Phase-Separation Phenomena in Solutions of Poly(2,6-dimethyl-1,4-phenylene Oxide). I. Thermodynamic Parameters of Solutions in Toluene

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Synopsis

New experimental data have been collected on thermodynamic properties of solutions of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in toluene. The Flory-Huggins interaction parameters g have been determined from light scattering measurements. These values are in agreement with values obtained by osmotic measurements at low concentrations and they allow the calculation of a melting point curve which fits the experimental melting points. No liquid-liquid phase separation can be calculated, as was concluded in a preceding paper. Spinodals could not be detected by light scattering or DSC-measurements. This also indicates that liquid-liquid phase separation does not occur. The phase separation on cooling of a PPO-toluene solution is thus believed to be a crystallization phenomenon.

INTRODUCTION

When a homogeneous solution of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO* resin) in toluene is cooled, the solution exhibits a phase separation visible by an increase of turbidity. This phenomenon has been explained in two different ways:

1. Crystallization of the polymer. The temperature at which turbidity appears (on slow cooling) is called the crystallization point.¹ It is possible that the solvent participates in the crystal structure.²

2. Liquid-liquid phase separation, and subsequent crystallization of polymer from the concentrated phase. In this case the temperature of appearance of turbidity with a very slow cooling rate (1°C/48 hr) has been taken as a point on the cloud point curve, and with a faster cooling rate (1°C/10 min) as a point on the spinodal.³

The melting-point curve, obtained by heating the phase-separated solutions, has the same meaning in both approaches. The first explanation is the most straightforward one. It, however, does not provide an explanation for the fact that depending on the rate of cooling there can be found two temperatures at which the solution becomes homogeneous on heating.³ The second interpretation was mainly based on the change-over of the phase boundaries of the system PPO-toluene in comparison with the ternary system PPO-toluene-ethanol.³ On and near the binary side, PPO-toluene, of the ternary diagram it was possible

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to determine three phase-transition temperatures, whereas in a system with more ethanol present, only liquid-liquid phase separation occurred. It seemed that the cloud point curve of this ternary system could be extrapolated to the binary PPO-toluene side. When cooled at a fast rate the solution becomes homogeneous again at or near this cloud point curve, which also points to liquid-liquid phase separation. As a last point of this interpretation it was stated that the liquid-liquid phase separation preceded a crystallization of the polymer-rich phase. This could explain the occurrence of the three-phase boundaries which have been found in the experiments.

In the present paper some additional experiments are described which allow a better choice to be made between the proposed mechanisms.

THEORETICAL

General Thermodynamic and Kinetic Framework

In polymer solution, the free enthalpy (Gibbs free energy) of mixing is usually expressed in the form of the Flory-Huggins equation.⁴ In this paper we will write the Flory-Huggins equation using weight fractions, and with a free-enthalpy correction parameter g according to Koningsveld^{5,6}

$$\Delta G_m = RT \left[w_0 \ln w_0 + \sum_i \frac{M_0}{M_i} w_i \ln w_i + g w_0 w \right] \quad (1)$$

where ΔG_m is the free enthalpy of mixing of M_0 grams of solution; w_0 is the weight fraction of the solvent; w_i is the weight fraction of polymer component i , w is the total weight fraction of the polymer, M_0 is the molecular weight of the solvent, and M_i is the molecular weight of the polymer component i .

Equation (1) can be used to describe liquid-liquid phase separation. When the free enthalpy of mixing of a homogeneous solution of a given composition is higher than the free enthalpy of a combination of two liquid phases having the same total composition, the homogeneous mixture will separate into two phases. In a graphical representation for a binary system, the compositions are given by the common tangent to the ΔG_m versus composition curve. Between the common tangent and the points of inflection the curve is concave upwards, which means that the solution is stable towards fluctuations limited to neighboring compositions, but unstable against formation and growth of a nucleus with a composition across the instability gap. This mechanism of phase separation is called nucleation and growth. Between the points of inflection the ΔG_m curve is concave downwards. This means that the solution is unstable towards any concentration fluctuation and such a solution will separate into two phases instantaneously. This mechanism is called spinodal demixing. Therefore, upon temperature lowering in a system which shows liquid-liquid phase separation one will first pass through a region in which nucleation and growth can occur: the points at which the phase separation starts constitute the binodal. When this nucleation mechanism is retarded, spinodal demixing can occur, starting at the spinodal curve. If the empirical correction factor g is known, both binodal and spinodal curves can be determined. On the other hand, if the spinodal could be determined experimentally, it should be possible to calculate g .

