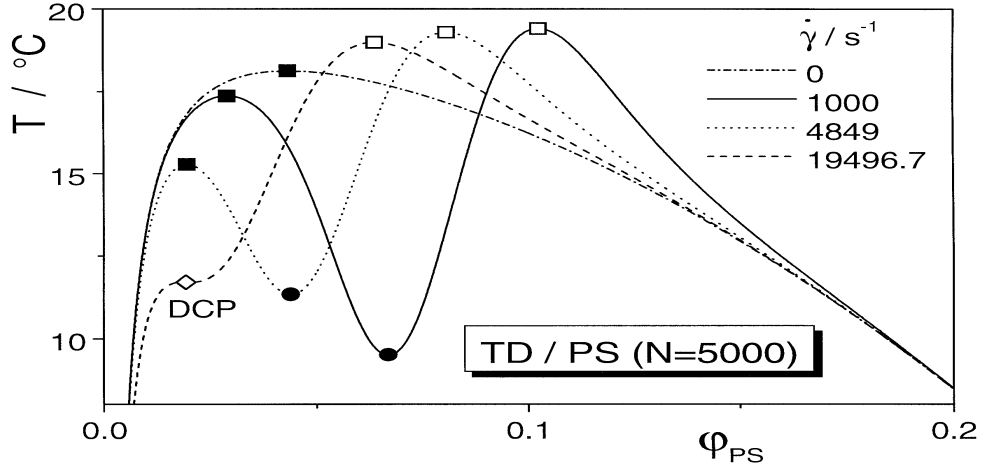

Figure 2. Spinodal lines of the stagnant system and for the different shear rates indicated in the graph. Stable critical points (open and full squares) are situated in the maxima and the unstable ones (full circles) in the minima of the curves; these two types of critical conditions coincide at the double critical point (DCP, open diamond) located at a shoulder of the spinodal.

Three phase lines. The spinodals of the above graph demonstrate that a situation like that shown in the scheme of Figure 1 (two ranges of instability in a certain temperature range) is typical for the flowing system. In accord with the unusual shape of G(φ), the phase diagram exhibits a very complex binodal, as can be seen in Figure 3 for a shear rate of 1000 s^{-1}.

The fact that a system flows changes the phase diagram in several ways. At low polymer concentrations the region of complete miscibility increases markedly (shear induced mixing) whereas the opposite effect (shear induced demixing) results at larger polymer contents. The latter fact was overlooked in the previous paper on this subject because of the inaccuracies of the graphical method applied then. In an intermediate composition range, at the eulytic point (2), the shift of the demixing temperature is particularly pronounced. For the flowing system the binodal curves are very complex and similar to phase diagrams calculated for mixtures of oligomers (8). In the cited paper the theoretical results are comprehensively discussed and the literature concerning exhaustively referenced. The present discussion uses the nomenclature of reference (8).

Upon the addition of polymer to the pure solvent the demixing temperature rises in the usual manner until it reaches the three phase line. Here the relevant binodal line intersects with another branch of the binodal and becomes metastable. In its further course it reaches the spinodal and exhibits a non-critical maximum. From this point onwards the binodal is unstable until it passes the spinodal again, in a non-critical minimum. The consecutive metastable part leads to the eulytic point which represents the middle of the three coexisting phases. Here the binodal becomes stable again, passes the stable extraordinary CP and runs to the last of the three coexistence points, intersecting another branch, and becomes metastable. After that a cusp (corresponding to the non-critical minimum discussed before) is reached; the binodal, now unstable, turns and runs to a second cusp related to the above-mentioned non-critical maximum. The binodal changes the direction, becomes metastable, passes the three phase line again, changing to stable. The further course of the binodal line is very similar to that of the unsheared system again.

