D.s.c. study of miscibility of polystyrene and poly(α-methylstyrene)

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The miscibility behaviour of blends of polystyrene and poly(α-methylstyrene) was studied by means of the differential scanning calorimetry. Three pairs of samples differing in their molecular weights were utilized, of which pair no. 2 had been previously investigated by means of light scattering (cloud points measurement). It is demonstrated that the onset of phase separation can be detected by noting any shift in the beginning and ending temperature of the glass transition region. By means of this technique, the phase diagram of one of the blends was determined and was found to agree well with the binodal curve calculated on the basis of the light scattering results. Some preliminary results obtained on the kinetics of phase separation show that even at temperatures only 30° above the glass transition temperature, a substantial phase separation occurs in less than a minute.

(Keywords: miscibility; blends; polystyrene; poly(α-methylstyrene); d.s.c.)

INTRODUCTION

Differential scanning calorimetry (d.s.c.) is utilized widely as a means of determining the miscibility of two polymers in a blend. The ease of operation of the d.s.c. instrument and the smallness of the sample size required make this a very popular technique. The criterion normally employed is that the two polymers are immiscible if two separate glass transition temperatures (T_g), characteristic of each polymer, are detected, while they are miscible if only a single T_g at an intermediate temperature is detected. If the blend composition is near the miscibility limit, however, such a criterion often fails to resolve the question of miscibility clearly, since then the T_g values of the two partially miscible phases might be too close to each other to be recognized as separate transitions. When the binodal (or critical) temperature of the blend lies within the scanning temperature range, the d.s.c. thermogram often exhibits either single or double T_g values depending on the cooling rate with which the sample was prepared prior to the scanning. No information on the binodal (or critical) temperature itself is normally obtainable from such scans.

The d.s.c. technique employed in the customary manner therefore provides only a very low resolution in detecting the miscibility of polymer blends. There are, however, ways to improve upon the resolution greatly by giving more careful attention to the sample preparation procedures and to the method of analysing the thermograms. In this study, we find that the determination of the initial and final temperature of the glass transition region affords a much more sensitive means of detecting the miscibility. We demonstrate that the method allows construction of an approximate phase diagram (binodal vs. composition) that agrees fairly well with that determined[1] by cloud point measurements. We also demonstrate that some limited amount of information can be obtained on the kinetics of phase separation.

Three different mixture samples of polystyrene and poly(α-methylstyrene) having different molecular weights were studied. The subtle differences in the thermograms arising from the differences in the upper critical solution temperature (UCST) of the blends in relation to the T_g were noted. The miscibility behaviour of this pair of polymers has been studied by other workers[2-4] by means of d.s.c., and also by us previously[1] using cloud point measurement. Comparison of the present results with these earlier studies is useful for evaluating the advantage of the present technique as a convenient means of revealing the phase behaviour of polymer blend systems.

EXPERIMENTAL

Materials

The characterization data for all the polymer samples used are summarized in *Table 1*. The two polystyrenes, designated 37KPS and 49KPS, were purchased from Pressure Chemical Company, who supplied their characterization data. Other polymer samples were synthesized in our laboratory by anionic polymerization under vacuum. Styrene was polymerized in benzene solution at room temperature for 12 h with n-butyl lithium as the initiator. α-Methylstyrene was polymerized in tetrahydrofuran solution at −78°C (dry ice

Table 1 Characterization data for the polymers used

Designation	Polymer	M_w	M_n	M_w/M_n
37KPS	Polystyrene[a]	37 000	35 000	1.06
49KPS	Polystyrene[a]	49 000	46 200	1.06
58KPS	Polystyrene	58 400	55 100	1.07
43KPMS	Poly(α-methylstyrene)	43 600	41 500	1.05
56KPMS	Poly(α-methylstyrene)	56 100	52 400	1.07
62KPMS	Poly(α-methylstyrene)	62 100	59 100	1.05

[a] Supplied by Pressure Chemical Company

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Table 2 Polymer pairs studied

	Component		
Pair no.	1	2	UCST
1	37KPS	43KPMS	388 K[b]
2	49KPS	56KPMS	467 K[a]
3	58KPS	62KPMS	505 K[b]

[a] Based on the cloud point data obtained previously[1]

[b] Calculated by use of the Λ value given by equation (2)

temperature) for 14 h also with n-butyl lithium as the initiator. The reaction time in all synthesized polymer samples was longer than necessary to ensure that the reaction went to completion. The molecular weight data shown were determined by gel permeation chromatography calibrated against standard polystyrene samples. The molecular weights for the poly(α-methylstyrene) samples were calculated through the use of the universal calibration curve in combination with intrinsic viscosity data.