In this work the g parameters have been determined by light scattering. The

g parameters obtained can be used to compute ΔG_m versus composition at several temperatures from which it can be judged, whether liquid-liquid phase separation could occur. Light scattering can also indicate the existence of a spinodal region, since the scattering intensity should increase enormously on approaching the spinodal curve. This has also been checked for the system under investigation. Furthermore, an attempt has been made to determine a spinodal temperature (if any) for the system PPO-toluene by fast-cooling experiments in differential scanning calorimetry. On increasing the cooling rate one should find a phase separation temperature for spinodal demixing which is independent of the cooling rate.

Finally, in terms of crystallization phenomena, one can also use the g parameter to calculate the lowering of the melting point of crystalline material in solutions of various polymer concentration.^{4,7,8} This allows the calculation of the melting point curve which can be compared with the experimental one.

Light Scattering

Measurement of the intensity of light scattered from a polymer solution at various concentrations and angles is a means for the determination of the chemical potential and the interaction parameters of the system.⁹

The equations derived by Scholte read:

$$-\left(\frac{\partial(\Delta\mu_0)}{\partial w}\right)_{M_n} = RT M_0 \left[\frac{2\pi^2 n_B^2}{N_A \lambda^4 R_B} \left(\frac{dn}{dw}\right)^2 \frac{w}{\rho(\alpha\Delta I)_{\theta=0}} + \frac{1}{M_n} - \frac{1}{M_w} \right] \quad (2)$$

and

$$-\left(\frac{\partial\mu}{\partial w}\right)_{MWD} = RT M_n \left[\frac{2\pi^2 n_B^2}{N_A \lambda^4 R_B} \left(\frac{dn}{dw}\right)^2 \frac{1-w}{\rho(\alpha\Delta I)_{\theta=0}} + \frac{1-w}{w} \left(\frac{1}{M_n} - \frac{1}{M_w}\right) \right] \quad (3)$$

where $\Delta\mu_0$ is the chemical potential of solvent in solution less the chemical potential of pure solvent; μ is the chemical potential of the polymer in solution; ΔI is the scattered light intensity from the solution minus that from the pure solvent, relative to the light intensity of pure benzene scattered perpendicular to the incident ray (scattering angle $\theta = 90^\circ$); α is the angle factor $(\sin \theta)/(1 + \cos^2 \theta)$; ρ is the density of the solution; n_B is the refractive index of benzene at wavelength λ of light; R_B is the Rayleigh factor of benzene; N_A is the Avogadro's number; (dn/dw) is the specific refractive index increment; and subscripts M_n and MWD indicate differentiation with respect to w at a fixed number average molecular weight and a fixed molecular weight distribution, respectively.

The right side of eqs. (2) and (3) can be determined experimentally. Integration of eq. (2) from very low values of w upwards then yields values of $\Delta\mu_0$. Differentiation of eq. (1) with respect to the number of moles of the various components yields, respectively:

$$\frac{\Delta\mu_0}{RT} = \ln(1-w) + \left(1 - \frac{M_0}{M_n}\right)w + \left\{g - (1-w)\frac{\partial g}{\partial w}\right\}w^2 \quad (4)$$

and

$$\left(\frac{\Delta\mu}{RT}\right)_{M_n} = \ln w + (1-w) - \frac{M_n}{M_0}(1-w) + \left\{g + w\frac{\partial g}{\partial w}\right\}\frac{M_n}{M_0}(1-w)^2 \quad (5)$$

It follows that the quantity

$$\chi_w = g - (1 - w) \frac{\partial g}{\partial w} \quad (5a)$$

can be calculated; χ_w is the well-known Flory-Huggins interaction parameter.