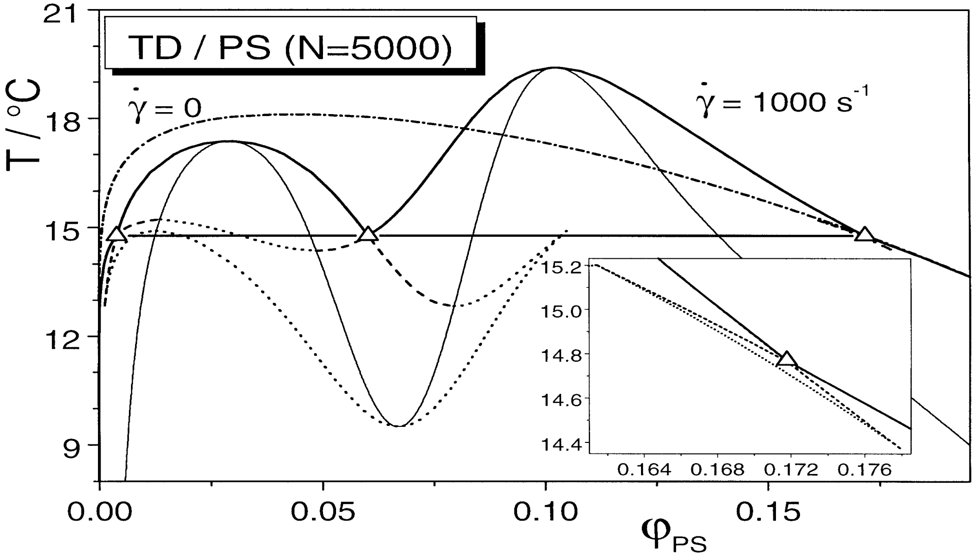

Figure 3. Binodal line for the quiescent system ($\dot{\gamma}$ = 0, dash-dotted) and phase diagram for a shear rate of 1000 s^{-1}. The thin solid line represents the spinodal line of the last graph. The thick lines stand for binodals; their stable, metastable and unstable parts are - as in Figure 1 - indicated by full, broken and dotted curves, respectively. Also shown is the three phase line (open triangles: coexisting phases) at the eulytic temperature (2). There is a break in the shape of the stable binodals (discontinuity in their slope) at that temperature as can be seen in more detail from the insert.

So far we have neglected a second part of the binodal line which is double-sigmoidal. Beginning at the left point of the three phase line a stable binodal runs to the stable ordinary CP and then to the second of the three coexisting phases where it intersects with the branch of the binodal discussed above and becomes metastable. The binodal then runs to lower temperatures until it passes the spinodal in a non-critical minimum becoming unstable. The binodal now leads to a cusp which corresponds to a non-critical maximum one encounters as one follows the curve further. At the cusp the binodal changes its direction and leads to the unstable CP at the minimum of the spinodal. Then it rises to higher temperatures, passing a second non-critical maximum and reaches a second cusp which corresponds to the above-mentioned non-critical minimum. A metastable branch leads back to the starting point of the classification of the double-sigmoidal line.

The coexistence of three liquid phases is a nonvariant situation (9), since the pressure is fixed for the actual phase diagrams. Therefore this state is found for exactly one temperature. The eulytic point is identical to the middle phase of the three coexisting phases.

Critical end point. Figure 4 shows what happens with the three phase line as the shear rate increases. The ordinary CP shifts to lower temperatures until it is no longer located in a maximum of the stable binodal but on a shoulder. This point marks the disappearance of the three phase line and represents a critical end point (CEP). The shear rate chosen for the phase diagram of Figure 4 is the last one for which a three phase line can be observed. If γ is raised only slightly the double sigmoidal curve submerges completely into the two phase area and the ordinary CP becomes metastable. As the shear rate is increased much further, the area covered by the double sigmoidal curve vanishes at the DCP.

