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Pressure-Pulse-Induced Critical Scattering of Oligostyrene in *n*-Pentane

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ABSTRACT: An experimental method has been developed for the determination of binodal and spinodal points in the temperature–pressure–concentration phase diagram of demixing systems. Intensities of scattered and transmitted light are measured as a function of pressure. It is shown that the intensity of the experimentally determined scattered light is completely different from the corrected light scattering intensity, which is calculated by turbidity corrections. Slow changes of the pressure can be used for isothermal experiments and fast pressure pulses for adiabatic procedures. These methods based on the theory of Debye are explained for two concentrations of the system oligostyrene/*n*-pentane.

1. Introduction

In the past several years increasing attention has been paid to phase separation kinetics. The demixing processes were most often performed by the temperature (*T*) jump method, to which we give a few references.[1-8] In a few cases, pressure (*P*) jumps were used.[3,9,10] The theoretical study of phase separation has also been actively pursued, including treatments of spinodal decomposition and models of nucleation.[11-16]

Most of the experiments have been on binary systems; polymer solutions have not received much attention.[17-20] The object of the present work is a systematic description of phase separation behavior in the system oligostyrene/*n*-pentane. A special feature of this system is the necessity to use oligostyrenes with molar masses in the range M = 900–1300 g mol^{-1}.

It seemed favorable to us to use a pressure jump, because it can be exerted more quickly than a temperature jump. A rapid pressure change leads to an essentially adiabatic change of the state of the system. The corresponding scattering intensities can be measured immediately. Also, under isothermal conditions the scattering phenomena can be followed with the same equipment, it being necessary only to wait for a time such that the adiabatic temperature change has faded out.

In order to study fast processes involved in phase separation, it is important to establish a comprehensive temperature–pressure–concentration phase diagram. For this reason we developed a technique which we designate as pressure-pulse-induced critical scattering (PPICS). The experimental procedure is similar to the pulse-induced critical scattering (PICS) which was introduced by Gordon et al.[21-23] Our PPICS technique can be used for the determination of binodal and spinodal points in a T–P–y diagram, where y is the mass fraction. Spinodal surfaces in a wide temperature, pressure, and concentration range far from the critical concentration have not previously been described in the literature. As a result of these measurements it is possible to calculate some thermodynamic properties of the system under consideration[24-38] and thus extend our knowledge beyond that obtained at atmospheric pressure.[39-45]

2. Apparatus

The equipment used is represented schematically in Figure 1. The determination of the binodal temperatures and pressures of the demixing systems are carried out in a high-pressure cell, made from nonferromagnetic stainless steel, the alloy nimonic 90. The cell, with three windows made from synthetic sapphire, can be operated up to temperatures of 400 °C and up to pressures of 2.2 kbar. The light source is a 5-mW He–Ne laser. The scattered light is measured at a scattering angle of 90° by a photomultiplier. The transmitted light is detected by a sensitive laser power meter with a silicon detector head (Model 460, EG & G). The signals of scattered and transmitted light are registered by a recorder. The pressure is generated by a screw press filled with hydraulic oil. The oligostyrene solution is separated by a mercury seal from the hydraulic oil. The pressure is determined by two calibrated pressure gauges up to 1.0 and 2.5 kbar with an accuracy of 0.1%. The pressure is also registered by the recorder via an electric resistance pressure gauge.

The high-pressure cell is surrounded by an exactly adjusted tempering jacket, through which water of constant temperature flows. The temperature of the thermostat is controlled with an accuracy of better than ±0.01 °C. In this way the temperature inside the high-pressure cell can be controlled to within ±0.02 °C and even better if the system is decoupled from fluctuations of the room temperature. For reaching temperatures below 20 °C, the thermostat is cooled by a cryomat. The absolute value of the temperature of the cell is measured with an accuracy of ±0.01 °C by a platinum resistance thermometer inside a hole in the outer part of the high-pressure cell. Temperature fluctuations are determined with an accuracy of ±0.002 °C by a thermocouple, which is placed directly in the oligomer solution. The thermocouple thus indicates temperature changes corresponding to adiabatic pressure changes.

A magnetic bar inside the high-pressure cell is rotated by a magnetic stirrer placed outside the cell, thus shortening the time for achieving isothermal conditions. The stirring is also necessary to homogenize the system, because diffusion around the miscibility gap is generally a slow process.

3. Materials

Oligostyrene. The samples were prepared anionically by initiation with *sec*-butyllithium.[46-50] The oligostyrene sample PSA 35 has a number-average molar mass given by $\bar{M}_n$ = 1000 g/mol and a molar mass ratio of $\bar{M}_w/\bar{M}_n$ = 1.1 where $\bar{M}_w$ is the weight-average molecular weight.

Solvent. *n*-Pentane was a puriss. p.a. product of 99.5% from Fluka. It was used without further treatment.

4. Light Scattering and the Spinodal

A schematic temperature–pressure–concentration phase diagram of a binary system with an upper critical solution temperature (UCST) is shown in Figure 2 in a semiperspective view. It is representative for the system of an oligostyrene in the solvent *n*-pentane.