When a spinodal is approached, the light scattering can reach very high values. Scholte¹⁰ has given an extrapolation procedure to determine the spinodal by plotting values of $1/(\alpha\Delta I)_{\theta=0}$ against $1/T$ or T (when the temperature range is not too large) and extrapolating to $1/(\alpha\Delta I)_{\theta=0} = 0$.

Melting-Point Depression

The melting-point depression equation for polymer-solvent systems derived by Flory⁴ and modified by Hoffman⁹ reads:

$$\Delta\mu_{f,u} = H_u^0 \frac{(T_m^0 - T_m)T_m}{(T_m^0)^2} \quad (6)$$

where $\Delta\mu_{f,u}$ is the chemical potential change for the melting of one mole of polymer segments; ΔH_u^0 is the molar enthalpy of fusion for the polymer repeat unit; T_m is the melting point in solution; and T_m^0 is the melting point of pure polymer.

At equilibrium between polymer crystals and a polymer solution, the following relations are valid:⁴

$$\begin{aligned} \mu_u^1 - \mu_u^{(0)} &= \Delta\mu_{M,u} \\ \mu_u^c - \mu_u^{(0)} &= \Delta\mu_{f,u} \end{aligned} \quad (7)$$

and

$$-\mu_{f,u} = \Delta\mu_{M,u}$$

μ_u^c is the thermodynamic potential of one mole of repeat units for the polymer in the crystalline state; $\mu_u^{(0)}$ is the thermodynamic potential of one mole of repeat units for the polymer in the standard state; μ_u^1 is the thermodynamic potential of one mole of repeat units for the polymer in solution and M refers to mixing, f to fusion.

Using eq. (5) and inserting a temperature and concentration dependent g of the form

$$g = g_0 + \frac{g_1}{T} + g_2w \quad (8)$$

(g_0 , g_1 and g_2 are constants), we obtain the following expression for the change in chemical potential upon mixing polymer and solvent.

$$\Delta\mu_{M,u} = RT \left[\frac{M_0}{M_n} \ln w - (1 - w) \frac{M_0}{M_n} - (1 - w) + \left(g_0 + \frac{g_1}{T} + 2g_2w \right) (1 - w)^2 \right] \quad (9)$$

Combining eqs. (6), (7), and (9) we find:

$$\Delta H_u^0 \frac{(T_m^0 - T_m)T_m}{(T_m^0)^2} = -RT_m \left[\frac{M_0}{M_n} \ln w + (1-w) \frac{M_0}{M_n} - (1-w) + (g_0 + \frac{g_1}{T_m} + 2g_2w)(1-w)^2 \right] \quad (10)$$

By solving eq. (10) for at least three sets of melting temperature versus composition data, we have a possibility in principle to determine g_0 , g_1 , and g_2 from experimental data.

Differential Scanning Calorimetry

As has been pointed out by Van Emmerik¹⁸ it is possible to determine the phase separation temperatures in this system by differential scanning calorimetry. When the phase separation is a result of nucleation and growth a certain induction or delay time has to be expected, irrespective of the type of phase separation. These delay times should become shorter with increasing undercooling. At temperatures below a spinodal even the smallest fluctuation in concentration is sufficient to destabilize the solution and therefore demixing must occur without a delay time.^{11,12} In DSC measurements spinodal demixing is in principle detectable, since phase separation temperatures should then become independent of the cooling rate.