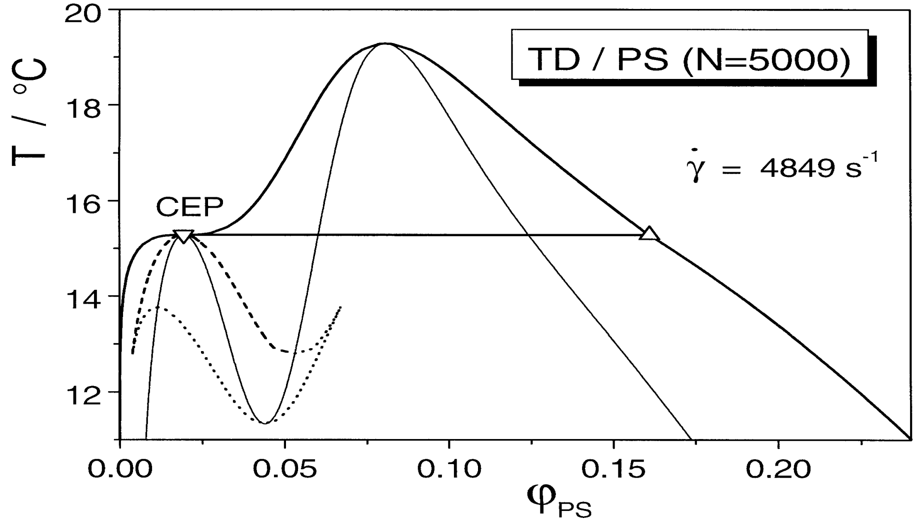

Figure 4. Phase diagram calculated for a shear rate of 4849 s^{-1}. Here two of three coexisting phases coincide in a critical end point (CEP) and the three phase line comes to an end. Lines as in Figure 3.

Isothermal sections. Figure 5 shows as an example an isothermal cut through the phase diagram at 14 °C. Two two-phase areas, separated by a homogeneous region, exist at low shear rates. At the present temperature three phases coexist at 186.5 s^{-1}. At higher $\dot{\gamma}$. values only one, comparatively broad two phase area is found. At the three phase line the stable binodal is continuous but not differentiable as in the T-φ_2-diagram.

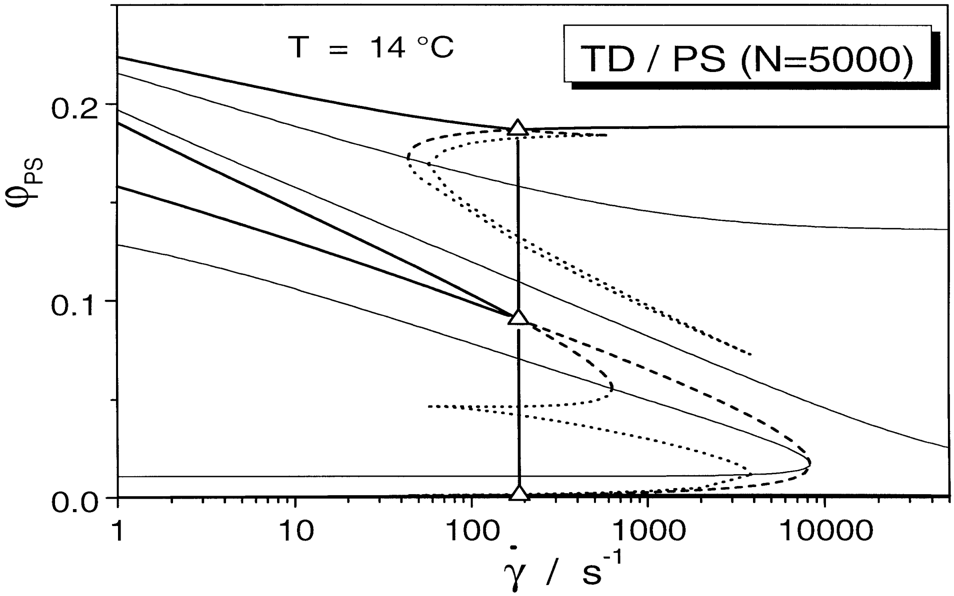

Figure 5. Spinodal lines and composition of coexisting phases as a function of shear rate at the indicated temperature. Lines and symbols as in Figure 3.

Critical lines and eulytic line. The following two figures summarize all shear effects resulting for the present system and the $\dot{\gamma}$ range of interest. The different lines traversing the T-φ_{PS}-$\dot{\gamma}$ space are shown in terms of their projection, either into the φ_{PS}-$\dot{\gamma}$ plane (Figure 6) or into the T-$\dot{\gamma}$ plane (Figure 7). Both graphs also give the compositions of the three coexisting phases.

The ordinary CL is stable until it reaches the critical end point at 4849 s^{-1} where it becomes metastable. This has already been described in the context of Figure 4. At 19 496.7 s^{-1} the ordinary CL meets the unstable CL in a heterogeneous double critical point (cf. Figure 2, giving more details). The extraordinary CL is detached from the ordinary and from the unstable CLs. Since the coexistence of three phases comes to an end at the CEP (where two of these phases merge) the third line (highest polymer concentration) has to terminate at the same shear rate.