Blend sample preparation

The two polymers for the blend were first dissolved together in toluene (2–3%) at room temperature. After filtering, the solution was poured into a large amount of methanol, and the precipitated fine powder was filtered and dried under vacuum at 85°C for at least a week. The dried powder was compression-moulded at 1.25 kbar under vacuum at room temperature (for 30 min) into a white circular film of 1.27 cm diameter and 0.03 cm thickness, from which a d.s.c. sample, weighing 9–11 mg, was cut.

D.s.c. measurements

The d.s.c. instrument (Perkin–Elmer DSC-2) was interfaced to a PDP 11/73 computer running under RT11/TSX-plus operating system. A 12-bit ADC board (Analog Devices RTI 1250) was used to convert the calorimetric (voltage) signal from the d.s.c. instrument into a digital form, the conversion being triggered by the temperature marker pulse generated by the instrument at the interval of 1/30 of a degree on both heating and cooling. A series of commands for d.s.c. operations, such as constant rate heating and cooling and isothermal annealing, could be stored in a program in the computer to enable unattended operation of the instrument over an extended time period. A typical measurement consisted of keeping the sample at 315 K for 5 min, heating at 20 K min^{-1} to an annealing temperature T_A, keeping it at that temperature for a length of time, and cooling at 80 K min^{-1} to 315 K, and this cycle was repeated several times in succession. A fresh sample gave a thermogram with minor irregularities in the first run, but if it was held at a temperature 10–20 K higher than the estimated UCST for 15 min or longer, all subsequent runs were completely reproducible within the instrumental noise level.

RESULTS AND DISCUSSION

The three polymer pairs studied in this work are listed in *Table 2*. Of these, pair no. 2 had been investigated previously[1] using cloud point measurements. Because of the high viscosity of these blends, the cloud temperatures were actually determined indirectly by first measuring the cloud points of ternary mixtures containing various proportions of dibutyl phthalate and then extrapolating the results to a zero amount of the latter. These were then fitted to the binodal curve calculated on the basis of the Flory–Huggins free energy of mixing (per unit volume of the mixture):

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln \phi_1 + (1/V_2)\phi_2 \ln \phi_2] + \Lambda \phi_1 \phi_2 \quad (1)$$

where V_1 and V_2 are the molar volumes of polymers 1 and 2, ϕ_1 and ϕ_2 are the volume fractions of the two polymers, and Λ is the interaction energy density between the two. The best fit to the experimental cloud points could be obtained by use of the value of Λ represented by:

$$\Lambda = 0.0608 + 0.0018\phi_2 - 0.000056T \quad (2)$$

where Λ is in cal cm^{-3}, ϕ_2 is the volume fraction of poly(α-methylstyrene) and T is in Kelvin. *Figure 1* shows the cloud points determined for pair no. 2 and the binodal curves calculated by means of equations (1) and (2) for the three polymer pairs. The broken line is the estimated T_g of the miscible blend, calculated according to:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (3)$$

with 373 and 444 K for T_g of polystyrene and poly(α-methylstyrene), respectively. The molecular weights of the polymers in these three pairs were chosen so as to have their UCST values near, but at different distances from, the T_g of the blends.