An isobaric cut at $P = P_1$ of the binodal surface shows the isobaric binodal curve $A_1A_3C_1B_3B_1$ which separates the homogeneous from the heterogeneous region. The latter

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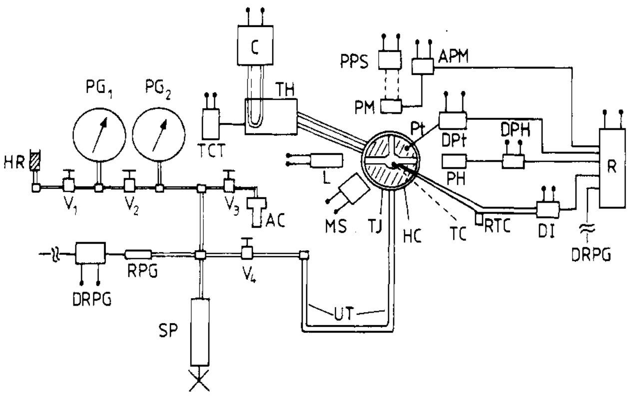

Figure 1. Schematic representation of the total apparatus: AC, autoclave; APM, photomultiplier analog indicator; C, cryomat; DI, thermocouple digital indicator; DPH, photometer digital indicator; DPt, digital indicator of the platinum resistance thermometer; DRPG, digital indicator of RPG; HC, high-pressure cell; HR, hydraulic oil reservoir; L, laser; MS, magnetic stirrer; PG1, pressure gauge 1.0 kbar; PG2, pressure gauge 2.5 kbar; PH, photometer silicon detector head; PM, photomultiplier; Pt, platinum resistance sensor; PPS, photomultiplier power supply; R, recorder; RPG, electric resistance pressure gauge; RTC, reference thermocouple; SP, screw press; TC, thermocouple; TCT, temperature controller; TH, thermostat; T, tempering jacket; UT, U-tube; V_1, V_2, V_3, V_4, ventils.

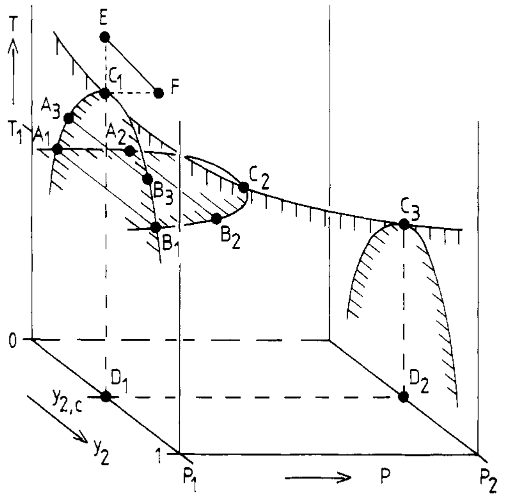

Figure 2. Schematic T–P–y phase diagram of a polystyrene–solvent system with an upper critical solution temperature with the representations $T(y_2)$ and $P(y_2)$; see text.

is situated on the dashed side of the curve. C_1 is the upper critical solution temperature corresponding to P_1 at which the coexisting phases corresponding to A_1, B_1 and A_3, B_3 become identical.[27,30,51-53]

The pressure dependence of the UCST is described by the critical curve $C_1C_2C_3$. The critical curve is assumed to be independent of the mass fraction of the oligomer y_2. This can be seen from the projection of the curve $C_1C_2C_3$ onto the pressure–concentration plane, giving the line D_1D_2 which is drawn parallel to the P-axis. A second isobaric cut is presented for the pressure for which the critical point is given by C_3. An isothermal cut of the binodal surface at the temperate T_1 shows the isothermal binodal curve $A_1A_2C_2B_2B_1$, which has an upper critical solution pressure at C_2. The heterogeneous region inside the binodal is also dashed.

Figure 3 shows such an isothermal P–y_2 phase diagram, which will help to visualize the pressure-pulse-induced critical scattering method.

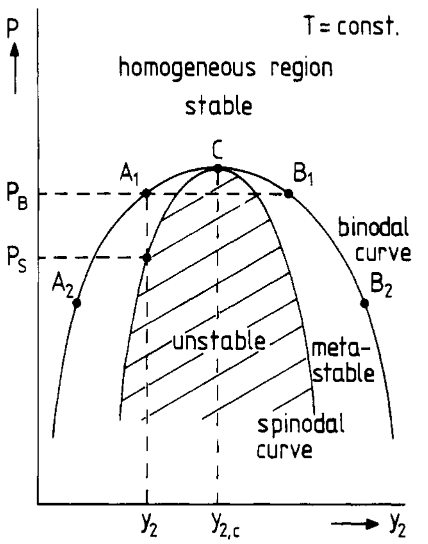

Figure 3. Typical pressure (P)–concentration (y_2) phase diagram for the system PSA 35/n-pentane.

