

# Thermodynamics of Polymer Solutions

All participants are requested to register the day before the hand-on training starts in the laboratory 01 131 building K to prepare the solutions (time required: approx. 1 h). Otherwise the experiment cannot be carried out within one day.

## Introduction

The practical importance of polymers is beyond doubt as becomes obvious in every-day life. The significance of these products is not restricted to the area of materials, macromolecules are also of great pharmaceutical importance and as essential modifying agents in many applications.

Most of the synthetic compounds are prepared and processed in the liquid state, i.e. in solution or in the molten state. Detailed knowledge on this state is therefore indispensable. In particular it is essential to know the limits of complete miscibility with a low molecular weight solvent as a function of temperature, pressure and composition. Furthermore it is often mandatory to be acquainted with shear induced changes in the segregation of a second phase, which may either be liquid or solid. The present experiments are meant to provide some insight into the physico-chemical features of polymer containing mixtures.

## Truly binary systems (non-uniformity $U=0$ )

For the present consideration we assume that the polymer consists (like typical low molecular weight compounds) of one kind of molecules only. In other words we assume that all polymer chain have the same length (molar mass). For synthetic polymers this assumption is never true. In this case the number average molar mass  $M_n$  - obtained by counting the molecules (osmosis) – is always less than the weight average  $M_w$  - resulting from weighting (light scattering). Concerning the definition of  $M_n$  and  $M_w$  please consult the literature. The width of the molecular weight distribution can be quantified by the molecular non-uniformity  $U$  defined as

$$U = \frac{M_w}{M_n} - 1 \quad (1)$$

In the limit of a uniform material  $U \rightarrow 0$ . With some polymerization or fractionation techniques it is possible to realize very small  $U$  values. In these cases the present consideration become approximately true.

## Phenomenology

An example for a typical phase diagram obtained for small  $U$  values is shown in Fig. 1 for the system@ cyclohexane/polystyrene. In this case a second liquid phase is segregated from the homogenous solutions upon cooling as well as upon heating. Only within a certain limited temperature range the components are completely miscible. For some systems the miscibility gap at low  $T$  and that at high  $T$  overlap. In this case it is impossible to observe complete miscibility at any temperature (constant pressure). There only exists a characteristic  $T$  where the polymer can take up the largest amount of solvent (swelling of the polymer) and the solvent is able to take up a limited amount of solute. With many systems one does not observe phase separation upon cooling, because the solvent solidifies before it becomes sufficiently poor to induce demixing. Analogously the solvent often boils off at atmospheric pressure before the two-phase state is reached.

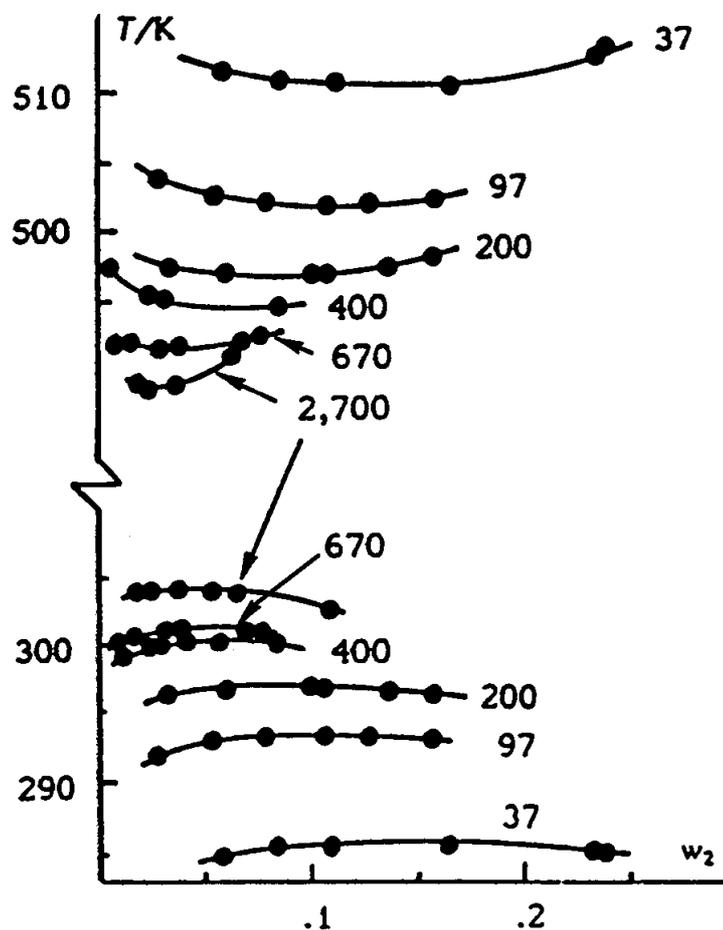


Fig. 1: Phase separation upon cooling and upon heating for the system cyclohexane/polystyrene and the indicated molar masses ( $M_w$  in kg/mole);

$w_2$  is the weight fraction of polystyrene.

Saeki, S, et al. *Macromolecules* 6(2), 246-250. 73.

The measuring data of Fig. 1 were obtained by cooling or heating a given homogeneous solution until it becomes turbid at the so called cloud point temperature  $T_{cp}$  because of the segregation of a second phase. The reason for this milky appearance lies in the normally pronouncedly different refractive indices of the components. The dependence of  $T_{cp}$  on the composition of the mixture is called cloud point curve. For small  $U$  the two cloud points belonging to a given molar mass and constant temperature (cf. Fig. 1) constitute the compositions of the coexisting phases. If one adds successively polymer to a certain amount of solvent one moves along a line parallel to the abscissa until the cloud point at the lower polymer concentration is reached. Up to that point the mixture is homogeneous. As further polymer is added, the first droplet of a second phase (gel phase) is segregated from this mixture (sol phase). The composition of the gel is in the present case given by the second cloud point at the given temperature. Adding more polymer does not change the compositions of the coexisting phases but only increases the volume of the polymer rich phase until the last droplet of the sol phase disappears. The mixture remains homogeneous up to the pure polymer. The line connecting the points representing the sol and the gel phase, respectively, for  $T=\text{const.}$  is called tie line.

A more detailed analysis of the phase diagram reveals that the two-phase regime can be subdivided into two areas, within one the mixture unstable within the other it is metastable. The line separating these regions is called spinodal line. Fig. 2 shows the situation schematically for a system exhibiting a so called upper critical solution temperature (UCST, phase separation upon cooling). In this case the tie lines degenerate into a single point (at the critical temperature  $T_c$  and at  $w_c$ , the critical weight fraction of the polymer;  $w_c$  is for  $U=0$  given by the maxima of the cloud point curves) as  $T$  is raised. For the opposite case (phase separation upon heating) we speak of a system exhibiting a lower critical solution temperature (LCST). Subject to the condition  $U = 0$  the ends of the tie lines (the so called coexistence curve) coincides with the cloud point curve.

For mixtures of low molecular weight compounds ( $U = 0$  is automatically fulfilled) the critical composition (extrema of the coexistence curves) are normally close to 1:1 mixture. With polymer/solvent systems  $w_c$  is the more shifted towards lower values, the higher the molar mass of the polymer becomes (cf. Fig. 1). In the limit of infinitely long chains  $w_c \rightarrow 0$ . The temperature at which this situation is reached, is normally called  $\Theta$  (theta temperature, cf. viscometric experiments). As can be seen from Fig. 1, there exist two theta temperatures for the system cyclohexane/polystyrene, one for endothermal conditions, corresponding to the UCSTs, and another one for exothermal conditions, corresponding to the LCSTs.

