D.s.c. studies on the phase separation of solutions of poly(2,6-dimethyl-1,4-phenylene ether) in decalin

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Phase separation phenomena in solutions of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in decalin were investigated by means of differential scanning calorimetry. Phase separation and gradual crystallization were observed on cooling a homogeneous solution of PPO in decalin. Phase separation temperatures of PPO solutions in decalin were determined at various concentrations. The heat of melting of crystals was found to be equal to 1285 cal/mol for the PPO–decalin system.

INTRODUCTION

Phase transition phenomena of poly(2,6-dimethyl-1,4-phenylene ether) have been described by several authors[1–3] who showed the crystallization of PPO to take place in solution.

Crystallization was found to occur only in the presence of certain solvents which play an important role in the formation of the crystal lattice. The melting point of the isolated crystalline material was reported to lie between 510–540K, glass transition occurring in the temperature range of 480–500K.

PPO–chloronaphthalene and PPO–toluene systems[1,3] were investigated by differential scanning calorimetry (d.s.c.). It was found that PPO crystallizes from toluene solutions by liquid–liquid phase separation[4,5].

Phase separation phenomena in PPO solutions in decalin were investigated and their results will be reported in the present paper.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) used in this study was obtained from the Institute of Industrial Chemistry, Warszawa, and had a number-average molecular weight, $\bar{M}_n$, of 25 000 and a viscosity–average molecular weight, $\bar{M}_v$, of 36 700. Its glass transition temperature, T_g, was found to be 491K. Decalin was used as received from the Veb Jenapharm–Apolda.

Measuring technique

The PPO samples were dissolved in decalin and the solutions kept in glass test-tubes. Homogeneous solutions of PPO were then cooled rapidly to a temperature of 273K and a semirigid material was obtained.

Small pieces of this semirigid material were then placed in volatile sample pans, phase separation temperatures being determined by means of a differential scanning calorimeter Perkin–Elmer DSC–2. Measurements were performed on samples weighing between 4 and 10 mg. The samples were heated in the differential scanning calorimeter up to a temperature of 453K and then gradually cooled to the required temperature at a cooling rate of 20K/min.

To determine the T_g of the sample of PPO we used the DSC–2 calorimeter. At a heating rate of 10K/min the sample was found to exhibit a wide endothermic peak having its maximum at about 521K and responsible for the fusion of the crystalline phase. The sample was then rapidly cooled to 350K at a cooling rate of 320K/min and subsequently heated again at a rate of 10K/min and a discontinuity in C_p (heat capacity) indicative of a glass transition T_g was observed at 491K.

RESULTS

Three phase separation temperatures were observed for the PPO–decalin system. On cooling (at a rate of 20K/min) a homogeneous solution of PPO in decalin from the temperature of 180K it was found that, at a certain temperature (T_1) an exotherm appeared over a relatively wide temperature range.

The same sample was then heated at a rate of 10K/min starting at a temperature below T_1. Two endothermic phase transition phenomena were observed on heating the sample. The first, rather wide temperature range corresponding to an initial endothermic effect was found to end at a temperature T_2 and a second endotherm was found to end at a temperature T_3. Reproducible results of measurements were obtained for several experiments.

A typical thermogram obtained for a 13.6% solution of PPO in decalin is shown in *Figure 1*. For samples of solutions allowed to stand for longer periods of time (20 min) at temperatures below T_1, the area of the second endothermic peak was found to increase while that of the first decreased. The values of the temperature T_2 and T_3 were nevertheless the same. Temperature T_3 was taken as the melting point T_m of the polymer crystals in solution.

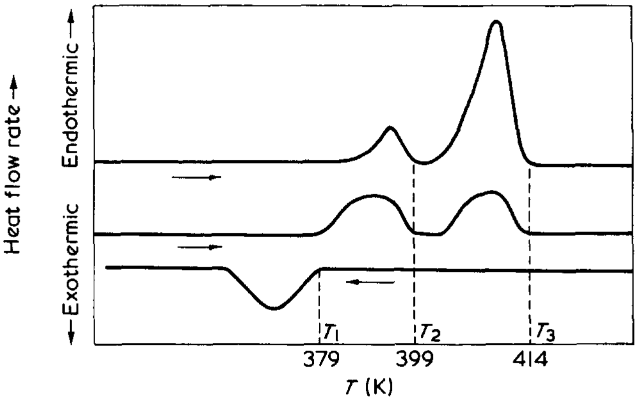

Figure 1 Phase separation temperatures and heat effects determined with d.s.c. for 13.6 wt % poly(2,6-dimethyl-1,4-phenylene oxide)–decalin solution

