

Deconvolution of Scanning Calorimetric Signals Obtained for Aqueous Mixtures of Poly(Oxypropylene) Oligomers[†]

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High-sensitivity differential scanning calorimetric (HSDSC) data obtained for mixtures of poly(oxypropylene) (POP) oligomers, of different molecular masses, in aqueous solution have been deconvoluted using a previously reported mass action thermodynamic model of aggregation (Armstrong, J.; *et al. J. Phys. Chem.* **1995**, *99*, 4590) to investigate polymer aggregation/phase separation in these mixed systems. The data shows that POP oligomer solutions will phase separate at well defined temperatures as the POP solution is warmed. The data obtained shows no scan rate dependence which prompts the hypothesis that phase separation is adequately described by a nucleation and growth mechanism. It is concluded that the nucleation step is observable by HSDSC while the growth phase is calorimetrically silent. The model derived parameters indicate that the phase transitions occurring at the lower temperature are only slightly modified compared to those values obtained for the respective single-polymer solutions, whereas the higher temperature transitions are markedly altered. A descriptive model is proposed which is used to explain the obtained results. Essentially the model suggests that the higher molecular mass component, which phase separate at lower temperatures, aggregates and phase separates independently of the lower molecular mass component. However, depending upon the molar ratio of the two components, the lower molecular mass component will, at the appropriate temperature, either join the already existing high molecular mass component aggregates or will form separate aggregate nuclei.

Introduction

Water soluble polymers formed from ethylene oxide (EO) and propylene oxide (PO) and block copolymers formed from both these monomers show interesting solution behavior.^{1,2} It is proposed that in aqueous solution these polymers form an extensive hydrogen bonded structure with the aqueous solvent.^{2,3} Hydrogen bond formation is an exothermic process and thus, as anticipated, experimental measurements of the differential enthalpic contribution to the free energy of mixing is negative.⁴ Any increase in water structure associated with the creation of the hydrogen bonded system on the other hand gives rise to a decrease in entropy thereby producing an opposing contribution to the free energy of mixing. An increase in temperature of the polymer solution provides the thermodynamic driving force for the increasing disruption of the hydrogen bonded structure, which eventually gives rise to polymer phase separation.⁵ A large body of experimental evidence^{4,6,7} has also been successfully explained using a model that assumes that a small number of polar polymer conformations are favored at low temperatures. As the temperature rises, a greater number of nonpolar molecular conformers become energetically preferred. The diminishing interaction between the nonpolar conformers and the solvent is thus the driving force for phase separation.

In a previous publication we reported scanning calorimetric data obtained for phase separations observed in aqueous

solutions of polyoxypropylene (POP).⁸ The enthalpic component associated with the separation of POP was, as expected, endothermic. One particular feature of the investigation was the specific way in which the data was analyzed. Despite the fact that clouding more or less coincides with the start of the calorimetric transition, the calorimetric data obtained appeared to be adequately described by a mass action aggregation model rather than a phase separation model. It was concluded that phase separation, as observed by scanning calorimetry, consists of the formation of small aggregates which then proceed to form a separate phase. Clearly such a proposal corresponds satisfactorily with the nucleation and growth explanation of phase separation⁹ in the metastable region of the phase diagram: the metastable region being that section of the phase diagram between the phase boundary and the spinodal, the point at which $(\partial^2 G_{\text{mix}}/\partial \phi^2)_{T,P} = 0$. The aggregation step was regarded as being the enthalpically active stage. Growth, on the other hand, was judged to be calorimetrically silent.⁸ The purpose of this paper is to report a continuation of this investigation using mixtures of POP oligomers in aqueous solution and to extend the analysis of the scanning calorimetric data further by model fitting the signals obtained for these aqueous systems.

Experimental Details

Four POP samples were used in this investigation of molecular mass 725, 1000, 2000, and 4000 g mol⁻¹. These were obtained from Aldrich Ltd., Dorset, U.K. and were used as received. P237 (notional molecular formula EO₆₁PO₃₉EO₆₁) of molecular mass 7700 g mol⁻¹ was obtained from ICI Chemicals, Cleveland, U.K. Single- and double-component polymer solutions were prepared at room temperature using doubly distilled deionized water. These solutions were then injected into the sample cell of a MC-2 differential scanning microcalorimeter (Microcal, Inc., Amherst, MA). Once in the

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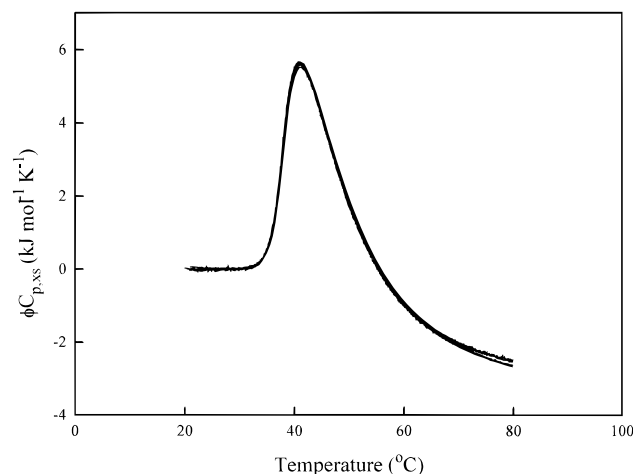


Figure 1. Superposition of data obtained for a POP 1000 solution (5 g dm⁻³) at five different scan rates ranging between 10 and 90 K hr⁻¹. Scan rates employed are (i) 12.6, (ii) 20.3, (iii) 44.7, (iv) 57.9, and (v) 83.4 K hr⁻¹.