EXPERIMENTAL

Light Scattering

The light scattering experiments were performed with a Sofica 42000 M photogoniidiffusometer. The wavelength used was 546 nm (unpolarized light). There was no need for extra neutral filters with the intensities measured. Temperatures at which experiments were performed were 25, 55, and 75°C. Temperature control was within 0.1°C, with an external thermostat. The toluene used was Baker Analyzed Reagent p.a. grade which was distilled and dried by molecular sieves (4 Å). The PPO sample used had $\bar{M}_n = 21.600$ and $\bar{M}_w = 37.700$ as determined by osmometry and light scattering, respectively. The solutions were freed from dust by filtration through a 0.45μ Millipore filter. With this filter only solutions with $w \leq 0.1$ could be filtered because the viscosity at higher concentrations.

Melting-Point Depression

Homogeneous mixtures of PPO-toluene were made by weighing the appropriate amounts of PPO and toluene in small glass tubes, which were degassed, flushed with nitrogen, and sealed under vacuum at liquid nitrogen temperature. The sealed glass tubes were heated in an oil bath to obtain a homogeneous solution. These solutions were cooled very slowly (1°C/48 hr) in a thermostat until the solutions became turbid. Melting points were determined visually by heating the turbid solution very slowly, until the solution again became clear. The melting points were confirmed by differential scanning calorimetry measurements.

Differential Scanning Calorimetry

Solutions were made in the glass tubes as mentioned above. After the tubes were cooled and broken, samples were put into liquid type sample pans. Only those pans which showed no weight loss after 24 hr at 90°C were used. DSC measurements were performed with a Perkin Elmer DSC-2 apparatus.

RESULTS

Light Scattering

In Figure 1 a typical scattering plot is shown from which the extrapolation of $\alpha\Delta I$ to $\theta = 0$ was made. The extrapolation of $(w/(\alpha\Delta I)_{\theta=0})$ values to $w = 0$ yielded a weight average molecular weight of 37.700 which is in accordance with the previously determined value. For the calculation of $(\partial\mu/\partial w)_{MWD}$ and $[\partial(\Delta\mu_0)/\partial w]$, the following constants have been used.

$$\text{At } T = 25^\circ\text{C}; n_B = 1.502 \quad R_B = 16.3 \times 10^{-6} \text{ (cm}^{-1}\text{)}$$

The values of n_B^2/R_B occurring in eqs. (2) and (3) have been corrected for temperature effects with the Lorentz-Lorenz equation (n_B) and data of Cohen and Eisenberg¹³ (for R_B), and yield

$$(n_B^2/R_B)_{55^\circ\text{C}} = 0.908 (n_B^2/R_B)_{25^\circ\text{C}}$$

$$(n_B^2/R_B)_{75^\circ\text{C}} = 0.847 (n_B^2/R_B)_{25^\circ\text{C}}$$

The densities at 25°C and 55°C were taken from Ref. 3 and the densities at 75°C were calculated with the relations given in Ref. 1.

The calculated values $\Delta\mu_0$ and χ_w are shown in Table I. Figure 2 shows χ_w

Fig. 1. Light scattering at different concentrations of PPO in toluene at 55°C.

TABLE I
Chemical Potentials and Interaction Parameters for PPO-Toluene Solutions

Temperature, °K	w	$-\Delta\mu_0 \times 10^{-6}$, erg/mole	χ_w
298	0.005	0.591	0.40
	0.01	1.305	0.40
	0.02	3.10	0.407
	0.05	11.25	0.421
	0.10	35.02	0.437
328	0.005	0.607	0.39
	0.01	1.443	0.40
	0.02	3.439	0.404
	0.05	13.00	0.412
	0.10	39.05	0.435
348	0.005	0.703	0.38
	0.01	1.58	0.38
	0.02	3.80	0.392
	0.05	14.48	0.402
	0.10	45.43	0.422

as a function of concentration and temperature. The values of χ_w at 75°C are probably somewhat too low in comparison with the values at 25°C and 55°C because the densities calculated from the equations of Shultz¹ are lower than those found by Van Emmerik³ at higher temperatures, thus yielding higher $\Delta\mu_0$ values and a lower χ_w . The concentration dependence of χ_w , however, is the same for the three temperatures. The χ_w values are in agreement with the values $\chi = 0.38 \pm 0.04$ at low concentrations, determined with osmometry in this laboratory for the determination of the number average molecular weight, and by Barrales-Rienda and Pepper.¹⁴

It can be concluded that the temperature dependence of χ_w is very small for this system, but there is a distinct concentration dependence (Fig. 2).