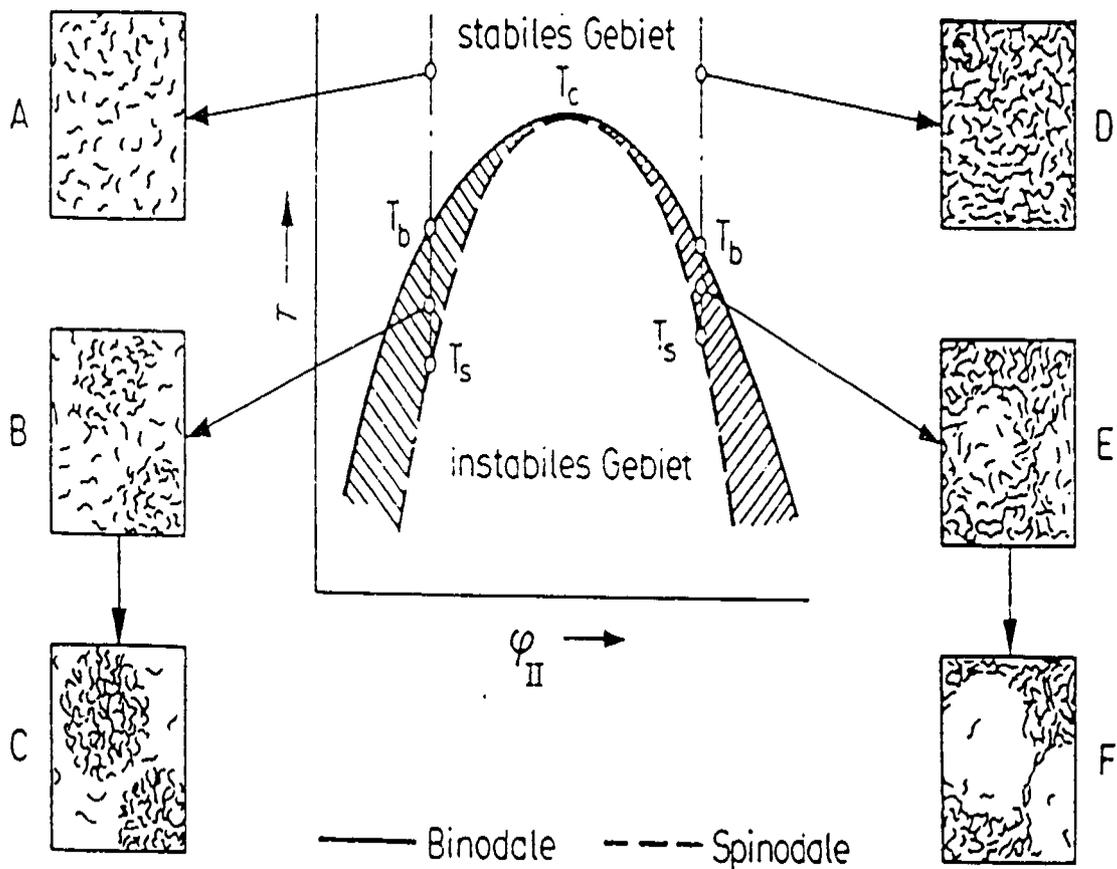
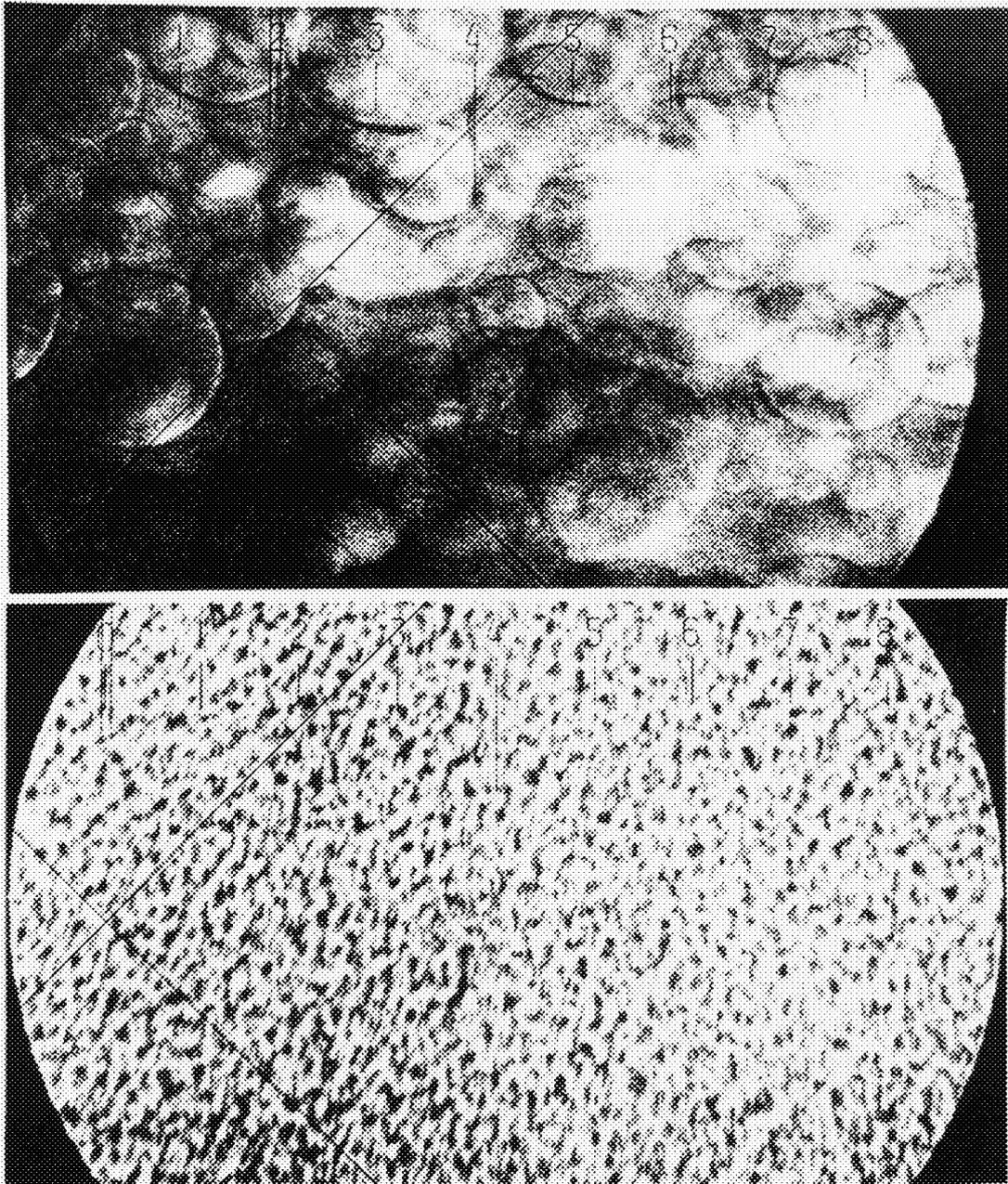


Fig. 2: Schematic phase diagram (after Derham and Goldsbrough and Gordon 1974) for solutions of a molecularly uniform polymer. Polymer lean phase (sol): A stabile; B metastable; C unstable, segregation of a gel phase. Polymer rich phase (gel): D stabile; E metastable; F unstable, segregation of a sol phase.

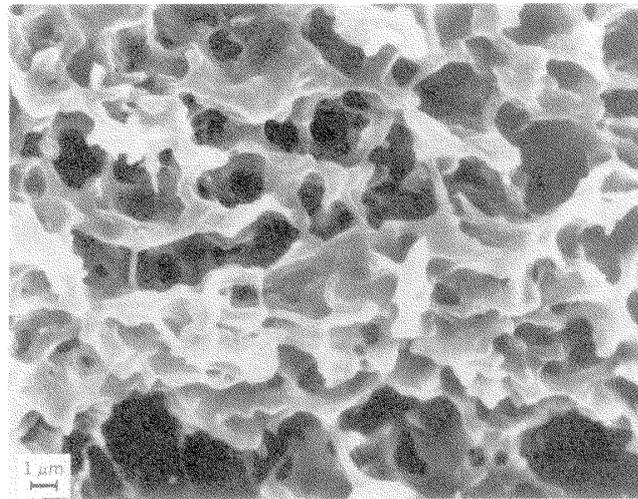
Binodal curve and spinodal curve touch each other at the critical point. Within the metastable regime a solution may remain homogeneous upon standing for a very long time, despite the possibility to reduce the Gibbs energy upon phase separation. Under these conditions the demixing process takes place via nucleation and growth. For values of temperature and composition located inside the spinodal line, on the other hand, phase separation takes place spontaneously, because any fluctuation in concentration will inevitably right away lead to a reduction in the Gibbs energy. Consistent with the different demixing processes, the morphology of the two phase systems looks markedly different as demonstrated in Fig. 3.



*Fig. 3: Micrographs of the phase separated system phenetol/polyisobuten 87. Upper picture: A solution was slowly cooled from the homogeneous region (75 °C) to 25 °C into the metastable region (1 K/h; mechanism: nucleation and growth). Lower picture: This time a solution was cooled rapidly into the unstable region (1 K/s; mechanism: spinodal decomposition); M. Heinrich thesis, Mainz 1991*

In the case of a nucleation and growth mechanism the individual droplets of the minor phase formed in the early state of the process grow slowly. They are dispersed in the matrix of the corresponding coexisting phase and can become rather large. For spinodal decomposition,

on the other hand, the size of the coexisting phases is usually at least one order of magnitude less and the morphology is co-continuous, i.e. for each phase it is possible to find paths through the entire system without the necessity of penetrating into the other coexisting phase. With mixtures of low molecular weight liquids these structures are quickly lost upon standing. The driving force for this process is the minimization of the interface (contributing to high values of the Gibbs energy). Eventually the coexisting phases are separated macroscopically and divided by a meniscus. With polymer mixtures the morphologies prevailing at the early stages of phase separation are often frozen in (e.g. because of the glassy solidification of one phase upon cooling) and constitute the basis of some special properties of such blends. Fig. 4 shows an example for the spatial distribution of the phases in a commercial product.



*Fig. 4: Scanning electron micrograph of a 70/30 blend of EPM and polypropylene; the EPM phase was extracted with heptane, leaving the PP.*  
*Encyclopedia of Polymer Sci. Vol. 9, p. 779*

### *Binodals and spinodals*

The following discussion in terms of phenomenological thermodynamics is based on the Gibbs energy,  $G$ , of the system. Quantities referring to one mole of mixture are characterized by a stroke above the symbol ( $\bar{X}$ ), those referring to one mole of segments (where the segment can be defined arbitrarily and is normally defined by the volume of the solvent or set 100 mL/segment) by a double stroke ( $\overline{\overline{X}}$ ). The latter option is considerable more suitable for polymer containing systems, because of the fact that one mole of a truly high molecular material has a mass of approximately one ton. It is, however, essential to keep in mind that mole

fractions are still the basis for all thermodynamic consideration due to the fact that segments are bound together and do not constitute independent units.