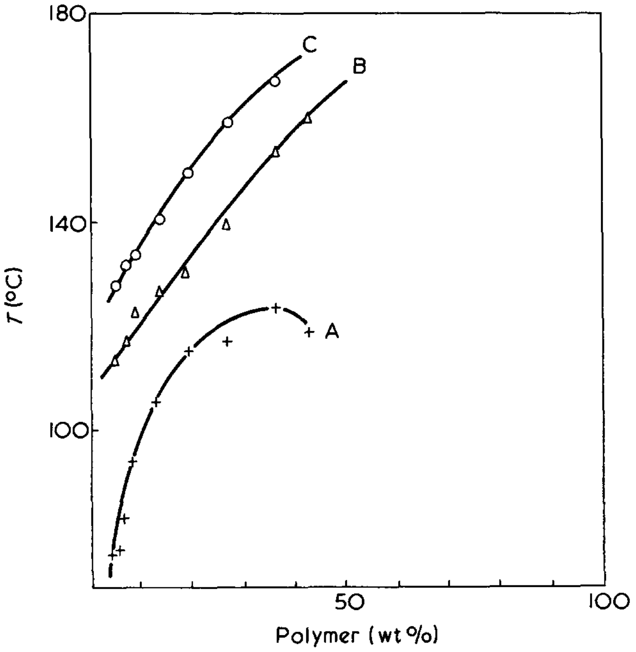

Figure 2 Phase separation temperatures of poly(2,6-dimethyl-1,4-phenylene oxide)–decalin solutions, determined by DSC–2. A, spinodal curve; B, cloud-point curve; C, melting point curve. ●, Spinodal temperatures; △, cloud-point temperatures; ○, melting point temperatures

Figure 2 shows phase transition temperatures expressed as a function of polymer concentration in the PPO solutions investigated.

PPO samples taken out of the solution exhibited a certain degree of crystallinity in differential scanning calorimetry measurements. The melting point determined for these samples by d.s.c. was found to be equal to ~510K, values between 503–533K being determined using the Boetiis hot stage.

Using Smolders equation[3] for the lowering of the melting point of a polymer, the heat of fusion of the polymer can be determined:

$$\frac{T_m^0 - T_m}{(T_m^0)^2} = R/\Delta H_u^0 \left\{ \frac{M_0}{\bar{M}_n}\ln w_1 + (1 - w_1)\frac{M_0}{\bar{M}_n} - (1 - w_1) + (g_0 + 2g_1 w_1)(1 - w_1)^2 \right\} \qquad (1)$$

where ΔH_u^0 is the heat of fusion of pure crystalline polymer; T_m^0 is the melting point of pure crystalline polymer; T_m is the melting point of polymer crystals in solution; M_0 is the molecular weight of the solvent; $\bar{M}_n$ is the number-average molecular weight of polymer; w_1 is the weight fraction of polymer and R is the gas constant.

Equation (1) was derived from the expression for the Gibbs free energy of mixing[2] in which g, the interaction parameter is linearly dependent on concentration and temperature[2,3] and is given by:

$$g = g_0(T) + g_1(T)w_1 \qquad (2)$$

where g_0, g_1 are empirical correction parameters (functions of T)

Following a method described in the literature[2] and taking the data from the cloud-point curve (*Figure 2*) the empirical equations (3) and (4) for the parameters g_0 and g_1 were determined:

$$g_0 = \frac{1999.9 - 12.1\,(T - 273)}{RT} \qquad (3)$$

$$g_1 = \frac{2197.6 - 4.6\,(T - 273)}{RT} \qquad (4)$$

Using the values from the melting point curve (*Figure 2*) and the values of g_0 and g_1 earlier determined from equations (3) and (4), and taking $T_m^0 = 510$K, a plot of $(T_m^0 - T_m)/(T_m^0)^2$ against

$$\frac{M_0}{\bar{M}_n}\ln w_1 + (1 - w_1)\frac{M_0}{\bar{M}_n} - (1 - w_1) + (g_0 + 2g_1 w_1)(1 - w_1)^2$$

was obtained.