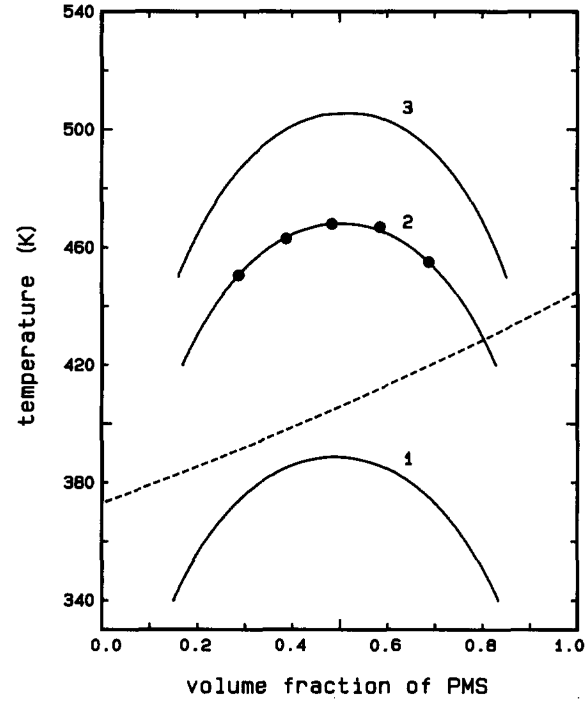

Figure 1 The solid curves are the binodal curves calculated by means of the Flory–Huggins free energy of mixing with the Λ value given by equation (2). Curves 1–3 refer to the polystyrene–poly(α-methylstyrene) pairs of different molecular weights listed in *Table 2*. ●, The experimental cloud points[1] obtained with pair no. 2, from which the best-fitting Λ value represented by equation (2) was previously evaluated. The broken curve gives the T_g of the miscible blend against composition

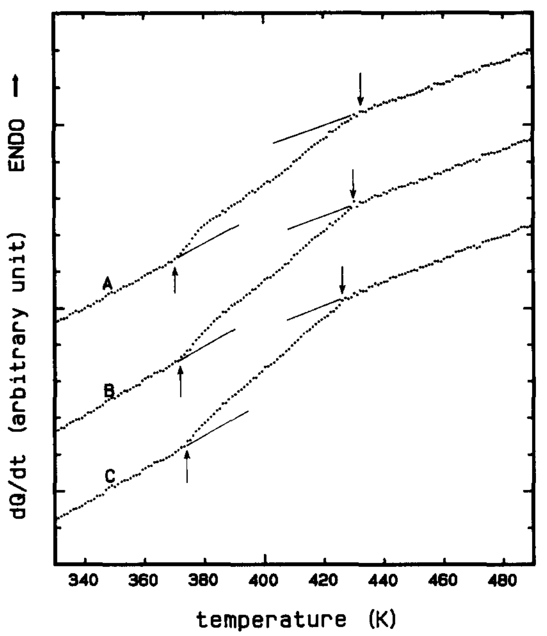

Figure 2 D.s.c. thermograms of a sample of pair no. 3 (containing 50% polystyrene) determined after the sample was cooled to 315 K from 520 K at different cooling rates: A, 20; B, 40; C, 80 K min^{-1}. The arrows indicate the beginning and the end of the glass transition region, as determined by the onset of deviation of the thermogram from the extrapolated liquid or glass line. The glass transition region has clearly broadened with slower cooling rate, indicating that some phase separation has occurred during the slow cooling

Effect of cooling rate

For pairs no. 2 and 3, for which the UCST lies above T_g, the degree of miscibility of the samples annealed at high temperature and cooled to lower temperature depends on the rate of cooling. *Figure 2* shows the effect of cooling rate observed with a sample of pair no. 3 (containing 50% polystyrene). The sample was first annealed for 20 min at 520 K (which is about 15 K above its UCST) to attain a miscible state, and then was cooled to 315 K at a cooling rate of either 20, 40 or 80 K min^{-1}. Subsequent scanning at a 20 K min^{-1} heating rate produced the thermograms A, B and C shown in *Figure 2*. The sample cooled at 20 K min^{-1} gives a clear indication of the presence of two phases noted, for example, by the glass transition of the polystyrene phase at around 380 K. The sample cooled at 80 K min^{-1}, on the other hand, shows only a single smooth transition extending from around 376–426 K. The result discussed below indicates also that the cooling rate of 80 K min^{-1} is indeed rapid enough to prevent phase separation of samples of pair no. 2 and 3 in most cases. We note in *Figure 2* that the glass transition region becomes progressively wider as the cooling rate is lowered. This suggests the possibility that the beginning and the end of the glass transition region can be utilized as indicators of the progress of phase separation process.