When g is taken as a function of concentration and temperature [eq. (8)], combination with eq. (5a) gives

$$\chi_w = g_0 + \frac{g_1}{T} + 2g_2w - g_2 \quad (11)$$

From the experimental light scattering data we thus find in a first approximation

Fig. 2. The interaction parameter χ_w as a function of concentration and temperature. (●) 25°C, (○) 55°C, (△) 75°C.

Fig. 3. $(\partial\mu/\partial w)_{MWD}$ for PPO-toluene solutions at different temperatures. (●) 25°C, (○) 55°C, (Δ) 75°C.

Fig. 4. Extrapolation plot to determine the spinodal.

that $g_1 = 0$. From data plotted in Figure 2, g_2 and g_0 can then be determined. The slope of the curve yields $g_2 = 0.19 \pm 0.02$ and from χ_w at $w = 0$ a value of $g_0 = 0.58 \pm 0.02$ is obtained. In Figure 3 a graphical representation of $(\partial\mu/\partial w)_{MWD}$ versus composition is shown. It can be seen from this figure that $(\partial\mu/\partial w)_{MWD}$ also has only a slight dependence on T . The spinodal (if it exists) is located at $1/(\alpha\Delta T)_{\theta=0} = 0$; this means that high-fluctuation scattering occurs on approaching a spinodal point.

From Figure 4 it appears that the extrapolation to $1/(\alpha\Delta T)_{\theta=0} = 0$ leads to an extremely low spinodal temperature; about 180°K. In the temperature range studied there is no indication for high-fluctuation scattering. Hence a spinodal curve is not present in the temperature region of interest.

Melting-Point Depression

Melting temperatures determined visually with an accuracy of $\pm 1^\circ\text{C}$ are given in Table II as a function of the polymer concentration. The results agree very well with other literature data.^{1,3} The inverse melting points plotted versus the

TABLE II
Melting Temperature of PPO Solutions in Toluene

w	$T_m, ^\circ\text{K}$
0.1	334
0.2	345
0.3	359
0.4	373
0.5	389

weight fraction of polymer in the solution, show a practically linear relation (Fig. 5), over the large concentration range covered. Therefore, the melting-point depression cannot be used to discriminate between contributions of g_1/T and g_2w in eq. (10). From the light scattering experiments it follows that g_1/T is very small and we have already concluded that $g = g_0 + g_2w$ can be used in eq. (10).

Since data on ΔH_u^0 range from 6 to 20 cal/g¹⁵ and data on T_m^0 from 510–545°K^{3,16} it is not feasible to calculate g_0 and g_2 directly from melting-point data. With the data obtained from light scattering: $g_0 = 0.58$ and $g_2 = 0.19$ a good fit of the experimental melting points was found using $T_m^0 = 545^\circ\text{K}$, $\Delta H_u^0 = 9.5$ cal/g and also using $T_m^0 = 535^\circ\text{K}$ with $\Delta H_u^0 = 9.8$ cal/g: both data sets give the “calculated” line from Figure 6. This type of experiment, obviously is not a very sensitive means of obtaining thermodynamic data. For lower g_0 values, good fits can be obtained also, but only when using somewhat higher ΔH_u^0 values. The ΔH_u^0 and T_m^0 values chosen remain within the range reported in the literature. For $g_2 = 0$ a fit can only be obtained by choosing large g_0 values. Then the normal type of liquid–liquid phase separation should occur with a maximum in the cloud point curve at low polymer concentration.⁴ This type of phase separation is not found for toluene as a solvent. It has to be concluded that g_2w contributes appreciably to the total g as was found in the light scattering results. Qualitatively, the melting point data are in agreement with the results for g from the light scattering data. Melting-point data are not very suitable to obtain quantitative information on $g(T,w)$.

