DIFFERENTIAL SCANNING CALORIMETRY OF POLY-(2,6 DIMETHYL-1,4 PHENYLENE-OXIDE)-TOLUENE SOLUTIONS

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Abstract—A study has been made by differential scanning calorimetry of the phase separation phenomena of solutions of poly(2,6 dimethyl-1,4 phenylene-oxide) (PPO) in toluene. Upon cooling a homogeneous solution, liquid-liquid phase separation always precedes crystallization effects. By assuming the correction parameter g (in the expression for the chemical potential difference of the solution) to be temperature-dependent, the value of the heat of fusion is calculated to be 8.2 cal g^{-1} for PPO-toluene crystals.

INTRODUCTION

SEVERAL studies have been performed on the transition properties of poly(2,6 dimethyl-1,4 phenylene-oxide).^{*(1,2,3)} These studies showed that crystallization of PPO occurs if dilute solutions of PPO-solvent mixtures are allowed to stand for a rather long period at a phase separation temperature. Even then crystallization is poor and will be destroyed by thermal treatment. Experimental results indicated the importance of the solvent, since crystallization occurred only in the presence of certain organic liquids which played an important role in building up the crystal lattice. Melting points of the carefully dried material were reported as between 510–540 K, glass transition temperatures between 480 and 500 K.

A differential scanning calorimetry study has been made of PPO- α -chloronaphthalene solutions in order to measure the melting point depression temperatures.⁽¹⁾ The curve thus obtained could be explained by the theory of melting point depression of polymer solutions with a temperature and concentration independent interaction parameter.

We have studied phase separation phenomena in concentrated PPO-toluene solutions which showed that crystallization of PPO is always preceded by liquid-liquid phase separation.^(4,5) Computer calculations with a temperature and concentration dependent interaction parameter gave good agreement between the calculated and experimental phase separation curves.⁽⁶⁾ If melting point depression theory is adapted with such a parameter, values can be obtained for the heat of fusion of PPO-toluene crystals.

The results obtained by differential scanning calorimetry are reported in this paper.

EXPERIMENTAL

The poly(2,6 dimethyl-1,4 phenylene oxide) used was characterized by $\bar{M}_n = 25000$ and $\bar{M}_w = 39000$ $T_g = 495 \text{ K}$.

PPO-toluene samples were weighed in glass tubes, flushed with nitrogen and sealed under vacuum.

Complete dissolution occurred in a thermostat bath at an appropriate temperature. Homogeneous solutions in these tubes were brought into liquid N_2 which caused such fast cooling that no visible

* PPO.

phase separation took place and the solution turned completely into the glassy state. The tubes were opened, small pieces were cut off the sample and hermetically sealed in the sample pans normally used for liquids.

To determine the T_g of the samples, the sealed pans were heated upon a heating stage to 150°, after a certain time quenched in liquid nitrogen, and quickly transferred into the calorimeter (DSC-1B) already kept at -100°. After the temperature equilibrium was restored, T_g could be determined at a heating rate of 8°/min.

The contents of the sample holder were between 8 and 15 mg. To determine the heat effects due to phase separation at other temperatures, the sample holders were heated in the DSC to 150° and subsequently cooled in the DSC to the appropriate temperature.

THEORY OF MELTING POINT DEPRESSION

For an equilibrium between polymer crystals and a polymer solution, the following relation is valid:⁽⁷⁾

$$\mu_u^c - \mu_u^{(0)} = \mu_u^1 - \mu_u^{(0)}. \quad (1)$$

μ_u^c = thermodynamic potential of one mole of repeating units for the polymer in the crystalline state.

$\mu_u^{(0)}$ = thermodynamic potential of one mole of repeating units for the polymer in the standard state.

μ_u^1 = thermodynamic potential of one mole of repeating units for the polymer in solution.

This relation is equal to

$$- \Delta\mu_{f,u} = + \Delta\mu_{M,u} \quad (2)$$

f stands for melting, M for mixing.