Once the size of a segment is defined (e.g. in terms of volumes), one can calculate the number  $N_i$  of segments of a polymer species  $i$  as

$$N_i = \frac{\bar{V}_i}{\bar{V}_{seg}} \quad (2)$$

In many cases the molar volume of the solvent is set equal to the molar volume of the segment. The Gibbs energy of  $n_1$  moles of component 1 and  $n_2$  moles of component 2 is calculated from the segment molar or molar quantities as

$$\Delta G = \overline{\Delta G} (n_1 N_1 + n_2 N_2) = \overline{\Delta G} (n_1 + n_2) \quad (3)$$

The coexistence of different phases under equilibrium is bound to the condition that the chemical potential  $\mu$  must be identical in all phases. We are presently only interested in liquid/liquid phase equilibria (i.e. the two phases have the same state of aggregation); this means that we need only account for differences in the Gibbs energy of mixing and can write

$$\Delta\mu_i' = \Delta\mu_i'' \quad (4)$$

For many purposes volume fractions  $\varphi$  are employed as composition variables. For a binary mixture containing components that are made up of more than one segment,  $\varphi$  is given as

$$\varphi_i = \frac{n_i N_i}{n_1 N_1 + n_2 N_2} \quad (5)$$

With the definition of the chemical potential of component 1

$$\Delta\mu_1 = \left( \frac{\partial \Delta G}{\partial n_1} \right)_{p,T,n_2} \quad (6)$$

and analogously of component 2 we obtain the following relations (cf. eq(2))

$$\begin{aligned} \Delta\mu_1 &= \left( \frac{\partial \left[ (n_1 N_1 + n_2 N_2) \overline{\Delta G} \right]}{\partial n_1} \right)_{p,T,n_2} = \\ &= N_1 \overline{\Delta G} + (n_1 N_1 + n_2 N_2) \left( \frac{\partial \overline{\Delta G}}{\partial \varphi_1} \right) \left( \frac{\partial \varphi_1}{\partial n_1} \right) \end{aligned} \quad (7)$$

where

$$\left(\frac{\partial \varphi_1}{\partial n_1}\right) = \frac{1}{n_1} \varphi_1 \varphi_2 \quad (8)$$

so that eq (7) becomes

$$\Delta\mu_1 = N_1 \Delta\bar{G} + N_1 \frac{n_1 N_1 + n_2 N_2}{n_1 N_1} \varphi_1 \varphi_2 \left(\frac{\partial \Delta\bar{G}}{\partial \varphi_1}\right) \quad (9)$$

After some rearrangement we obtain

$$\Delta\mu_1 = N_1 \left( \Delta\bar{G} + (1 - \varphi_1) \frac{\partial \Delta\bar{G}}{\partial \varphi_1} \right) \quad (10)$$

In terms of molar quantities this equation reads

$$\Delta\mu_1 = \Delta\bar{G} + (1 - x_1) \frac{\partial \Delta\bar{G}}{\partial x_1} \quad (11)$$

Because of the above relations one can obtain the chemical potential of component 1 by means of the tangent to the curves describing the composition dependence of the Gibbs energy of mixing from the intercept with the ordinate ( $\varphi_1 = 1$ ), as demonstrated in the lower part of Fig. 5. Analogously the chemical potential of component 2 results from the intercept at  $\varphi_2 = 1$ . The chemical potentials of a given component must be identical in the coexisting phases as formulated in eq (4). In case the system exhibits limited mutual solubility it is therefore possible to determine the composition of the coexisting phases by means of a common tangent (double tangents, cf. upper curves in the lower part of Fig. 5). Repeating this construction for different temperatures and plotting  $T$  on the ordinate and the corresponding compositions on the abscissa yields the binodal curve shown in the upper part of Fig. 5.

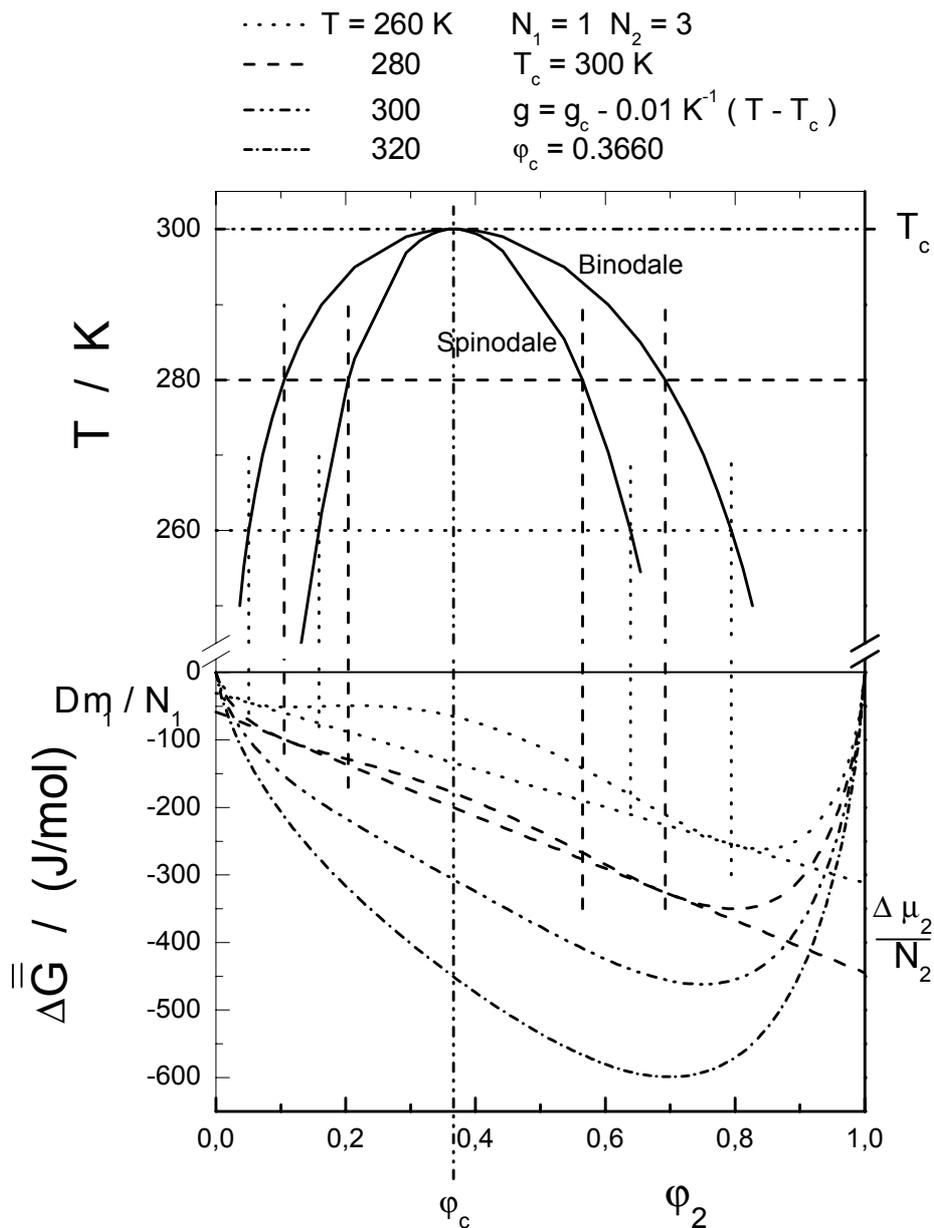


Fig. 5: How to construct a phase diagram knowing the composition dependence of segment molar Gibbs energy of mixing

Another totally equivalent possibility to determine the composition of the coexisting phases makes use of the condition that the Gibbs energy of any equilibrium system must become minimum. Out of any conceivable combination of coexisting phases the one with the lowest Gibbs energy of the entire system will under these conditions be realized. To find that minimum for a given over-all (brutto) composition of the mixture  $\phi_2^b$ , one calculates the Gibbs energy  $G^b$  of the entire system for all possible pairs  $\phi_2' < \phi_2^b$  and  $\phi_2'' > \phi_2^b$ . Fig. 6

gives an example for this procedure, for the thermodynamic conditions used to calculate the uppermost curve of the lower part of the previous diagram and setting  $\phi_2^b$  equal to 0.1.