At constant pressure and temperature, the phase corresponding to A_i coexists with the phase corresponding to B_i, with i = 1, 2, 3. Stable and metastable regions are separated from the unstable one by the spinodal curve. If the pressure of a solution with the initial concentration y_2 is lowered below the spinodal pressure P_S, the concentration fluctuations will lead to a spontaneous phase separation called spinodal decomposition.[11-13] Between the binodal pressure P_B and the spinodal pressure P_S a phase separation *may* take place. The intensity of light I_θ scattered at an angle θ is caused by density and concentration fluctuations. This was derived by Smoluchowski[54] and Einstein[55] and later extended to polydisperse polymer solutions by others.[56-58] The theory gives a relation between I_θ and the second derivative of the change of the specific free enthalpy of mixing, ΔG, with respect to the concentration y_2 in a binary system:

$$\left(\frac{\partial^2 \Delta G}{\partial {y_2}^2}\right)_{T,P}$$

The spinodal surface in the T–P–y_2 space is the limiting surface enclosing the essentially unstable region. Under isobaric or isothermal conditions the intersection of the spinodal surface by a P–T plane results in the spinodal curve, which for a binary system is defined by:[27-30]

$$(\partial^2 \Delta G / \partial {y_2}^2)_{T,P} = 0 \tag{1}$$

The determination of spinodal points allows the calculation of the thermodynamic properties of the solution with relatively high accuracy.[30,59,60] According to the existing theories spinodal (sometimes called pseudospinodal[69]) temperatures and pressures can be determined by the extrapolation of the reciprocal light-scattering intensity $(I_{\theta=0})^{-1}$ to zero values as a function of temperature or pressure. Here I_θ is the intensity of the scattered light at a scattering angle θ.

This method of extrapolation was initiated by Debye and co-workers[61-63] and has been exploited by Scholte[64,65] and Gordon et al.[21-23] The intensity of the scattered light has been formulated by Debye and others:[61-63,66-68]

$$\frac{I_\theta}{I_0} = \frac{4\pi^2 V_s \alpha^*}{R^2 \lambda^4} \frac{KP(\theta)}{\phi_2 \frac{\partial}{\partial \phi_2}\left(\frac{\Pi}{kT}\right) + \frac{16\pi^2 {\phi_2}^2 H^*}{kT\lambda^2} \sin^2 \frac{\theta}{2}} \tag{2}$$

I_0 is the intensity of the primary beam at the scattering volume V_s and λ the wavelength of the light in the solution.

For unpolarized light α^* is given by $(1 + \cos^2\theta)/2$. Also, ϕ_2 is the volume fraction of the oligomer, Π is the osmotic pressure, and R the distance between the scattering volume and the detector. The optical constant K is a function of the refractive index and the refractive index increment, $P(\theta)$ is the well-known particle scattering function, and H^* depends on interaction energies between the different molecules and on the range of the intermolecular forces.

Along the spinodal surface, on which also the critical curve is situated, the first term in the denominator vanishes, because according to eq 1 the second derivative of the specific free enthalpy of mixing with respect to the mass fraction vanishes. The relation between $(\partial\Pi/\partial\phi_2)_{T,P}$ and $(\partial^2\Delta G/\partial y_2^2)_{T,P}$ is given by

$$\left(\frac{\partial\Pi}{\partial\phi_2}\right)_{T,P} = \frac{1}{\tilde{V}_1}\left(\frac{\partial\phi_2}{\partial y_2}\right)_{T,P}\left(\frac{\partial^2\Delta\tilde{G}}{\partial y_2^2}\right)_{T,P} \qquad (3)$$

where $\tilde{V}_1$ is the partial specific volume of the solvent. Equation 3 is derived by use of the well-known thermodynamic relations which are valid for constant values of T and P:

$$\Delta\tilde{G} = y_1\Delta\tilde{\mu}_1 + y_2\Delta\tilde{\mu}_2 \qquad (4)$$

$$\Delta\tilde{\mu}_1 = -\tilde{V}_1\Pi \qquad (5)$$

where $\Delta\tilde{\mu}_i$ is the partial specific free enthalpy (chemical potential) of component i. Furthermore the Gibbs–Duhem equation is used and the assumption made that $\tilde{V}_1$ is not dependent on the composition.

If the second term in eq 2 is negligible, we expect the reciprocal scattering intensity to become zero, when I_θ^{-1} is extrapolated to spinodal conditions. This can be done, for instance, by a change of pressure for a given oligomer concentration. It is completely analogous to the extrapolation procedure first used by Debye and co-workers, where instead of the intensive variable P the temperature T at the critical concentration was used. As was shown by Debye and co-workers, the first term in the denominator of eq 2 can be represented by the expression[61–63]

$$\phi_2\frac{\partial}{\partial\phi_2}\left(\frac{\Pi}{kT}\right)_{T,P} = a|T - T_C|; \qquad T \geq T_C, \quad \text{for an UCST} \qquad (6)$$

where T_C is the critical temperature and a is a constant. At a critical point we have $(dT/dP)_C \approx (\Delta T/\Delta P)_C = (T - T_C)/(P - P_C) = b$, where b is related to thermodynamic quantities.[25–30] For small values of ΔT and ΔP it is a constant. Inserting this relation into eq 6 we get

$$\phi_2\frac{\partial}{\partial\phi_2}\left(\frac{\Pi}{kT}\right)_{T,P} = ab|P - P_C| \qquad (7)$$

This equation tells us that the first term in the denominator of eq 2 vanishes also if the pressure P reaches the critical pressure P_C.