Beginning and end of the glass transition region

The calculated binodal curve for pair no. 1 lies below the T_g curve at all compositions. The blend will therefore be unable to phase separate and remain miscible at all temperatures once it is made miscible by annealing above its T_g. *Figure 3* shows the series of thermograms obtained with samples of this blend containing various proportions of poly(α-methylstyrene). The single glass transition region occurs at a progressively higher temperature as the composition shifts from pure polystyrene towards pure poly(α-methylstyrene). The glass transition region is noticeably broader when the two components are present in comparable amounts. This phenomenon, which occurs with many other compatible blends, was noticed also by other workers[5], and is probably due to the existence of concentration fluctuation in the miscible blends. One can define the beginning (T_{gb}) and the end (T_{ge}) of the glass transition region by drawing straight lines through the glass and liquid regions, respectively, and noting the points of deviation of the actual thermograms from these straight lines. By adopting some consistent method of determining these temperatures (*Figure 2*), it is possible to evaluate them within an uncertainty of a few degrees at most. The temperatures T_{gb} and T_{ge} thus obtained are plotted as circles in *Figure 4*.

Samples of pairs 2 and 3 would also be in a miscible state if they are annealed at temperatures above their respective UCST and then quenched to room temperature. As discussed above, the results in *Figure 2* indicate that an 80 K min^{-1} cooling rate should be rapid enough to prevent phase separation during the cooling. Samples of pairs 2 and 3, prepared by such a 'quenching' procedure, were scanned at a 20 K min^{-1} heating rate, and the temperatures T_{gb} and T_{ge} evaluated, as described above, are plotted as squares and triangles in *Figure 4*. The T_{gb} and T_{ge} values for pair no. 2 agree well with those obtained with pair no. 1, thus indicating that the 'quench' was completely successful. Samples of pair no. 3 exhibit some deviation in their T_{gb} and T_{ge} values from those for pair no. 1, apparently indicating that the 'quench' may not have been completely successful in some cases because of the larger temperature difference between the binodal and the T_g.

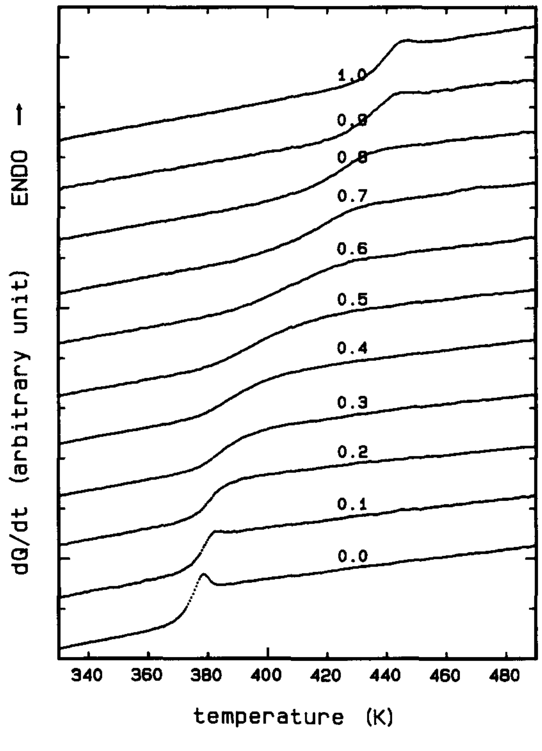

Figure 3 A series of thermograms obtained with samples of pair no. 1 containing the various fractions of poly(α-methylstyrene) indicated. Since the UCST of this blend is estimated to be below the T_g, these curves represent the thermograms obtainable with completely miscible blends