A least squares straight line plot was obtained, which is in full agreement with current theory. The slope of the straight line obtained is equal to $R/\Delta H_u^0$, and it was therefore possible to determine the heat of fusion of a PPO re-

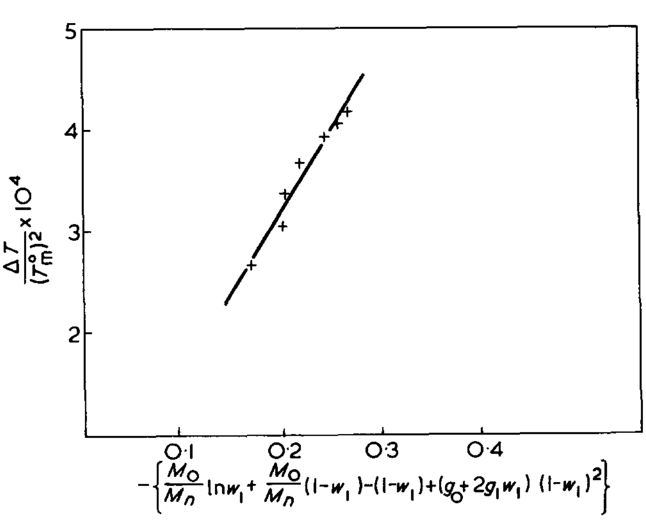

Figure 3 A plot of $\Delta T/(T_m^0)^2$ against

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

peating unit, $\Delta H_u^0 = 1285$ cal/mol repeating unit of a PPO. When PPO crystallizes in the absence of solvent we obtain from this value:

$$\Delta H_u^0 = 10.7 \text{ cal/g of the polymer.}$$

DISCUSSION

When comparing our results with those of Smolders[3], who studied the system PPO–toluene, it can be stated that crystallization of the PPO in decalin proceeds in a different manner.

Thus, in the case of the PPO–toluene system, the phase separation process taking place on cooling involves the formation of two liquid phases, and then PPO crystallizes in one of them. On the other hand, in the case of the PPO–decalin system it may be assumed on the basis of our experimental results that a partly crystalline precipitate is formed.

It is significant that the second liquid phase is not formed for the PPO–decalin system. The exothermic peak obtained on cooling and starting at the temperature T_1 is thought to reflect processes taking place below the spinodal decomposition temperature i.e. processes involving the formation of ordered structures by phase separation, crystallization and other processes.

On heating the samples from a temperature below T_1, two endothermic peaks ending at temperatures T_2 and T_3 may be observed. The appearance of these peaks may be interpreted as follows. The peak ending at T_2 is thought to represent a decrease of the degree of order in the system corresponding to the dissolution of the amorphous phase. The peak ending at T_3 is assumed to represent a decrease of the degree of order in the system due to the melting of the crystalline phase present in it. Results of our measurements carried out for 13% solutions of PPO in decalin clearly show the melting point of crystals (414K) to be considerably lower than that of the single PPO crystals (510K). Knowledge of the lowering of the melting point of polymer crystals makes it possible to calculate other properties of the system studied. Using a procedure similar to that of Smolders[3] the g_0 and g_1 interaction parameters, which are only a function of temperature in the Gibbs free energy of mixing equation, and using the equation (3) for the lowering of the melting point of the polymer, we obtained a value for the heat of fusion of pure, crystalline polymer equal to 1285 cal/mol, or $\Delta H_u^0 =$ 10.7 cal/g of polymer. This value is considerably lower than that found by X-ray methods (12–20 cal/g)[1] and slightly lower than the value determined by Smolders for the system PPO–toluene[3].

If we exclude the possibility of making such large experimental errors, we may then attempt to explain the phenomenon observed by assuming the possible formation of a different crystal lattice.

The possibility of formation of a crystal lattice comprising, besides the molecules of the polymer, the built-in molecules of the solvent used has already been described in the literature[5,6]. We think that the same phenomenon is responsible for the effects observed by us for the system PPO–decalin.

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