Geometrically the equivalence of eq 6 and 7 can be demonstrated by means of the construction of $(\Delta T/\Delta P)_C$ in Figure 2. ΔT is given by the distance EC_1 at the critical pressure $P_C = P_1$. ΔP is taken from the slope $(\Delta T/\Delta P)_{y_{2,C}}$ and given by C_1F at the temperature belonging to C_1. Therefore there is a complete thermodynamic equivalence in changing the temperature from E to C_1 and changing the pressure from F to C_1.

It has been shown that eq 6 is valid along the spinodal curve with T_S instead of T_C in eq 6.[54,55,58,64,65,69] These considerations based on the Debye theory tell us that the concentration fluctuations are responsible for the light scattering near the critical point. By a change in the temperature or the pressure the critical state can be reached.

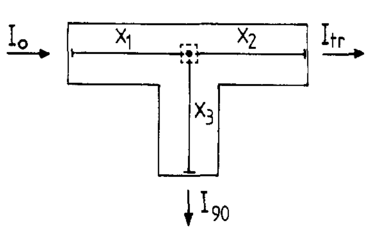

Figure 4. Schematic geometry of the optical pathway in the high-pressure cell.

5. Correction of the Intensity of the Scattered Light

Close to a miscibility gap, the critical opalescence caused by the concentration fluctuations is responsible for a strong turbidity. Consequently, the scattered light originating from a well-defined scattering volume and detected at an angle θ is considerably reduced by the turbidity of the medium. First of all, the primary beam is attenuated by the turbidity before entering the scattering volume. Second, the intensity of the scattered light is attenuated also because the beam passes through the turbid solution before reaching the detector. Thus some corrections are necessary. Especially in high-pressure equipment, where the distance between the scattering volume and the windows may be a few centimeters, this correction is of considerable importance. Results with a shorter optical pathway are described at the end of section 6. The geometry of the optical pathway of the high-pressure cell is schematically represented in Figure 4. A narrow beam of a He–Ne laser with intensity I_0 enters the high-pressure cell in the direction of the arrow. After the passages x_1 and x_2 the intensity of the primary beam I_0 is reduced to the intensity of the transmitted beam, I_{tr}. The scattered beam leaves the cell at the scattering angle θ after having passed through the solution the distance x_3. The intersection of primary and scattered beams gives the scattering volume. The total apparatus has been constructed in such a way that all correction factors have been worked out by Carr and Zimm and others.[70,71] This is mainly achieved by the use of a laser source and apertures at all windows that are small in relation to the path of the light beams. Following partly an application of Lambert's law as given by Maron and Lou,[72] we obtain

$$I_{tr} = I_0 e^{-\tau(x_1+x_2)} \qquad (8)$$

Here τ is the turbidity, which can be calculated from values of I_{tr}, I_0, and the known distances x_1 and x_2. The intensity of the primary beam at the scattering volume is given by

$$I_{0,x_1} = I_0 e^{-\tau x_1} \qquad (9)$$

The scattered light is measured after having passed through the solution along the distance x_3. Therefore the attenuation of the scattered light I_{90} at $\theta = 90°$ has to be corrected once more to give the intensity to be determined experimentally:

$$I_{90}^{\text{exp}} = I_{90}e^{-\tau x_3} \qquad (10)$$

Before calculating I_{90}^{corr} from I_{90}^{exp}, the quantity I_{90} has also to be corrected for density fluctuations of the solvent, because only the concentration fluctuations are relevant for the spinodal extrapolations. In so doing we assume that the density fluctuations of the solutions are the same as those of the pure solvent. Because only I_{tr} and I_{90}^{exp} can be determined in the experiments, the property I_{90} has to

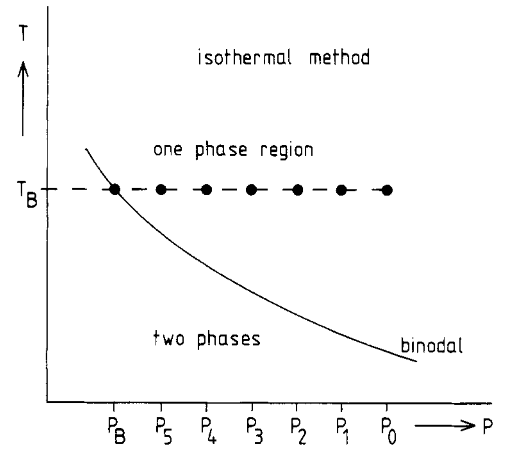

Figure 5. Schematic representation of the isothermal PPICS extrapolation technique in a temperature versus pressure phase diagram.

be calculated from I_{tr} and I_{90}^{exp} with the simple attenuation corrections of eq 8–10.