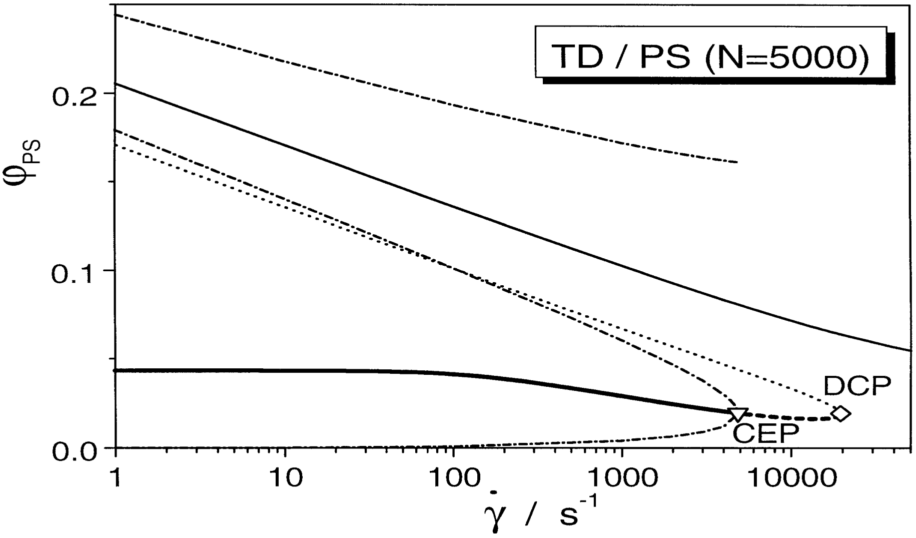

Figure 6. Projection of the critical lines (solid: stable, broken: metastable, dotted: unstable) and of the three coexisting phases (dash-dotted) into the φ_{PS}-$\dot{\gamma}$-plane. The critical end point and the double CP are also indicated.

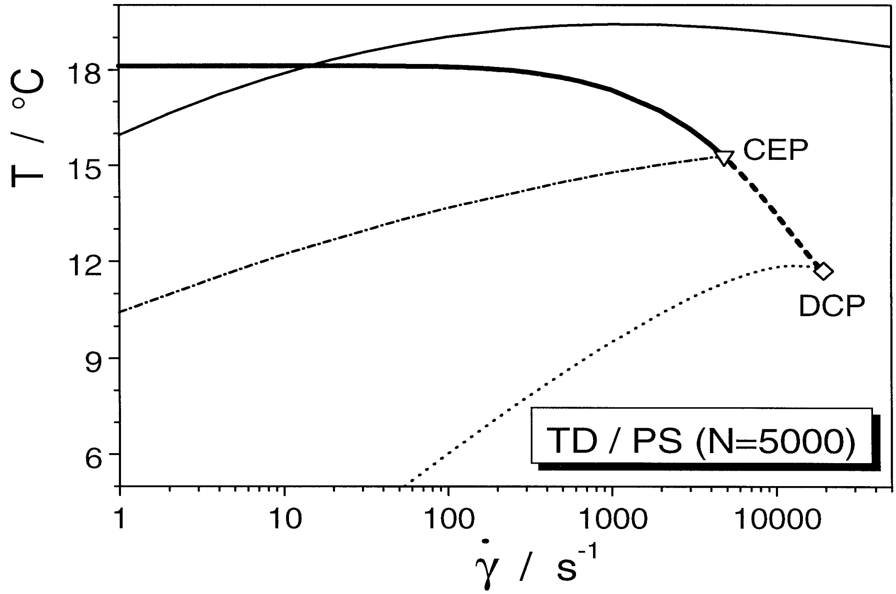

Figure 7. Projection of the critical lines and the three coexisting phases into the T-$\dot{\gamma}$-plane. Lines and symbols as in Figure 6.

Conclusion/Outlook

For the present polymer solution, which demixes at low temperatures, three types of critical points can be observed and three liquid phases coexist under certain conditions. For polymer blends the situation is even more complicated than for the polymer solution discussed here. One spectacular feature is the occurrence of shear induced closed miscibility gaps. This experimentally observed (10) prediction of theoretical calculations (11) implies that systems with LCST can in the sheared state under special condition also demix upon cooling and similarly blends with UCST upon heating.

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