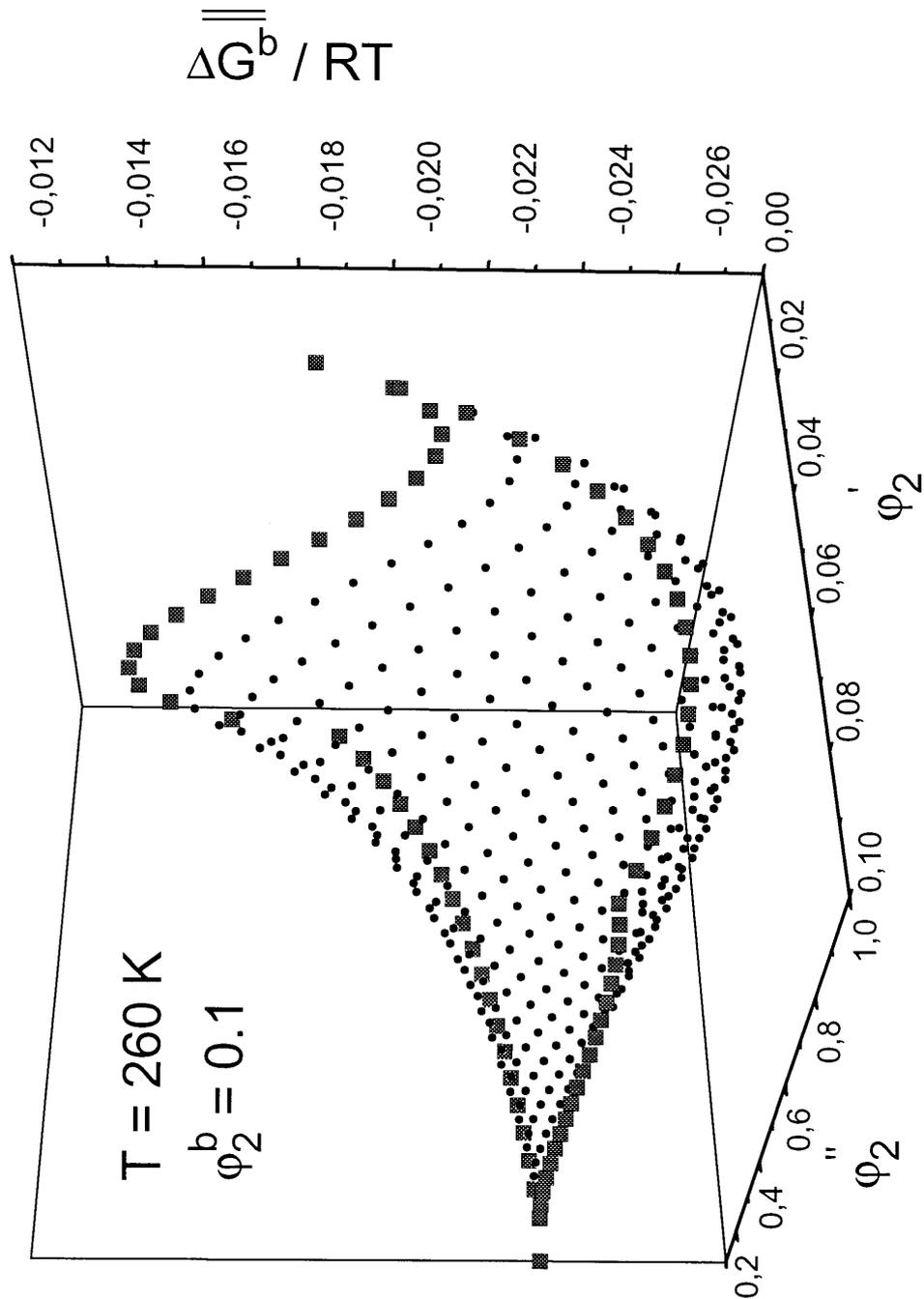


Fig. 6: Segment molar Gibbs energy of mixing for a phase separated system (constant over-all composition  $\phi_2^b = 0.1$ ) as a function of the composition of the coexisting phases.

The exact location of the minimum is hard to read from this representation. For this reason we reduce the number of variables by one, introducing  $\Delta\varphi_2 = \varphi_2'' - \varphi_2'$  and keeping (for purely heuristic reasons) the phase volume ratio constant at the equilibrium value. The result of this evaluation is shown in the following graphs for various  $\varphi_2^b$  values. It is self-evident that the tie lines calculated from the minima in  $G$  must not depend on the over-all starting composition (lying inside the two phase regime). Another interesting feature consists in the fact that  $G$  may initially rise as  $\Delta\varphi$  becomes larger (Fig. 7) before the minimum is reached. This behavior is indicative for the passage of metastable states.

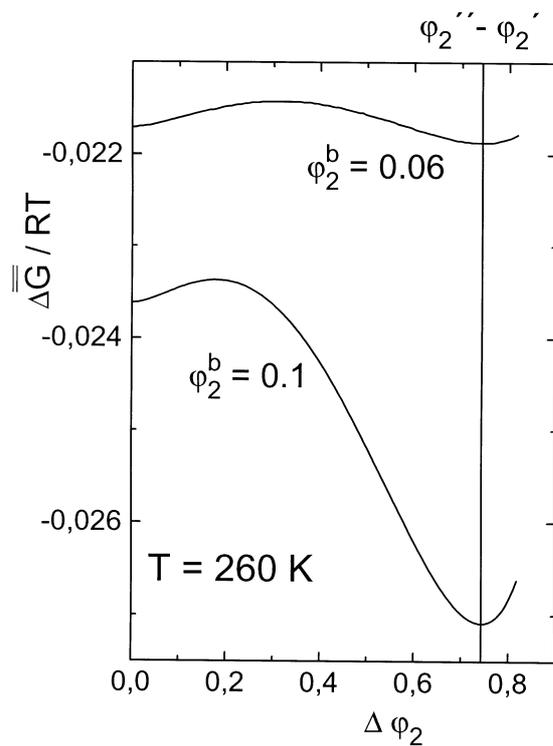


Fig. 7: Segment molar Gibbs energy of mixing for a phase separated system (at the indicated over-all compositions) as a function of the difference  $\Delta\varphi_2$  in the composition of the coexisting phases.

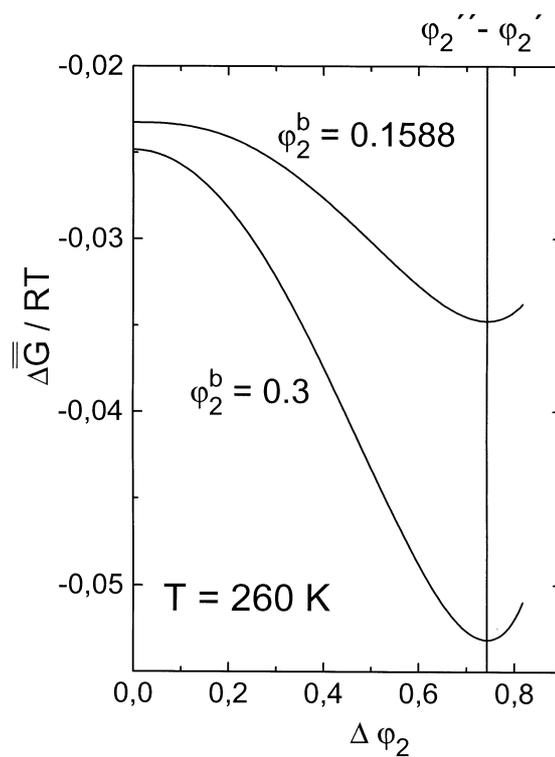


Fig. 8: As. Fig. 7 but for different over-all composition

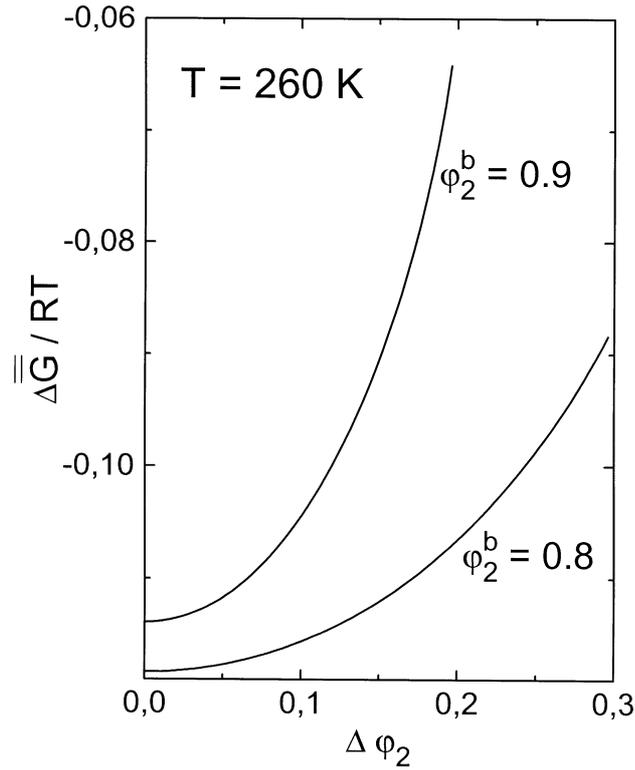


Fig. 9: As. Fig. 7 but for different over-all composition

The upper curve of Fig. 8, corresponding to  $\phi_2^b = 0,1588$ , is the first one, which does no longer exhibit the initial ascend upon rising the over-all polymer concentration. This implies that we have chosen an over-all composition located on the spinodal line. As this  $\phi_2^b$  value is surpassed the mixtures become unstable instead of metastable.

In case one selects a  $\phi_2^b$  value located inside the homogeneous region of the phase diagram the Gibbs energy of the hypothetically phase separated mixture increases steadily as  $\Delta \phi_2$  rises. This situation is depicted in Fig. 9.

The points of inflection of the curves of the lower part of Fig. 5, representing the spinodal conditions in terms of Gibbs energy, are mathematically given by the condition

$$\frac{\partial^2 \overline{\Delta G}}{\partial \phi_2^2} = 0 \quad (12)$$

In the critical point of the system, where the binodal line and the spinodal line touch, the minima and the points of inflection coincide and the third derivative also becomes zero

$$\frac{\partial^3 \overline{\Delta G}}{\partial \phi_2^3} = 0 \quad (13)$$

In the vicinity of the critical composition of the system and close to the critical temperatures the curve  $\overline{\Delta G}(\phi_2)$  is almost linear as demonstrated in Fig. 5.