For the thermodynamic extrapolations, I_{90} is the only interesting property. Because I_{90} is obtained by the corrections mentioned, we also call this property the corrected light-scattering intensity I_{90}^{corr}, as introduced before by Chu and co-workers for isobaric experiments:[69]

$$I_{90} \equiv I_{90}^{corr} \tag{11}$$

In the following experiments it is assumed, that I_{90}^{corr} is not far from $I_{\theta=0}^{corr}$, which can be expected for oligomer solutions.[59] The spinodal pressure P_S was determined by means of a linear extrapolation of the reciprocal corrected light-scattering intensity versus P to zero values of $(I_{90}^{corr})^{-1}$ starting at pressures far above P_S.

6. Spinodal and Binodal Points of the System Oligostyrene/*n*-Pentane

Figure 5 shows a schematic binodal curve in the temperature–pressure phase diagram of the system oligostyrene/*n*-pentane with a constant concentration of oligostyrene.

There are two ways for the determination of binodal and spinodal points with a change of the pressure: an isothermal and an adiabatic method. First we describe the isothermal method. The measurements are realized at the temperature T_B. The values of the transmitted light I_{tr} and the scattered light I_{90}^{exp} are registered for the pressure P_0. The values are constant after a time of 5–10 min, which is necessary for equalization of the temperatures. A fast pressure decrease is coupled to an adiabatic temperature decrease. For the pressures $P_1, P_2, ..., P_5$ the data of I_{tr} and I_{90}^{exp} are registered in the same way.

Figure 6 shows I_{tr}, $(I_{90}^{exp})^{-1}$, and $(I_{90}^{corr})^{-1}$ against the pressure P for an isothermal experiment at the temperature T = 13.21 °C and the critical mass fraction $y_{2,C}$ = 0.400 in the system PSA 35/*n*-pentane. This critical concentration was determined separately by measurements of the phase volume ratios at atmospheric pressure.[39,41,43,44] The $(I_{90}^{exp})^{-1}$ curve initially decreases with decreasing pressure, passes through a minimum, and then increases up to the binodal pressure which is identical with the spinodal pressure at this mass fraction of the oligostyrene. The I_{tr} curve shows a nonlinear decrease with decreasing pressure and finally becomes zero. Because of eq 8–10, the quantity $(I_\theta^{corr})^{-1}$ also becomes zero at this pressure. Therefore we have $P = P_S$. As $y_2 = y_{2,C}$, this has to be the critical pressure P_C, which has to coincide with P_B. The $(I_{90}^{corr})^{-1}$ versus P curve is totally linear, as predicted by the Debye theory, and becomes zero at $P_S = P_C = P_B$.

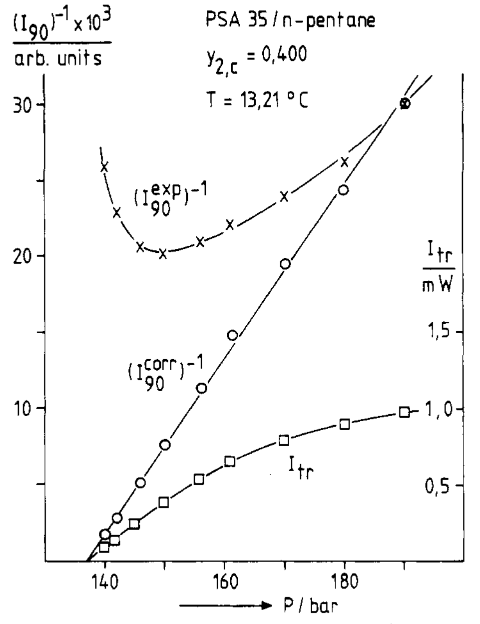

Figure 6. Pressure dependence of I_{tr}, $(I_{90}^{exp})^{-1}$, and $(I_{90}^{corr})^{-1}$ at the temperature T = 13.21 °C for the critical concentration $y_{2,C}$ = 0.400 in the system PSA 35/*n*-pentane.

The determination of the binodal pressures P_B is much more difficult, because first of all two new liquid phases have to be formed out of a homogeneous phase. This causes a sudden increase of the scattered light. Although it is known that binodal temperatures or pressures can be determined by the extrapolation of phase volume ratios of coexisting phases to zero or infinity, we had to find other criteria for the determination of the binodal pressure, because the phase volume ratios could not be measured in the high-pressure equipment.

The binodal (threshold) pressure was determined by means of a technique in which the difference of the transmission and scattered light intensities of a stirred and an unstirred solution was taken as a criterion for the demixing. If the conditions of temperature and pressure correspond to the state of a homogeneous solution, no differences of the cited light intensities could be observed whether the solution was stirred or not. For a set of T and P in the heterogeneous area, a difference of the light intensities could be clearly seen. In this case it was observed that the transmission light intensity was lower and the scattered light intensity was higher after stirring the solution with respect to the unstirred solution. The difference of the light intensities is caused by the different dispersions of the new phase in the scattering volume according to whether the solution is stirred or not. It should be mentioned, however, that the measurements of a "stirred solution" were performed directly after switching off the stirrer.

All binodal pressures P_B were determined with this technique. For the critical concentration $y_2 = y_{2,C}$ = 0.400, all binodal pressures were found to be the same as the spinodal pressures P_S.