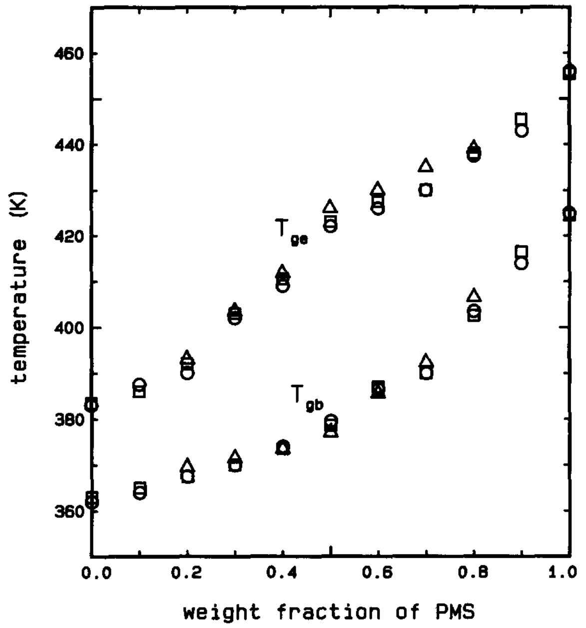

Figure 4 The beginning, T_{gb}, and the end, T_{ge}, of the glass transition region are plotted against the composition of the blend. ○, Values obtained for pair no. 1, and represent miscible blends. □, Values from samples of pair no. 2 which were cooled at 80 K min^{-1}. The good agreement between the two indicate that the cooling rate was sufficient to prevent phase separation during cooling. △, Values obtained for samples of pair no. 3 which were also quenched at 80 K min^{-1}, but the cooling rate apparently was not fast enough to arrest phase separation completely in some cases

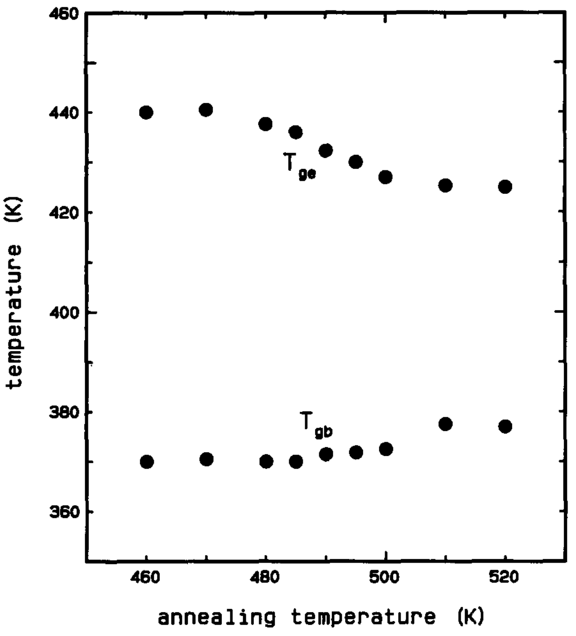

Figure 5 A sample of pair no. 3 containing 50% polystyrene was annealed at various temperatures and the beginning and the end of the glass transition region were noted from the thermograms obtained after 80 K min^{-1} quench. The progressively increasing separation between T_{gb} and T_{ge} with lower annealing temperature indicates the increasing degree of phase separation

The values of T_{gb} and T_{ge} obtained with pairs 1 and 2, and plotted in *Figure 4*, are now taken as the indicator of miscibility. A sample which has undergone phase separation will contain in it some regions richer in polystyrene and other regions poorer in polystyrene than the overall composition. As a consequence, its d.s.c. curve will show a T_{gb} lower than the T_{gb} expected of a homogeneous blend of the average composition. Similarly, its glass transition region will be extended to a higher temperature than is indicated by the T_{ge} values for pairs 1 and 2 in *Figure 4*. For example, the data shown in *Figure 5* were obtained with a sample of pair no. 3 containing 50% polystyrene, which was first annealed at 520 K for 20 min to make it homogeneous, and then annealed at various temperatures below the UCST for further 20 min. As the annealing temperature is decreased, the spread between T_{gb} and T_{ge} increases, suggesting a progressively increasing extent of phase separation. In fact, by matching the observed T_{gb} with the T_{gb} in *Figure 4*, we can estimate the composition of the styrene-rich phase in the phase-separated sample. Similarly, by matching the observed T_{ge} with the T_{ge} in *Figure 4*, we can estimate the composition of the (α-methylstyrene)-rich phase. The result is shown in *Figure 6*, in which the data is compared with the binodal curve estimated by means of the Flory–Huggins free energy of mixing with the Λ value represented by equation (2). The agreement between the phase compositions determined from T_{gb} and T_{ge} and the calculated binodal is surprisingly good, although the difficulty of evaluating T_{gb} and T_{ge} precisely obviously introduces fairly large scatter in the deduced phase compositions.