### *Flory-Huggins theory*

Processes taking place at constant temperature and constant pressure are normally dealt with in terms of changes in the Gibbs energy  $\Delta G$ , which are made up of an enthalpy contribution  $\Delta \overline{H}$  and an entropy contribution  $\Delta \overline{S}$  according to

$$\Delta \overline{G} = \Delta \overline{H} - T \Delta \overline{S} \quad (14)$$

where  $T$  is the absolute temperature.

Perfect mixing takes place athermally ( $\Delta \overline{H} = 0$ ) and the volume of the mixture does not differ from the sum of the volumes of its constituents (volume of mixing  $\Delta \overline{V} = 0$ ). In this case the driving force for the formation of a molecularly disperse mixture consists exclusively of the changes in entropy associated with the mixing process, i.e. in the higher number of arrangements of the molecules in the mixed state. The just described limiting situation is usually called perfect mixing (by approximation sometimes realized with mixtures of gases or mixed crystals) and the following relation holds true

$$\frac{-\Delta \overline{S}^{perf}}{R} = x_1 \ln x_1 + x_2 \ln x_2 \quad (15)$$

where  $R$  is the universal gas constant and  $x_i$  are mole fractions. For the Gibbs energy of mixing we thus obtain

$$\Delta \overline{G}^{perf} = -T \Delta \overline{S}^{perf} \quad (16)$$

Real mixture normally deviate considerably from the behavior described above. In order to maintain a well defined reference state one introduces so called excess quantities, measuring the deviation from perfect mixing, as formulated in the following equations.

$$\Delta \overline{G} = \Delta \overline{G}^{perf} + \Delta \overline{G}^E \quad (17)$$

where

$$\Delta \overline{G}^E = \Delta \overline{H} - T \Delta \overline{S}^E \quad (18)$$

This procedure is very useful for mixtures of low molecular weight compound. For polymer solutions and polymer blends the deviation from perfect conduct is, however, so pronounced that another reference behavior is advantageous.

For linear macromolecules Flory and Huggins have therefore developed the concept of combinatorial mixing. To this end each molecule is subdivided into individual segments, which are in their size usually fixed by the volume of the solvent or (by definition) by a volume of 100 mL/segment (cf. page 6). This approach uses a lattice onto which the different segments of the individual molecules can be placed, as shown by the two-dimensional sketches of Fig. 10.

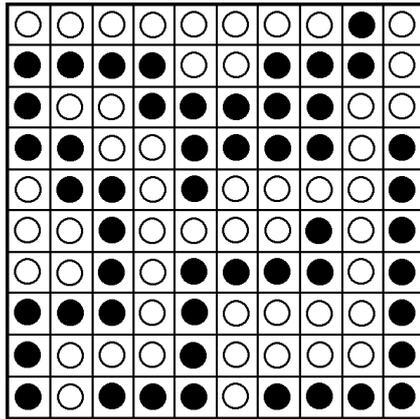


Fig. 10a: Lattice model for a mixture of low molecular weight compounds

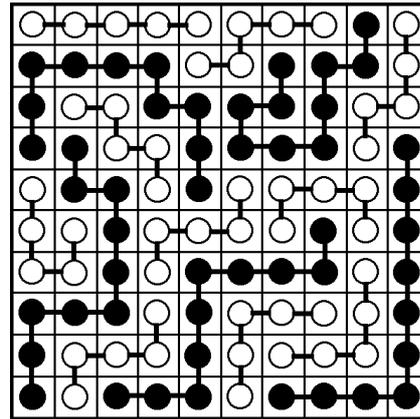


Fig. 10b: Lattice model for a mixture of chain molecules

The situation for a mixture of low molecular weight compounds ( $N_1 = N_2 = 1$ ) is depicted in *part a* of this graph for an equal number of black and white entities. Let us assume that this sketch stands for one mole of mixture. The combinatorial entropy can then be easily calculated from eq (19). *Part b* of this Figure differs from *part a* only by the fact that we invariably connect 5 of the white molecules and 10 of the black molecules by a chemical bond to form a white penta-mer ( $N_1 = 5$ ) and a black deca-mer ( $N_2 = 10$ ). As a consequence of this action we have reduced the number of moles from 1 to 0.15, without changing the mass of the system. From the manifold of possibilities to place the *segments* of the chain molecules on the lattice, the authors have come to the following expression for the so-called combinatorial entropy of mixing for one mole of *segments* (instead of molecules), which is again an idealization like the corresponding expression for the perfect entropy of mixing

$$\frac{-\Delta \overset{=}{S}^{comb}}{R} = \frac{1}{N_1} \varphi_1 \ln \varphi_1 + \frac{1}{N_2} \varphi_2 \ln \varphi_2 \quad (19)$$

By analogy to mixtures of low molecular weight components we quantify the deviation from this limiting behavior. To this end we introduce residual contribution according to

$$\overline{\Delta G} = \overline{\Delta G}^{comb} + \overline{\Delta G}^R \quad (20)$$

Initially  $\overline{\Delta G}^R$  was considered to be exclusively of enthalpic nature and a composition independent interaction parameter, here called  $g'$ , was introduced by means of the following relation

$$\frac{\overline{\Delta H}}{R T} = g' \varphi_1 \varphi_2 \quad (21)$$

$g'$  was meant to measure  $\frac{1}{2}$  of the change in enthalpy associated with the destruction of a contact between two segments of component 1 and two segments of component 2 to yield two contacts between a segment of 1 and a segment of 2. Despite the fact that experiments have very early demonstrated convincingly that  $g$  is neither independent of composition nor necessarily of enthalpic nature, this formalism is still widespread and helpful for the understanding of some central features of polymer containing mixtures. For the integral Gibbs energy of mixing per mole of segments the Flory-Huggins equation reads

$$\frac{\overline{\Delta G}}{R T} = \frac{1}{N_1} \varphi_1 \ln \varphi_1 + \frac{1}{N_2} \varphi_2 \ln \varphi_2 + g \varphi_1 \varphi_2 \quad (22)$$

where  $g$  is redefined as

$$g = \frac{\overline{\Delta G}^R}{R T \varphi_1 \varphi_2} \quad (23)$$

and contains enthalpic as well as entropic contributions.

The integral Flory-Huggins interaction parameter  $g$  is experimentally inaccessible. The only information that is available stems from the measurement of chemical potentials, normally that of the solvent (e.g. via vapor pressure measurements or via osmosis). For crystalline polymers the chemical potential of the polymer in the mixture becomes accessible from liquid/solid equilibria. In view of this situation and because of the already mentioned concentration dependence of  $g$  we must differentiate the integral equation (22) and end up with the following expressions

$$\frac{\partial}{\partial \varphi_2} \frac{\overline{\Delta G}}{R T} = -\frac{1}{N_1} + \frac{1}{N_2} - \frac{1}{N_1} \ln \varphi_1 + \frac{1}{N_2} \ln \varphi_2 + g (\varphi_1 - \varphi_2) + \frac{\partial g}{\partial \varphi_2} \varphi_1 \varphi_2 \quad (24)$$

$$\frac{\partial^2 \frac{\Delta \bar{G}}{RT}}{\partial \varphi_2^2} = \frac{1}{N_1 \varphi_1} + \frac{1}{N_2 \varphi_2} - 2g + 2 \frac{\partial g}{\partial \varphi_2} (\varphi_1 - \varphi_2) + \frac{\partial^2 g}{\partial \varphi_2^2} \varphi_1 \varphi_2 \quad (25)$$

$$\frac{\partial^3 \frac{\Delta \bar{G}}{RT}}{\partial \varphi_2^3} = \frac{1}{N_1 \varphi_1^2} - \frac{1}{N_2 \varphi_2^2} - 6 \frac{\partial g}{\partial \varphi_2} + 3 \frac{\partial^2 g}{\partial \varphi_2^2} (\varphi_1 - \varphi_2) + \frac{\partial^3 g}{\partial \varphi_2^3} \varphi_1 \varphi_2 \quad (26)$$

By means of the above relations one obtains the following expression for the chemical potential of component 1

$$\frac{\Delta \mu_1}{RT N_1} = \frac{1}{N_1} \ln \varphi_1 + \left( \frac{1}{N_1} - \frac{1}{N_2} \right) \varphi_2 + \chi \varphi_2^2 \quad (27)$$

where  $\chi$  is given by

$$\chi = g + \varphi_1 \frac{\partial g}{\partial \varphi_1} = \frac{\Delta \mu_1^R}{RT N_1 \varphi_2^2} \quad (28)$$

and for the chemical potential of component 2

$$\frac{\Delta \mu_2}{RT N_2} = \frac{1}{N_2} \ln \varphi_2 + \left( \frac{1}{N_2} - \frac{1}{N_1} \right) \varphi_1 + \xi \varphi_1^2 \quad (29)$$

where  $\xi$  is given by

$$\xi = g + \varphi_2 \frac{\partial g}{\partial \varphi_2} = \frac{\Delta \mu_2^R}{RT N_2 \varphi_1^2} \quad (30)$$