Figure 7 shows two isothermal plots of $(I_{90}^{corr})^{-1}$ versus P. Curve A represents an oligostyrene/*n*-pentane solution with 30% by weight of oligostyrene at T_B = 14.15 °C. This solution belongs to the maximum threshold temperature in the temperature–concentration phase diagram. It should be recalled that the maximum threshold point of a polydisperse polymer solution is not identical with the critical point.[17-20,31,39-44,75] This is evident also for the sample used in this paper, although the anionically pre-

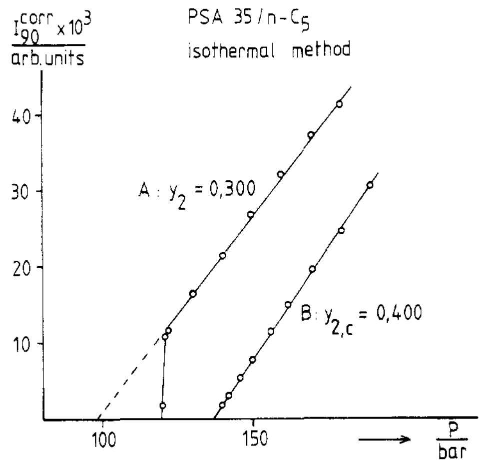

Figure 7. Isothermal extrapolation procedure for the determination of binodal and spinodal points: (A) $y_2 = 0.300$, $T_B = T_S = 14.16$ °C, $P_B = 119$ bar, $P_S = 98$ bar; (B) $y_{2,C} = 0.400$, $T_B = T_S = 13.21$ °C, $P_B = P_S = 137$ bar.

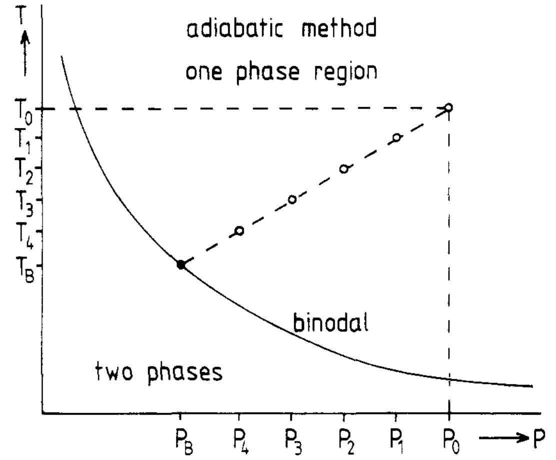

Figure 8. Schematic representation of the adiabatic PPICS extrapolation technique in a temperature versus pressure phase diagram.

pared sample was fractionated several times. For the following results and the discussion this rather small influence of polydispersity is disregarded.

Curve A shows a long linear range which is interrupted by a steep decrease of $(I_{90}^{corr})^{-1}$ with decreasing pressure down to extremely low values (zero), where the pressure $P_B = 119$ bar is reached. This pressure is identical with the binodal pressure P_B which was found by the stirring technique described above. The linear extrapolation of the colinear points starting at high pressures to $(I_{90}^{corr})^{-1} = 0$ yields the spinodal pressure $P_S = 97$ bar. Curve B describes the behavior of an oligostyrene/*n*-pentane solution with 40% by weight oligostyrene at $T_B = 13.21$ °C. This solution belongs to the critical concentration $y_{2,C}$. For this critical concentration all data points lie on a single straight line, which means that the binodal pressure P_B and the spinodal pressure P_S coincide.

The second possibility for the determination of P_B and P_S is an adiabatic method, which is explained schematically by using Figure 8.

Starting from the coordinates T_0 and P_0 a sudden change of the pressure from P_0 to P_1 is carried out. As the change takes only 1 s the process is an adiabatic one. If the light-scattering intensity is measured by automatic registration, the back step to P_0 is produced immediately afterward. This procedure is repeated for the pressures P_2–P_4. Every pressure pulse consists of two jumps in opposite directions. Because of a short pressure jump decrease ΔP, there is an adiabatic or isentropic temperature decrease ΔT at the moment when the new pressure is reached. The temperature T_i corresponding to the pressure P_i is given by

$$T_i = T_0 - \Delta T_i; \qquad i = 1, 2, ... \tag{12}$$

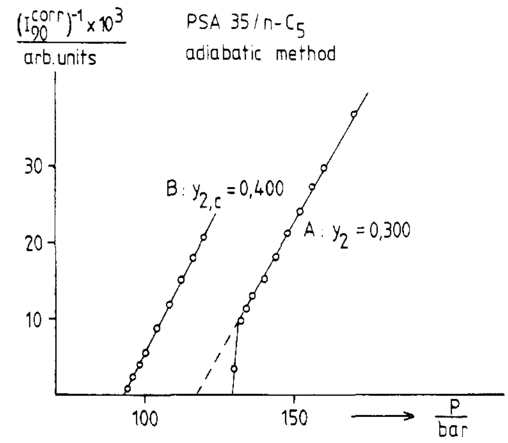

Figure 9. Adiabatic extrapolation procedure for the determination of binodal and spinodal points: (A) $y_2 = 0.300$, $T_B = 13.31$ °C, $P_B = 129$ bar, $T_S = 13.06$ °C, $P_S = 117$ bar; (B) $y_{2,C} = 0.400$, $T_B = T_S = 15.74$ °C, $P_B = P_S = 93$ bar.