Phase diagram

A more reliable way of constructing an experimental phase diagram is to prepare a series of samples having different compositions of a given pair of polymers, and then determine the lowest temperatures at which each of the samples can be annealed without inducing phase separation. As a criterion for phase separation, we again utilize the width of the glass transition region. *Figure 7* shows the thermograms obtained with a sample of pair no. 3 containing 30% polystyrene which was annealed at various temperatures (in the order indicated by the four

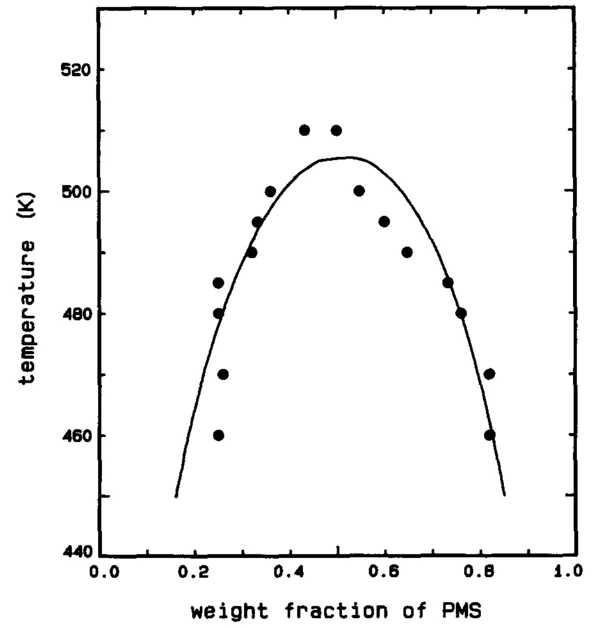

Figure 6 By comparing the T_{gb} and T_{ge} values given in *Figure 5* with those in *Figure 4*, approximate compositions of the phase-separated regions were estimated (●). The curve is the binodal calculated by means of the Flory–Huggins free energy of mixing with the Λ value as given by equation (2)

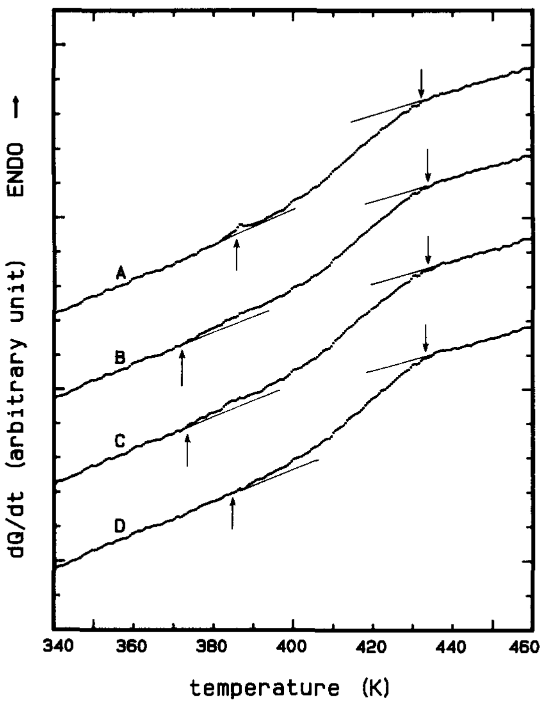

Figure 7 A sample of pair no. 3 containing 30% polystyrene was annealed at various temperatures and then cooled to 315 K at 80 K min^{-1} before the thermograms shown were obtained. A, annealed at 495 K for 20 min; B, annealed at 480 K for 20 min; C, annealed at 485 K for 30 min; D, annealed at 490 K for 20 min. The width of the glass transition region is clearly different between curves B and C on the one hand and curves A and D on the other hand, indicating that the binodal of the blend lies in the temperature interval between 485 and 490 K