By using Eqn. (2), the following relation can be derived for the depression of the melting temperature:⁽⁷⁾

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) / v_1 = (RV_u / \Delta H_u V_1) (1 - BV_1 v_1 / RT_m). \quad (3)$$

T_m = melting temperature of the polymer crystals in solution.

T_m^0 = melting temperature of the pure crystalline polymer.

V_u = molar volume of the repeating unit.

V_1 = molar volume of the diluent.

ΔH_u = heat of fusion.

B_1 = interaction parameter of the solvent-solute pair.

v_1 = volume percentage diluent.

R = universal gas constant.

Using expression (3) a plot of the quantity

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) / v_1$$

against v_1/T_m should give a straight line. This has been reported to be the case for the system PPO- α chloronaphthalene.⁽¹⁾ For PPO-toluene solutions, this is not the case. The system PPO-toluene can be described using an interaction parameter, g , in the

expression for the free energy of mixing⁽⁶⁾ which is linearly dependent on concentration and temperature $g = g_0(T) + g_1(T)w_1$.

Then $\Delta\mu_{M,u}$ is given by

$$\frac{\Delta\mu_{M,u}}{RT} = \frac{M_0}{M_n} \ln w_1 + (1 - w_1) \frac{M_0}{M_n} - (1 - w_1) + (g_0 + 2g_1w_1)(1 - w_1)^2. \quad (4)$$

M_0 = molecular weight of the solvent.

M_n = number average molecular weight of the polymer.

w_1 = weight fraction of the polymer.

g_0 and g_1 = empirical correction parameters (dependent only on T).

Taking⁽⁸⁾

$$\Delta\mu_{f,u} = \Delta H_u^0 \cdot \frac{\Delta T \cdot T_m}{(T_m^0)^2}. \quad (5)$$

A combination of Eqns. (2), (4) and (5), replacing T by T_m gives

$$\begin{aligned} \Delta H_u^0 \cdot \frac{\Delta T \cdot T_m}{(T_m^0)^2} = & -RT_m \left\{ \frac{M_0}{M_n} \ln w_1 + (1 - w_1) \frac{M_0}{M_n} - (1 - w_1) \right. \\ & \left. + (g_0 + 2g_1w_1)(1 - w_1)^2 \right\}, \end{aligned} \quad (6)$$

or

$$\begin{aligned} \frac{\Delta T}{(T_m^0)^2} = & -R/\Delta H_u^0 \left\{ \frac{M_0}{M_n} \ln w_1 + (1 - w_1) \frac{M_0}{M_n} - (1 - w_1) \right. \\ & \left. + (g_0 + 2g_1w_1)(1 - w_1)^2 \right\}. \end{aligned} \quad (7)$$

The only term which is a function of temperature in the right-hand side of Eqn. (7) is the term⁽⁶⁾ $(g_0 + 2g_1w_1)$, with

$$g_0 = \frac{566 \cdot 0 - 6 \cdot 7 (T_m - 273)}{RT_m}, \quad (8)$$

$$g_1 = \frac{1251 \cdot 8 - 0 \cdot 7 (T_m - 273)}{RT_m}. \quad (9)$$

Plotting $\Delta T/(T_m^0)^2$ against the term in brackets on the right-hand side of Eqn. (7) and taking account of (8) and (9), a straight line should be obtained with slope equal to $-R/\Delta H_u^0$.

RESULTS

In the system PPO-toluene, three-phase separation temperatures can be detected.⁽⁴⁾

When a homogeneous solution is cooled in the DSC at a rate of $16^\circ \text{ min}^{-1}$, an exotherm is observed at a certain temperature T_1 .

Upon recooling of such a solution, a very broad endotherm is observed ending at temperature T_2 . When reheating occurs a certain time after the exotherm

FIG. 1. Phase separation temperatures and heat effects determined with differential scanning calorimetry for a 30 per cent of weight poly(2,6 dimethyl-1,4-phenylene-oxide)-toluene solution.

effect has been observed, then next to the broad endotherm effect a second endotherm heat effect is observed at a temperature higher than T_2 , ending at the temperature T_3 . In Fig. 1 this is shown for a 30 per cent of weight PPO-toluene solution.