ΔT is calculated from the well-known thermodynamic relation[73,74]

$$\left(\frac{\partial T}{\partial P}\right)_S \approx \left(\frac{\Delta T}{\Delta P}\right)_S = \frac{TV\alpha}{C_p} \tag{13}$$

Here T, V, α, and C_p are the temperature, volume, expansion coefficient, and heat capacity at constant pressure of the solution. V, α, and C_p can be approximately calculated from the values for the pure components assuming additivity relations.

Figure 9 shows two adiabatic plots of $(I_{90}^{corr})^{-1}$ versus P. Curve A is characteristic for a solution of 30% by weight of oligostyrene. The binodal pressure is found to be at $P_B = 129$ bar where the curve drops down and intersects with the P-axis. With the adiabatic method the stirring technique was not used, because sedimentation or flotation of the new phases could not be expected to happen in 1 s in the scattering volume. Therefore the pressure at which the steep decrease of the reciprocal light-scattering intensities was observed was taken as the binodal pressure, as in the isothermal case described before. The calculated binodal temperature is 13.31 °C. The spinodal pressure is ascertained from the linear extrapolation of the reciprocal corrected scattering intensities versus pressure by the intersection with the P-axis and is given by $P_S = 117$ bar with a corresponding calculated spinodal temperature of $T_S = 13.06$ °C. Plot B again shows the corresponding curve for the critical concentration. As in the isothermal experiment the measurements are well represented by a single straight line. From this we deduce the result $P_S = P_B$. The calculation of the spinodal temperature T_S and binodal temperature yields $T_B = T_S = 15.74$ °C.

The agreement of the isothermally and the adiabatically measured points for the critical concentration of oligostyrene in *n*-pentane can be illustrated in a temperature–pressure phase diagram shown in Figure 10. It can thus be stated that the experimental results for the two different methods can be represented by a single isopleth showing no systematic deviations for the adiabatically or isothermally determined values.

In Figure 11 we present the experimental results of the binodal and the spinodal points for an oligostyrene/*n*-

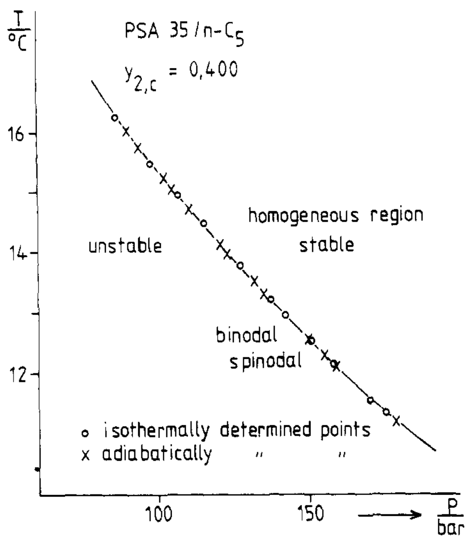

Figure 10. $T(P)$ binodal isopleth (equal to the spinodal isopleth) for the PSA 35/n-pentane system at the critical concentration $y_{2,C} = 0.400$.

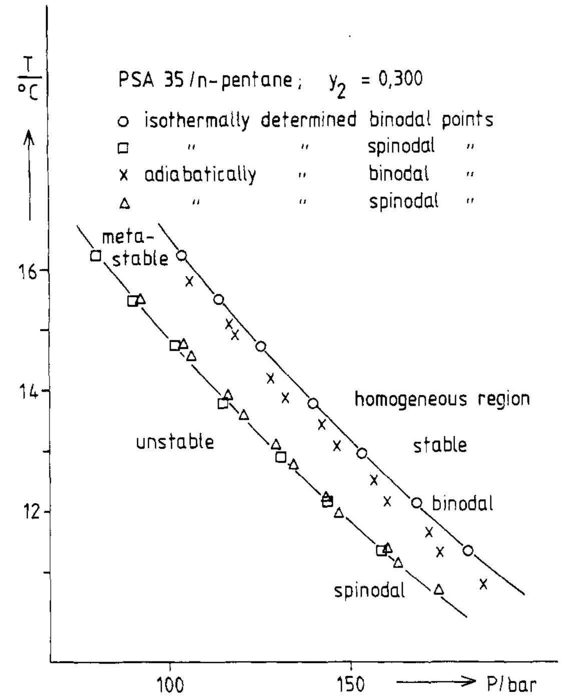

Figure 11. $T(P)$ binodal isopleth and spinodal isopleth for the system PSA 35/n-pentane system; $y_2 = 0.300$.

pentane solution of $y_2 = 0.300$. Isothermally and adiabatically determined spinodal points may be fitted in a single spinodal isopleth. Deviations from the common curve are in the range of experimental accuracy.