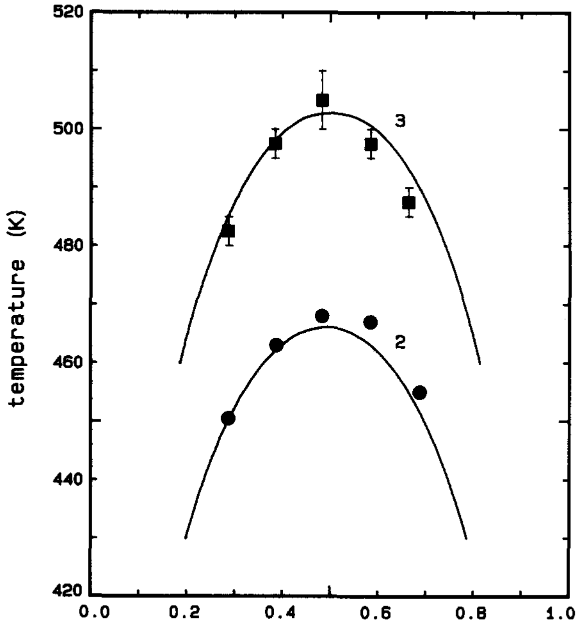

Figure 8 ■ (with error bars), The binodals for samples of pair no. 3 determined by the procedure illustrated in *Figure 7*. ●, The cloud points[1] previously determined for samples of pair no. 2. These two sets of data are fitted by the calculated curves based on the Flory–Huggins free energy of mixing with a single Λ value expressed by equation (4)

curves from top to bottom). There is not much difficulty in differentiating the miscible state (thermograms A and D), obtained by annealing at 495 and 490 K, and the phase-separated state (thermograms B and C), obtained by annealing at 480 and 485 K. On the basis of the data in *Figure 7*, we thus conclude that the binodal of the sample lies between 485 and 490 K. The experimental binodals determined in this way are plotted in *Figure 8* as squares, each with a corresponding error bar. The circles in the figure are the cloud points obtained for pair no. 2 by extrapolation of the dibutyl phthalate concentration to zero. These two sets of data were fitted by binodal curves calculated from equation (1) with a single set of Λ value, and the best fitting value of Λ is given by:

$$\Lambda = 0.06125 + 0.0008\phi^2 - 0.0000565T \qquad (4)$$

which differs from equation (2) (obtained previously from the cloud point data alone) insignificantly.

Kinetics of phase separation

Utilizing essentially the same procedure of examining the width of the glass transition region, one can even obtain some information on the time required for the phase separation to occur. *Figure 9* shows thermograms obtained with a sample of pair no. 3 containing 50% polystyrene. The sample was first annealed at 520 K (above its UCST) for 20 min, cooled at 80 K min^{-1}, and then scanned at 20 K min^{-1} (up to 490 K) to obtain curve D. The sample was then kept for 1 min at 490 K, cooled at 80 K min^{-1}, and then scanned at 20 K min^{-1} (again up to 490 K) to obtain curve C. After additional annealing for 1 min at 490 K, scan B was obtained, and after a further 2 min annealing (total cumulative annealing of 4 min) scan A was obtained. From curves D to C the glass transition region is clearly seen to have broadened, but no further changes are recognizable from curves C to B to A.