Fig. 5. Reciprocal melting points vs. concentration in the PPO-toluene system.

Fig. 6. Melting points for the PPO-toluene system. (—) calculated, (O) Shultz, (●) this work.

Differential Scanning Calorimetry

Phase separation upon cooling appears in DSC measurements as an exothermic peak. The temperature at which the peak begins corrected as needed,⁷ is taken as the phase separation temperature. The phase separation temperature depends largely on the scanning speed (see Fig. 7). Since phase separation temperatures decrease steadily with increase in scanning speed these experiments show that we are in the region of nucleation and growth. Thus even at the highest possible scanning speed, with temperatures far below those of the spinodal determined earlier,³ the spinodal has not been reached.

DISCUSSION

Some attempts to determine the thermodynamic parameters g and χ for the system PPO-toluene have been published previously.

The determination of the χ parameters by Shultz and McCullough¹ agrees qualitatively with the present results when their inverse temperature dependence of χ is replaced by a concentration dependence. We have shown that within the series of melting point versus concentration data it is impossible to distinguish between the two dependences. Since Shultz and McCullough assumed a χ parameter independent of concentration, only a temperature dependence was found. The light scattering experiments in his work indicate that the temperature dependence is very small and that there is a distinct concentration dependence. We believe that the light scattering experiments published earlier¹⁸ and the conclusions based on them, are erroneous. The difference in the light scattering results is probably caused in part by the pretreatment given to the solutions. We found that small amounts of water in toluene, and filtration of the solution with a filter of larger pore size, gave very high and less reproducible scattering values. Moreover, Figure 2 of Ref. 18 corresponds nearly totally with the value of $(\partial\mu/\partial w)_{MWD}$, due to the last factor inside the brackets in our eq. (3) which arises from the molecular weight distribution. This contribution is zero only at $w = 1$, so extrapolation to $(\partial\mu/\partial w)_{MWD} = 0$ to find the spinodal was not possible. Both these points, χ values and extrapolation procedure, led to the

Fig. 7. Phase separation temperatures on cooling as determined by DSC at various scanning rates.

invalid conclusion that the occurrence of liquid-liquid phase separation was demonstrated by light scattering measurements.

The values for χ_w found in this work by light scattering agree with those from osmometry; these values can be used to derive g and describe the melting-point curve satisfactorily. These g values do not give a liquid-liquid phase separation gap in the region studied. To obtain a liquid-liquid phase separation a minimum value of χ_w of 0.5 must occur in a solution of a polymer of infinite molecular weight, and a χ_w must not depend on the concentration.⁴ For a lower molecular weight polymer and a concentration dependent χ_w , higher values of this parameter are needed for a liquid-liquid phase separation. In addition, when liquid-liquid phase separation occurs there should be a spinodal not too far below the cloud point curve. Because this spinodal cannot be detected, neither by light scattering nor by DSC, it is unlikely that liquid-liquid phase separation occurs in this system between 273 and 373°K.

The calculation of g parameters from the "cloud point curve" obtained by slow cooling, as was done by Van Emmerik and Smolders¹⁹ raises serious doubts, since it was incorrectly assumed that the g parameters for two cloud-point curves are the same at their point of intersection. A final comparison with other data is possible for the ternary system PPO/polystyrene/toluene where no liquid-liquid phase separation occurs.¹ Hence it can be expected that the interaction between PPO and toluene is not very different from that between polystyrene and toluene.²⁰ Indeed the χ parameters found for polystyrene-toluene⁶ are of the same magnitude as the values for PPO-toluene found in this work. This supports our conclusion that the phase-separation phenomenon observed for PPO-toluene is a crystallization phenomenon and not a liquid-liquid phase separation. The phenomenon of the two different temperatures at which a phase separated solution can become homogeneous will be dealt with in the second paper of this series.

To obtain more g values, high-pressure osmotic and vapor pressure measurements are presently being made in our laboratory. It is to be expected that a more accurate statement about the small temperature dependence of g can be made in a later stage.

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