If a homogeneous solution is cooled to a temperature just above T_1 and reheated immediately no effect is observed at all. When reheating occurs after the solution is held at a temperature just above T_1 for a certain time, a broad endotherm is observed which becomes larger as a function of ageing time at T_1 until a maximum is reached. The second endotherm appears only after the first endotherm is observed. In Fig. 2 this is shown for a 30 per cent of weight PPO-toluene solution.

FIG. 2. Heat effects determined with DSC for a 30 per cent of weight poly (2,6 dimethyl-1,4 phenylene-oxide)-toluene solution cooled at $T = 300$ K for various periods of time.

Samples of pure PPO, carefully isolated from solutions in a manner described elsewhere,⁽⁹⁾ did not show any crystallinity by DSC measurements or with X-ray diffraction.

Only those PPO samples isolated from solutions which were held at a phase separation temperature for a certain time (long enough so that the second endotherm was observed by DSC) gave an exotherm at $T = 510$ K. Hence these samples were partially crystalline. In all other samples, T_g was 495 K.

FIG. 3. Phase separation temperatures of poly(2,6 dimethyl-1,4-phenylene-oxide)-toluene solutions. Full lines: A, spinodal curve; B, cloudpoint curve; C, melting point curve, obtained earlier.⁽⁴⁾ ●, Spinodal temperatures; ▽, cloudpoint temperatures; ○, melting point temperatures, determined by DSC. ---, Glass transition temperatures determined earlier;⁽⁴⁾ ×, the same, determined by DSC.

In Fig. 3 all phase transition temperatures obtained by DSC calorimetric measurements are shown, together with the glass transition temperatures.

Since the lower temperature limit of the DSC is -100° , no glass transition temperatures could be determined in solution less than 20 per cent of weight PPO-toluene.

Also plotted in Fig. 3 are the phase separation results obtained earlier.⁽⁴⁾

Using data from Fig. 3 and taking $T_m^0 = 510$ K, in Fig. 4 $\Delta T/(T_m^0)^2$ is plotted against

$$-\left\{ \frac{M_0}{M_n} \ln w_1 + \frac{M_0}{M_n} (1 - w_1) - (1 - w_1) + (g_0 + 2g_1 w_1)(1 - w_1)^2 \right\}.$$

A linear dependence is obtained, in accordance with theory. The slope obtained by the least squares method, being equal to $R/\Delta H_u^0$, gives for one mole repeating unit $\Delta H_u^0 = 1365.0$ cal. If PPO crystallizes without toluene this would mean $\Delta H_u^0 = 11.4$ cal g^{-1} , a value also obtained by Schultz⁽³⁾ (11.63 cal g^{-1}).

FIG. 4. A plot of $\Delta T/(T_m^0)^2$ against

$$-\left\{ \frac{M_0}{M_n} \ln w_1 + \frac{M_0}{M_n} (1 - w_1) - (1 - w_1) + (g_0 + 2g_1 w_1)(1 - w_1)^2 \right\}.$$

Later work indicates⁽¹⁰⁾ that the unit cell of PPO, crystallizing with low molecular weight solvent, contains eight polymer segments and four solvent molecules. As a consequence $\Delta H_u^0 = 8.2 \text{ cal g}^{-1}$.