For the integral interaction parameter the following equations hold true

$$g = \frac{1}{\varphi_1} \int_0^{\varphi_1} \chi d\varphi_1 = \frac{1}{\varphi_2} \int_0^{\varphi_2} \xi d\varphi_2 \quad (31)$$

$$g = \varphi_1 \chi + \varphi_2 \xi \quad (32)$$

Demixing into two liquid phases is bound to the existence of a “hump” in the function  $\Delta \bar{G}(\varphi_2)$  as discussed earlier. The contribution  $\Delta \bar{G}^{\text{comb}}(\varphi_2)$  inevitably runs above its tangents and does consequently exclude demixing; it is only the residual contribution  $\Delta \bar{G}^R(\varphi_2)$ , which may induce phase separation as demonstrated in Fig. 11. Only if the interaction parameter  $g$  exceeds a certain critical value, depending on the chain lengths of the components, the devia-

tion from combinatorial behavior becomes large enough to produce the required hump. Under the (unreasonable) assumption that  $g$  does not depend on composition, all interaction parameter become identical and one can calculate the critical interaction parameter  $g_c$  and the critical volume fractions  $\varphi_c$  from the condition that the binodal curve and the spinodal curve touch each other as the conditions become critical. By means of the eqs (12) and (25) one can calculate the spinodal if  $g$  is known and with the eqs (13) and (26) the critical point becomes accessible. From (13) and (26) one obtains

$$\frac{1}{N_1 \varphi_{1c}^2} = \frac{1}{N_2 \varphi_{2c}^2} \quad (33)$$

$$\sqrt{N_1} \varphi_{1c} = \sqrt{N_2} (1 - \varphi_{1c}) \quad (34)$$

$$\sqrt{N_1} \varphi_{1c} + \sqrt{N_2} \varphi_{1c} = \sqrt{N_2} \quad (35)$$

$$\varphi_{1c} = \frac{\sqrt{N_2}}{\sqrt{N_1} + \sqrt{N_2}} \quad (36)$$

and from the eqs (12) and (25)

$$g_c = \frac{1}{2} \left( \frac{1}{N_1 \varphi_{1c}} + \frac{1}{N_2 \varphi_{2c}} \right) \quad (37)$$

Insertion of eq (36) yields

$$g_c = \frac{1}{2} \left( \frac{\sqrt{N_1} + \sqrt{N_2}}{N_1 \sqrt{N_2}} + \frac{\sqrt{N_1} + \sqrt{N_2}}{N_2 \sqrt{N_1}} \right) = \frac{1}{2} \left( \frac{(\sqrt{N_1} + \sqrt{N_2})^2}{N_1 N_2} \right) \quad (38)$$

Despite the deficiencies of the Flory-Huggins theory this approach is very helpful in understanding some basic features. For example the fact that the mutual miscibility associated with a certain unfavorable interaction between the components (positive  $g$  values) decreases rapidly as the number of segments  $N_i$  becomes larger. Similarly it explains that critical volume fractions around 0.5 can only be expected if the chain length of the components is not too different. Otherwise the critical composition is shifted to the side of the component containing fewer segments.

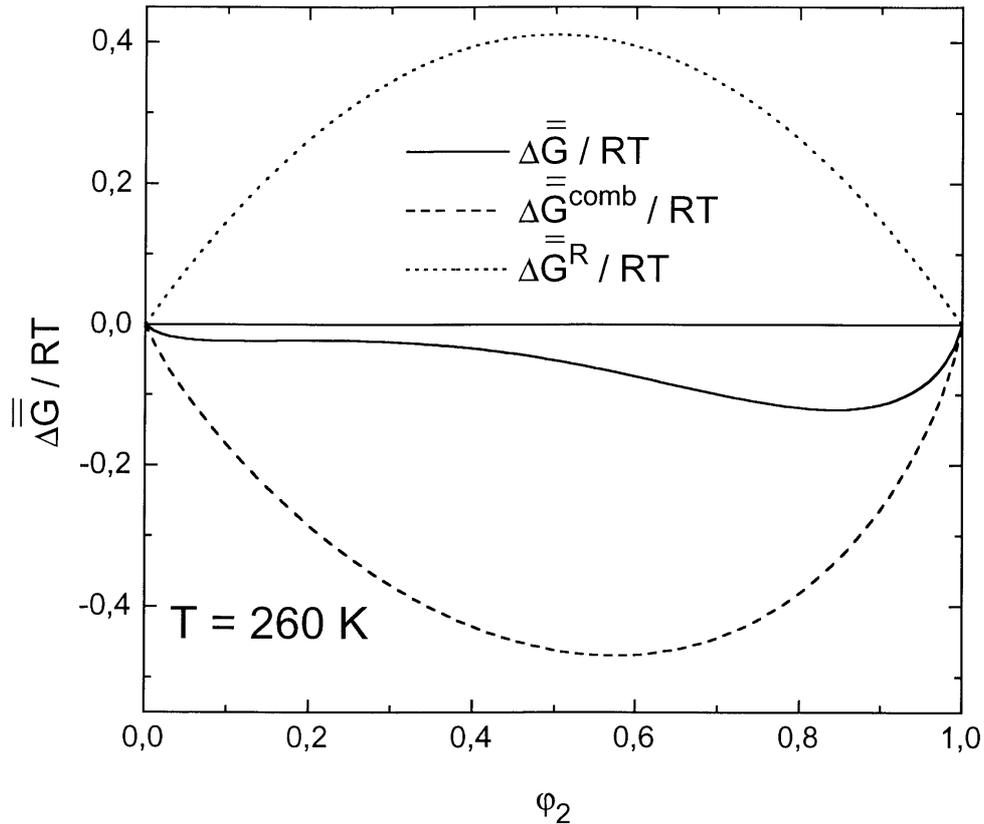


Fig. 11: Segment molar Gibbs energy of mixing and its combinatorial and non-combinatorial (residual) contributions as a function of composition.

### Quasi binary systems (non-uniformity $U > 0$ )

Synthetic polymers are seldom molecularly uniform. This implies that the number of species of their solution in a single solvent is typically on the order of several thousands, despite the fact that – chemically speaking – we have only two components. To indicate this feature we are in this case talking about *quasi*-binary systems. This short chapter describes some additional effects observed with such solutions. The example shown in Fig. 12 presents a phase diagram measured for solutions of polystyrene (most probable molecular weight distribution  $U = 1$ ) in cyclohexane.

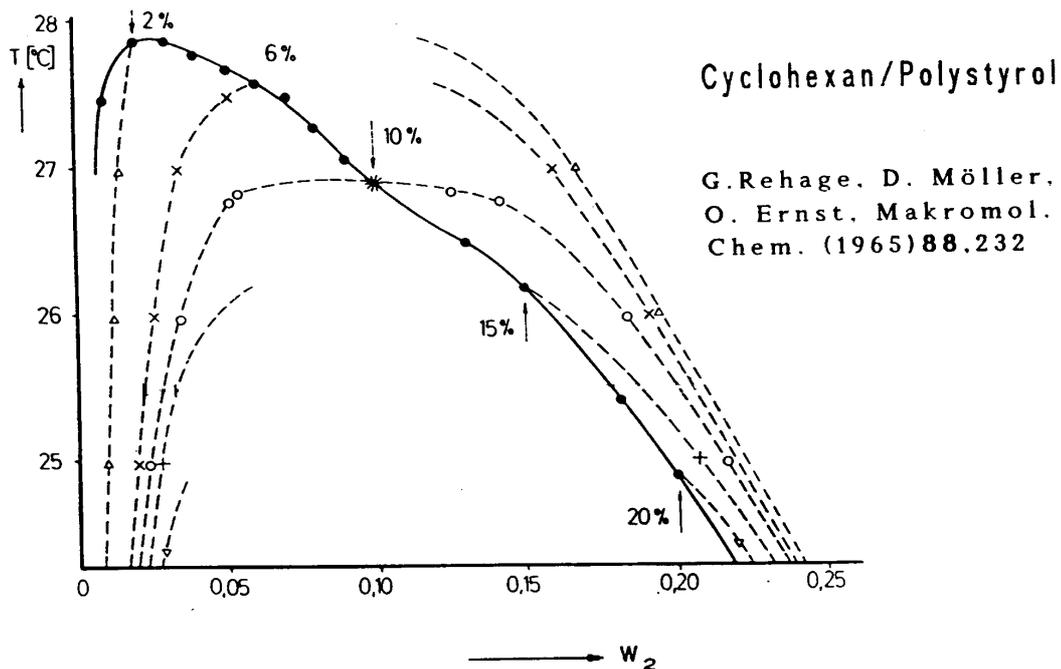


Fig. 12: Cloud point curve (full line) and coexistence curves for different over-all concentrations (broken lines) measured for the system cyclohexane/polystyrene

The most striking feature is the discrepancy between the cloud point curve (full line) and the binodal curves (connection of the end-points of the tie lines). Because of an uneven distribution of polymer species differing in molar mass upon the coexisting phases one obtains an individual binodal curve for each starting composition. Normally the binodal curves are interrupted and only for critical composition one obtains a closed curve passing through the critical point, which is shifted out of the maximum towards higher polymer concentration.

Upon phase separation the original polymer is fractionated. This means that the shorter chains accumulate in the polymer lean phase (sol) for entropic reasons (larger number of possible arrangements), whereas the longer chains prefer the polymer rich phase (gel) for enthalpic reasons (fewer unfavorable contacts between the polymer segments and solvent molecules). The distribution coefficient of the different polymeric species of a given sample varies considerably with chain length as can be seen from the GPC diagram (differential molecular mass distribution) shown in Fig. 13.