From Figure 11 we derive that isothermally and adiabatically determined *binodal* points do *not* coincide in a single binodal isopleth. With respect to the isothermally determined binodal isopleth (binodal in Figure 11) all adiabatically determined binodal points are shifted to lower pressures. We find that the difference between isothermal and adiabatic pressures is proportional to the amplitude of the pressure jump. Further, it is found that the isothermally measured binodal isopleth is nearly parallel to the spinodal isopleth.

All results in this paper have been obtained by corrected light-scattering intensities starting from Lambert's law. In most of our experiments the optical pathways were constant, with $x_1 = x_2 = x_3 = 13.15$ mm. In a further experiment we were able to show, for a critical concentration, that the extrapolated binodal and spinodal values are independent of the optical lengths, which were given by $x_1 = x_2 = x_3 = 5.95$ mm. This can be seen from Figure 12, in which measurements with a short and a long optical pathway coincide in a single critical spinodal isopleth, identical with the binodal isopleth. All results in this figure were obtained by the isothermal method. The coincidence of the spinodal points in a single isopleth confirms the correct application of the attenuation relations underlying the extrapolation procedure for the determination of spinodal pressures with (τx) going to infinity (see eq 8–10).

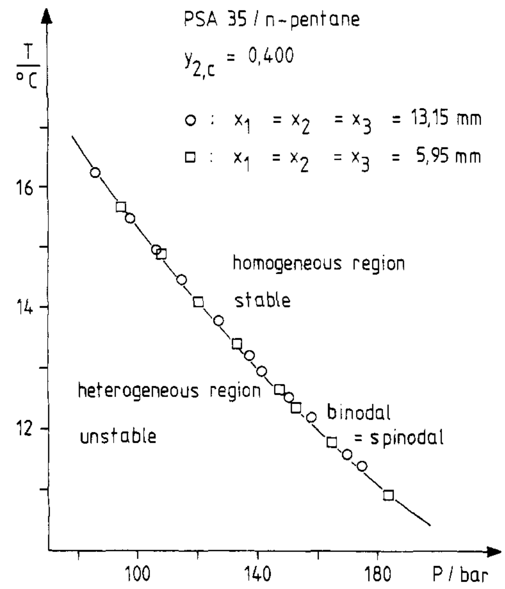

Figure 12. Coincidence of spinodal and binodal isopleths measured with long and short optical pathways at the critical concentration $y_{2,C} = 0.400$; see text.

7. Conclusion

The method of pressure-pulse-induced critical scattering has been developed for the determination of spinodal and binodal points in a T–P–y phase diagram. It is based on the extrapolation proposed by Debye and others, where changes of the temperature have been used to determine the reciprocal light-scattering intensities. In this paper it has been shown that pressure changes are completely equivalent to the changes of the temperature.

Isothermal and adiabatic procedures are presented and described in detail for two different concentrations of oligostyrene in n-pentane. For the critical concentration it is found that binodal and spinodal isopleths coincide in the pressure range under investigation. For concentrations $y_2 < y_{2,C}$ the isothermally and adiabatically determined coordinates can be represented by a single spinodal isopleth. The adiabatically measured binodal points in the T–P plane cannot be described by the isothermally measured isopleth. The derivation of adiabatically and isothermally determined coordinates is proportional to the amplitude of the pressure changes in the adiabatic experiment.

In an isothermal experiment the time for temperature adjustment takes nearly 500 s, whereas in the adiabatic pressure change the scattering values are registered in 1 s. Therefore the times at which the scattering intensities are measured are very different for the isothermal and the adiabatic technique. Both techniques have to give the same results for given values of T, P, and y_2, if all possible kinetic processes in the solution have taken place in the time needed for a pressure jump. This corresponds to the critical concentration. If there is a difference in the results with respect to the methods discussed, we have to conclude that some kinetic processes are taking place after the end of the pressure jump. This has been found for $y_2 < y_{2,C}$. These experiments show that the demixing process for the critical concentration and a noncritical one are different. This can be explained by the spinodal mechanism of demixing at the critical point, which was proposed by Cahn and Hilliard.[11-13] As the spinodal curve is tangent to the binodal at the critical concentration $y_{2,C}$, the smallest step into the region of heterogeneity leads into essentially unstable states.

For concentrations $y_2 \neq y_{2,C}$, a nucleation mechanism is assumed.[14-16] For every nucleation process a certain supersaturation concerning the pressure, temperature of concentration variables is necessary. In a short time only a few nuclei are formed in the metastable range, whereas after a longer time many more nuclei of the new phase are present. Therefore a much deeper step into the heterogeneous region is necessary to have a comparable effect for the number of nuclei present during the relatively short time of observation. As the isothermally determined binodal isopleth represents the limit between the homogeneous and heterogeneous phase regions, all adiabatically determined binodal points represent states in the heterogeneous phase area. Therefore only the isothermally determined binodal isopleth can be considered as the curve for thermodynamic equilibrium.

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Registry No. $H_3C(CH_2)_3CH_3$, 109-66-0; polystyrene, 9003-53-6.

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