DISCUSSION

PPO belongs to the class of slowly crystallizing polymers.⁽¹⁰⁾ Crystallization occurs only after very careful treatment of very dilute solutions. It is to be expected then that upon cooling concentrated solutions, crystallization will hardly occur. A general description of the phase separation phenomena of such solutions has been given by Papkov and Yefimova.⁽¹¹⁾

Upon cooling of a concentrated solution, liquid-liquid phase separation will take place, leading to a concentrated and a dilute phase. Two mechanisms of liquid-liquid phase separation are possible, viz. nucleation and growth of one of the phases or spinodal decomposition. Both mechanisms occur in PPO-toluene solutions.⁽⁴⁾ The nucleation process starts after induction periods which depend on temperature.⁽¹²⁾ If a homogeneous solution of PPO-toluene is cooled at a rate of $32^\circ \text{ min}^{-1}$, nucleation will not take place in a detectable amount and the spinodal area is entered. The solution in that case is not stable even to the smallest fluctuations in concentration and demixes instantaneously.⁽¹³⁾ This is shown as an exotherm at the spinodal temperature T_1 in Fig. 1, measured by DSC.

Direct reheating of the demixed solution, preventing crystallization, will cause a continuous change of the phase composition. This is observed on the DSC thermogram as a very broad endotherm. The temperature T_2 represents the cloudpoint of that solution. At this temperature the solution becomes homogeneous again and upon further heating no thermal effect is observed.

When a demixed solution is kept at the temperature of phase separation for a certain time, the concentrated phase will partially crystallize. If the polymer is isolated carefully from this solution, the thermogram shows a melting peak at 510 K.

The heat effect has such values that the percentage of crystallinity of the pure PPO can be estimated at about 2 per cent in solutions of 5 or 10 weight per cent PPO-toluene and even less in more concentrated solutions.

When demixed solutions in which crystallization has occurred are heated in the calorimeter, two broad endotherm peaks are observed. The first one is the heat effect caused by dissolution of the non-crystallized polymer, the second endotherm is the heat effect caused by the melting of the crystalline material.

The temperature where the solution becomes completely homogeneous again is taken as the melting point of that particular solution.

The melting point curve and the cloudpoint curve thus obtained are in agreement with those obtained previously.⁽⁴⁾ The spinodal curve, taken before as a five minutes time limit of phase separation after cooling, is several degrees higher.

The glass transition temperatures measured by DSC are much lower than those previously obtained. In earlier work, glass transition temperatures were obtained by microscopic observations for lower, and D.T.A. measurements for higher concentrations which for concentrations above 40 per cent PPO-toluene solutions, gave too high values.

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Résumé—On a étudié par calorimétrie différentielle les phénomènes de séparation de phase de solutions de poly(diméthyl 2,6 oxyde de phénylène 1,4) (PPO) dans le toluène. Pendant le refroidissement d'une solution homogène, la séparation de phase liquide-liquide précède toujours les effets de cristallisation. En supposant que le paramètre de correction g (dans l'expression donnant la différence de potentiel chimique de la solution) dépend de la température, on a calculé que pour des cristaux de PPO-toluène la chaleur de fusion était de $8,2 \text{ cal}^{-1}$.

Sommario—Mediante calorimetria differenziale esploratrice, si è eseguito uno studio sui fenomeni di separazione di fase di soluzioni di poli(2,6 dimetil 1-1,4 fenilene-ossido) (PPO) in toluene. In seguito a raffreddamento di una soluzione omogenea, la separazione della fase liquido-liquido precede sempre gli effetti di cristallizzazione. Supponendo che il parametro correttivo g (che esprime la differenza di potenziale chimico della soluzione) dipenda dalla temperatura, si è calcolato che il valore del calore di fusione per cristalli di PPO-toluene è di $8,2 \text{ cal g}^{-1}$.

Zusammenfassung—In Lösungen von Poly(2,6-dimethyl-1,4 phenylen) oxid (PPO) in Toluol wurde die Erscheinung der Phasentrennung durch differentielle Scanning Calorimetrie untersucht. Beim Abkühlen einer homogenen Lösung geht den Kristallisationseffekten immer eine Trennung in zwei flüssige Phasen voraus. Unter der Annahme, daß der Korrekturparameter g (in der Gleichung für die chemische Potentialdifferenz der Lösung) von der Temperatur abhängig ist, wird für die PPO-Toluol Kristalle ein Wert von 8.2 cal g^{-1} für die Schmelzwärme berechnet.