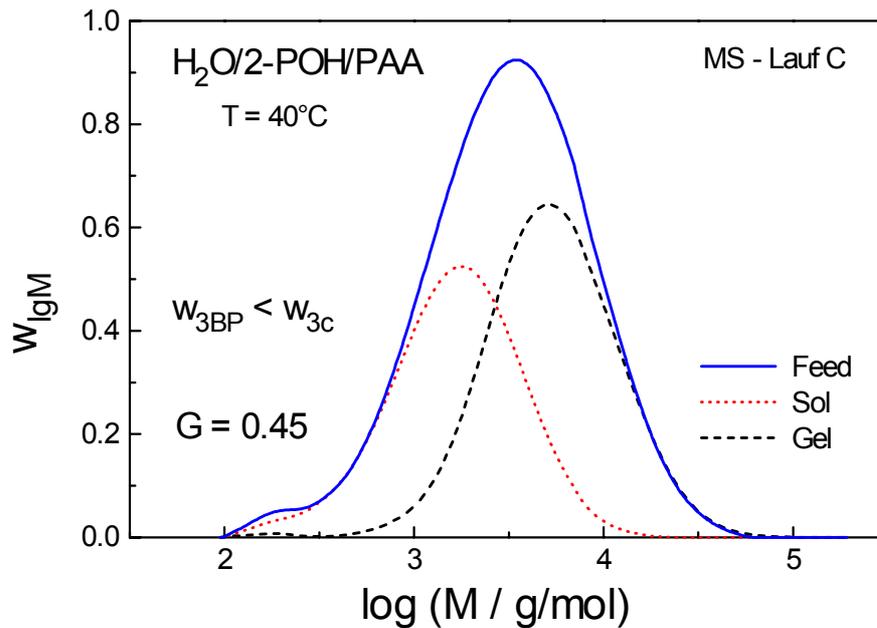


Fig. 13: Differential molar mass distribution of the starting polymer (feed) and of the polymer fractions contained in the coexisting phases (sol and gel) as determined by GPC experiments for the system water/2-propanol/poly(acrylic acid).  $G$  (not to be confused with the Gibbs energy) is the mass ratio of the polymer contained in the sol and in the gel, respectively. K. Meißner thesis Mainz 1994

In this graph the sum of sol and gel must yield the value of the starting material (feed). At the  $M$  value at which the curves for sol and gel intersect, 50% of the species that are present in the feed reside in each phase; below that characteristic  $M$  value the percentage is higher in the sol and above it in the gel phase. Liquid/liquid phase equilibria of the present kind are used for preparative fractionation on a technical scale. It is obvious that a sharp cut through the molecular weight distribution would be best. In reality fractionation is much less efficient. In order to quantify the success, one uses the so called Breitenbach-Wolf plot (Fig. 14). To that end the logarithm of the ratio of polymer with a given molar mass  $M$  that is found in the sol phase and in the gel phase, respectively, is mapped out as a function of  $M$ . In such graphs the ordinate value becomes zero at the  $M$  value at which the molecular weight distributions for sol and gel intersect. The steepness of the curves increases with rising quality of fractionation. In the unrealizable case of sharp cuts through the molecular weight distribution the curve would run parallel to the ordinate and its position on the  $M$  axis determines where this section takes place (i.e. fixes the  $G$  value, cf. Fig. 13).

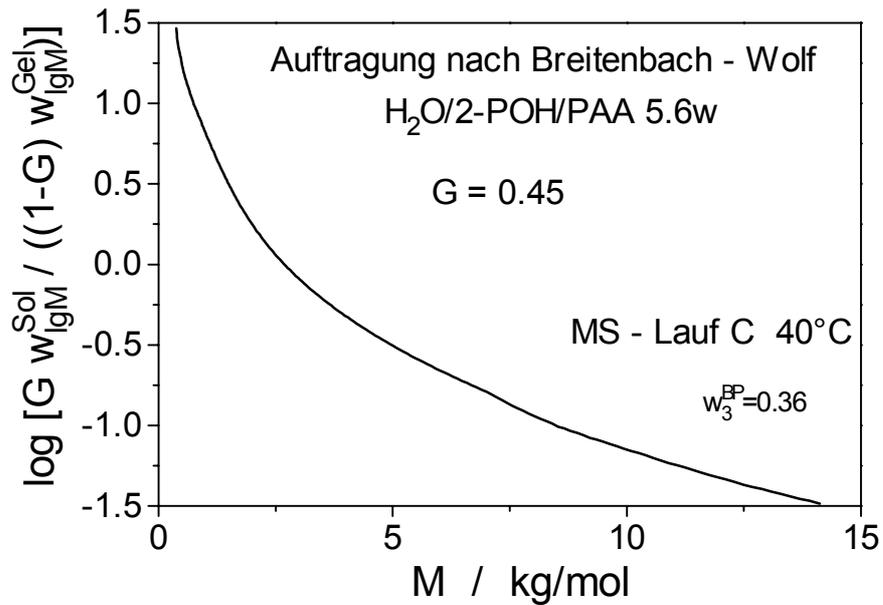


Fig. 14: Breitenbach-Wolf plot for the fractionation displayed in Fig. 13. K. Meißner thesis Mainz 1994

### Ternary systems

The description of three component systems requires three independent variables in the case of constant pressure:  $T$  and two composition variables. Because of the additional variable it is according to the Gibbs phase law possible that three phases coexist within a certain *range* of composition, in contrast to binary systems, for which only three phase *lines* are feasible.

#### *The Gibbs phase triangle*

In order to avoid three-dimensional representations one normally depicts the isothermal situation and uses the so-called Gibbs phase triangle for that purpose as demonstrated in Fig. 15.

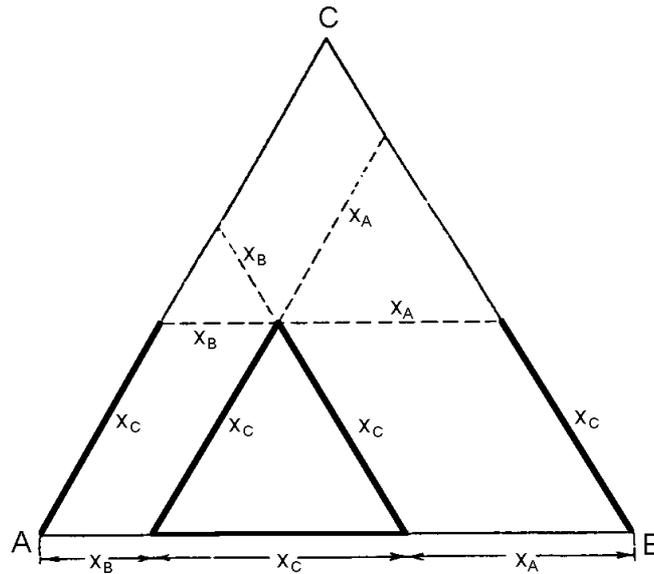


Fig. 15: How to read the composition of a ternary mixture in a Gibbs phase triangle

The corners of the triangle represent the pure components, the three edges (of unit length) the binary subsystems and the interior of the triangle stands for ternary mixtures. There are no restrictions concerning the particular nature of the composition variable, as long as the sum of all components yields unity. The most common method (out of several) to read the concentrations is demonstrated in Fig. 15

#### Gibbs energy of mixing

The extension of the integral Flory-Huggins equation to  $K$  components yields the following expression

$$\frac{\overline{\Delta G}}{RT} = \sum_{i=1}^K \frac{1}{N_i} \varphi_i \ln \varphi_i + \sum_{i=1}^{K-1} \sum_{j=i+1}^K g_{ij} \varphi_i \varphi_j \quad (39)$$

For its derivation it was tacitly assumed that interactions between two types of segments ( $ij$ ) suffice to describe the mixture and that no ternary interaction parameters  $g_{ijk}$  are required. For  $K = 3$  we obtain the relation for mixtures of three components.

For the construction of the phase diagram in terms of phenomenological thermodynamics (by analogy to that described for binary systems) we must now use a three dimensional representation as demonstrated in Fig. 16. The “hump” of the binary case becomes a “fold” in the ternary and the tangent turns into a tangential plane.