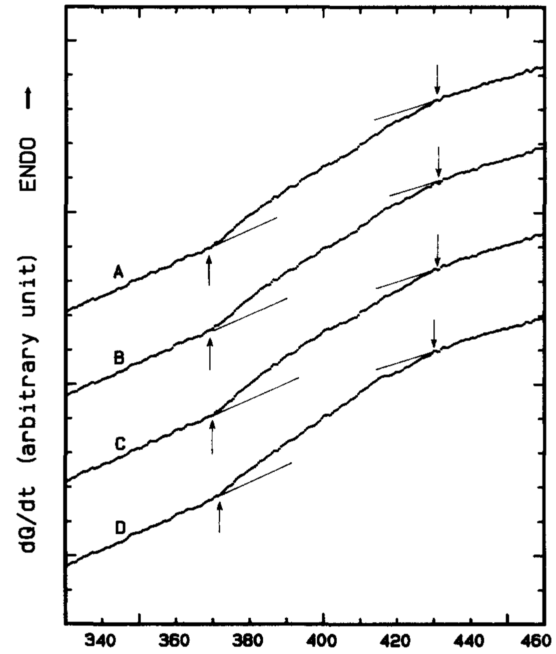

Figure 9 Thermograms obtained with a sample of pair no. 3 containing 50% polystyrene. Curve D was obtained when the sample was annealed at 520 K for 20 min to render it homogeneous. Curves C, B and A were obtained with the same sample after it was annealed for 1, 2 and 4 min (cumulatively) at 490 K. The shift in T_{gb} and T_{ge} between curves D and C indicates that a substantial phase separation has occurred at this temperature in less than a minute

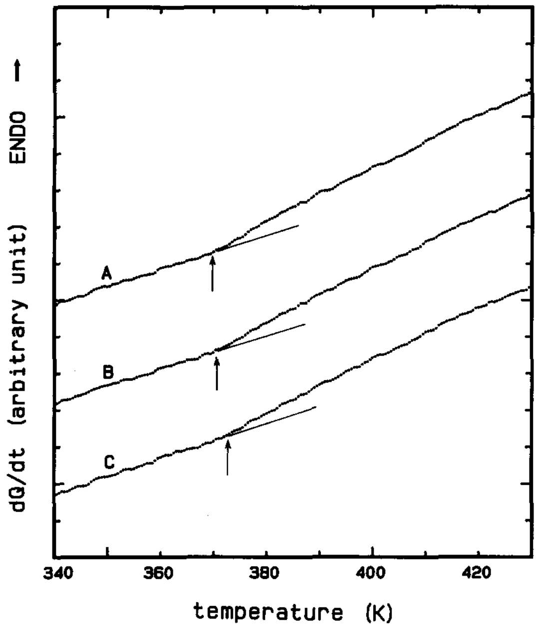

Figure 10 The same sample as that described in *Figure 9* was at first annealed at 520 K for 30 min (C) to make it homogeneous, and then annealed at 430 K for 1 min (B) and for 6 min (A). The lowering of T_{gb} from curves C to B indicates that a substantial degree of phase separation has occurred in less than a minute even at such a low temperature which is only about 30° above T_g

The result thus indicates that the phase separation of the sample at 490 K is substantially completed in less than a minute.

Figure 10 shows similar results obtained after annealing at 430 K, which is only about 30° above the glass transition temperature. The same sample used for the results in *Figure 9* was again annealed at 520 K for 30 min to make it homogeneous, and then it was annealed at 430 K for 1 min and then for an additional 5 min. Each curve shown in *Figure 10* was obtained after the sample was cooled at 80 K min^{-1} and scanned up to 430 K at 20 K min^{-1}. Because the T_{ge} of a 50/50 mixture is expected to lie above about 440 K, only the shift in T_{gb} was examined. The result in *Figure 10*, however, clearly shows that a considerable extent of phase separation has occurred already in 1 min at 430 K. We have an additional result obtained by annealing at 410 K, which indicates that even at such a low temperature (only about 10° above T_g) a downward shift in T_{gb} is clearly recognizable after 7 min of annealing.

Full quantitative information on the kinetics of phase separation undoubtedly requires a more quantitative technique, such as small-angle neutron scattering with deuterium-labelled samples. But the present result demonstrates that the d.s.c. measurement, performed in a systematic manner as described here, can provide a general outline of the phase diagram and the phase separation behaviour and can, at the least, serve as a rapid method of screening samples suitable for more detailed and time-consuming investigation utilizing light scattering or neutron scattering.

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