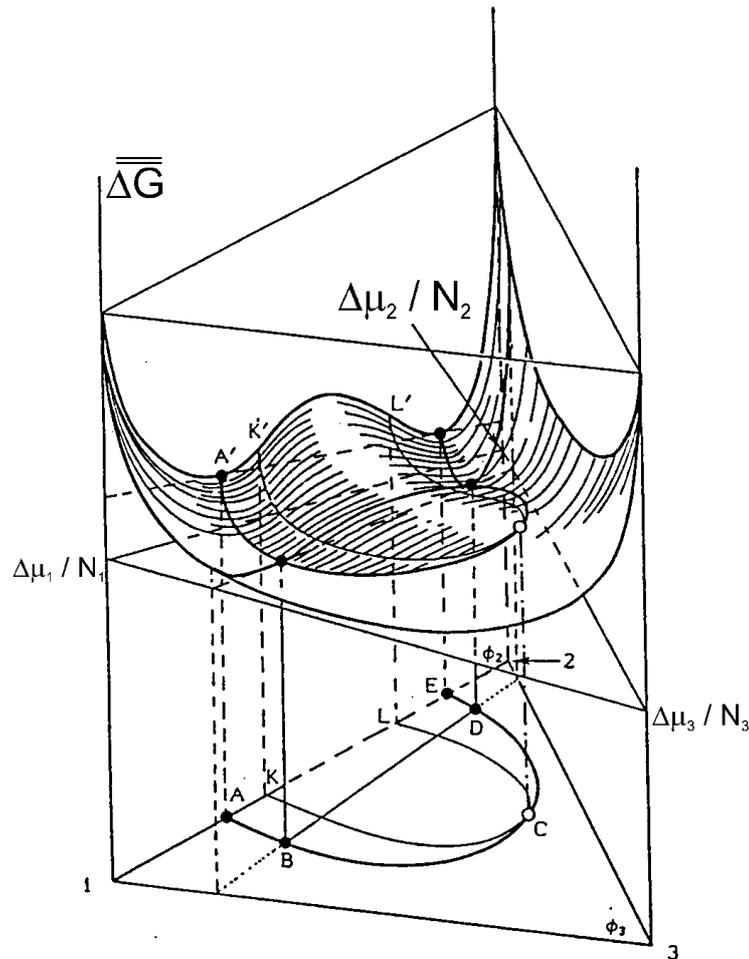


Fig. 16: Segment molar Gibbs energy of mixing for a ternary system as a function of its composition

### Cosolvency and co-nonsolvency

Bound to special thermodynamic conditions it is possible that a mixture of two low molecular weight liquids can dissolve any amount of a given polymer, whereas each of these liquids alone exhibits a miscibility gap with the polymer. How this phenomenon, termed cosolvency, looks like in a Gibbs phase triangle is shown in Fig. 17a. Similarly an area of immiscibility may show up for ternary mixtures, despite the fact that phase separation is absent for all three binary subsystems. This particular behavior, called co-nonsolvency by analogy to cosolvency is shown in Fig. 17b.

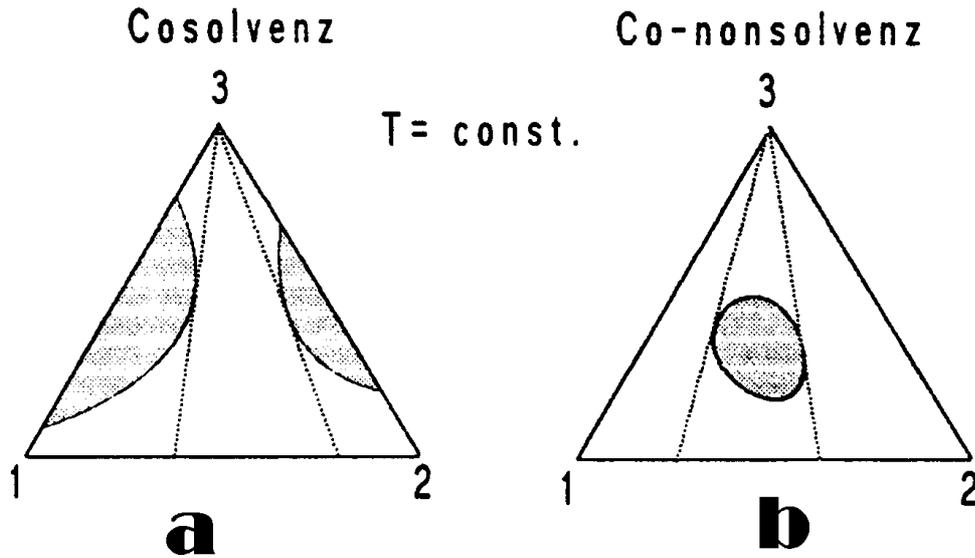


Fig. 17: Schemes describing the phenomena of cosolvency and co-nonsolvency

The easiest way to rationalize cosolvency is offered by the so-called single liquid approximation of Scott. It treats the mixture of the low molecular weight liquids 1 and 2 as one component (index <12>) and obtains for its interaction with the polymer (index 3) the following relation

$$g_{<12>3} = \varphi_1^* g_{13} + \varphi_2^* g_{23} - \varphi_1^* \varphi_2^* g_{12} \quad (40)$$

where the asterisks of the volume fractions indicate that these variables refer to the low molecular mixture only, according to

$$\varphi_i^* = \frac{\varphi_i}{\varphi_1 + \varphi_2} \quad \text{with } i = 1 \text{ or } 2 \quad (41)$$

According to this approach cosolvency is due to a very unfavorable interactions between the components of the mixed solvent (large  $g_{12}$ ), which do not yet suffice to induce their demixing but which are large enough to reduce  $g_{<12>3}$  below its critical value. In other words the formation a homogeneous mixture may lower the Gibbs energy of the ternary system more (because of the avoidance of 1-2 contacts via the insertion of polymer segments) than the prevention of the less unfavorable 1-3 and 2-3 contacts (associated with phase separation).

Co-nonsolvency can be explained by very favorable, normally negative  $g_{12}$  values. Under these conditions the third term of eq (40) may become dominant and  $g_{<12>3}$  can exceed its

critical value in spite of the fact that  $g_{13}$  and  $g_{23}$  are well below. Here the reason for demixing lies in the formation of many favorable 1-2 contacts in one of the coexisting phases.

### Exercises

1. Establishment of a phase diagram for the ternary system **acetone/diethyl ether/polystyrene**
  - a. Determination of cloud points at 0 °C by means of titration
  - b. Swelling experiments with the binary subsystems solvent/polymer
2. Swelling experiments with the system cyclohexane/polystyrene at room temperature
3. Interpretation of a plot of light transmittance as a function of temperature for a solution of polystyrene in cyclohexane of known composition with respect to its cloud point.
4. Draw a schematic phase diagram from the info of experiments 2 and 3, keeping in mind that the theta temperature of the system is 34 °C.
5. Determination of the molecular weight distribution of the polystyrene sample used and of the fractions obtained with the system acetone/2-butanone/polystyrene by means of GPC and evaluation of the fractionation efficiency by means of a Breitenbach-Wolf plot.
6. Calculation of  $g = g_c (1.29 + \text{group number} * 0.005)$  by means of the critical interaction parameter  $g_c$  for  $N_1=1$  and  $N_2=2$ . Also calculate the critical composition  $\varphi_c$ . Plot the combinatorial part and the residual part (for the calculated  $g$ ) of  $\Delta\bar{G}$  and  $\Delta\bar{G}$  itself as a function of composition and determine the tie lines and spinodal composition graphically.
7. Discuss the slopes of  $\Delta\bar{G}(\varphi_2)$  in the limit of  $\varphi_1 \rightarrow 0$  and  $\varphi_1 \rightarrow 1$  (analytically by differentiating the Flory-Huggins relation).

**Note:** Please do not copy the script when describing your experiments. The idea is that you make clear how the measurements were performed and evaluated. To this end it is recommended that the derivation of the relevant equations is presented or at least commented. Please collect the data in tables. Furthermore a reasonable estimate of the experimental uncertainties, differentiating between systematic and random errors, must be given.

### Experimental details

All participants are requested to show up in the lab 01 131 of building K (Welder-Weg 13, 1<sup>st</sup> story) to prepare the solutions (required time ca. 1-2 hours). Otherwise it is impossible to perform the experiments in one day.

### *Preparation of the solutions*

Note the weight of the flask (including a magnetic stirrer) and weigh in the required amounts of the components; write down the individual data.

ad item 5): Separate 50 mg of the gel phase and approximately 1.5 g of the sol phase formed by the system acetone/2-butanone/polystyrene that has formed upon standing at room temperature and deposit these solutions in a small glass flask. The volatiles are removed and the polymer is dried over night in the oven.

ad item 1a): Prepare a mixed solvent containing 3 parts (weight) of diethyl ether and 2 parts acetone. Prepare two sets of polystyrene solutions in this mixed solvent of the following concentrations: 5, 10, 15, 20 and 25 wt%.

ad items 1b and 2): Fill 1 g of polymer into each of three flasks (note the precise weight) and add one of the solvents acetone, diethyl ether or cyclohexane to prepare approximately 5 mL of the solutions. The solutions in acetone or diethyl ether are placed in the refrigerator over night, whereas that in cyclohexane is kept at room temperature.

### *Titration*

- a. Switch on the thermostat and the temperature control unit.
- b. Control the weight of the solutions prepared the previous day (to control loss of solvent)
- c. Cool the solution in an ice bath.
- d. Fill a burette that can be held at constant temperature with diethyl ether.
- e. Titrate the prepared homogeneous polymer solutions in the mixed solvent with diethyl ether until they become cloudy.
- f. The composition of the mixture at the cloud point is determined by weighting the flask.
- g. Empty the burette and rinse it with acetone.  
Fill it with acetone and repeat items e and f.
- h. Switch off all apparatus and clean all containers thoroughly.

### *Swelling experiments*

Decant the supernatant solvent and determine the solvent content of the swollen remaining polymer.

### *Cloud point curve*

The participants will be briefed on that in the lab.

### *GPC measurements*

Dissolve the three different polymer samples (starting material, polymer contained in the gel and in the sol phase, respectively) in THF such that the concentration amounts to approximately 2 mg/mL. Toluene is used as an internal standard for the calibration of the GPC curve. Additional information is supplied when the experiments are performed.

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