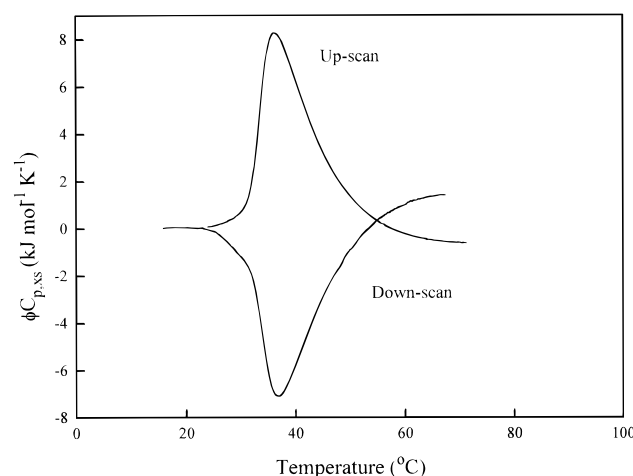


Figure 2. Upscan and downscan data obtained for a POP 1000 solution (10 g dm⁻³) at a scan rate of 30 K hr⁻¹.

calorimetric cells the samples were kept under nitrogen at a pressure of 1 atm to suppress bubble formation during scanning. The instrument is capable of scanning from -10 to 105 $^{\circ}$ C. The instrument is extremely sensitive, which means that low scan rates may be used. In this study all solutions were scanned at a rate of 1 K min⁻¹ with the exception of those scans reproduced in Figure 1 where the effects of scan rate were investigated and Figure 2 where the effect of up scanning and down scanning were investigated. For the former experiments, the POP 1000 solutions (5mM) were scanned at rates varying between 0.2 and 1.4 K min⁻¹. Within the limit of the instrumentation the signals showed no scan rate dependence. The lack of scan rate dependence of the signal demonstrates that the process is not subject to any kinetic limitation and may therefore be analyzed using equilibrium thermodynamic formulations.¹⁰ For the latter experiments the POP 1000 (5mM) solution was up scanned, kept for an hour at the high temperature, and then down scanned. No attempt was made to investigate the effect of prolonged or shorter periods of incubation at high temperature upon the down-scan signal.

Data Analysis. The underlying thermodynamic and mathematical treatment used in the analysis of the data has been outlined previously.^{8,21} The HSDSC output obtained for the polymer solutions comprises information on the way in which the power required to maintain temperature equality between

the sample and reference cells varies with temperature. Power is converted into apparent excess heat capacity, $\phi C_{p,xs}$, using the expression $P/(\sigma \times m)$ where P is power (J s⁻¹), σ is the scan rate (K s⁻¹) and m is the amount (expressed in g or mol) of polymer in the calorimeter. The calorimeter cell volume (for the instrument in our laboratory) is 1.1902 mL, thus for the single-component solutions m is easily determined. $\phi C_{p,xs}$ is given by the following expression

$$\phi C_{p,xs} = (\Delta H_{cal}(T_{1/2}) + \Delta C_p(T - T_{1/2})) \frac{d\alpha}{dT} + \alpha \Delta C_p \quad (1)$$

where $\Delta H_{cal}(T_{1/2})$ is the value for the calorimetric enthalpy (obtained from integration of the HSDSC peak) at $T_{1/2}$ (the temperature at which $\alpha = 0.5$), α is the extent of reaction, ΔC_p is the change in heat capacity, and T is temperature.

$d\alpha/dT$ is given by the expression

$$\frac{d\alpha}{dT} = \frac{\Delta H_{vH} + \beta \Delta C_p(T - T_{1/2})}{RT^2} \times \left(\frac{1}{\frac{1}{\alpha} + \frac{n}{1-\alpha}} \right) \quad (2)$$

where ΔH_{vH} is the van't Hoff enthalpy (and is obtained from the van't Hoff isochore); β is the ratio of the van't Hoff enthalpy to the calorimetric enthalpy and is introduced so that the ratio of the heat capacity changes is the same as the ratio of corresponding enthalpy changes. Values for α may be obtained by solving the following expression:

$$\ln(\alpha) + (n-1)\ln(1-\alpha) - n \ln(1-\alpha) = \frac{\Delta H_{vH}}{R} \left(\frac{1}{T_{1/2}} - \frac{1}{T} \right) + \frac{\beta \Delta C_p}{R} \left(\ln \left(\frac{T}{T_{1/2}} \right) + \frac{T_{1/2}}{T} - 1 \right) \quad (3)$$

Data analysis of the signals comprised the following sequence of steps. The pretransition portion of each scan was identified and set equal to zero using the DA2 software supplied with the instrument. This has the effect of making the heat capacity of the system prior to phase transition equal to zero. The rest of the scan is correspondingly modified, and as a consequence, the heat capacity of the post transitional system is also altered. The heat capacity change ΔC_p , however, is not changed. The modified scans for the single component systems were then fitted to the above model using the model fitting package Scientist (MicroMath, Salt Lake City, Utah). Scientist uses a powerful minimization algorithm to obtain best fit parameters which adequately fit the data to the model. Additionally the software uses a robust root finder to determine values for α using eq 3.

To deconvolute the HSDSC output obtained for the aqueous mixtures, it was assumed that the apparent excess heat capacities of the aqueous mixtures resulted from a linear combination of the apparent excess heat capacities of the separate components and that the heat capacity changes ΔC_p for each transition could be obtained using the formula

$$\Delta C_{p_i} = \frac{\Delta H_{cal_i}}{\sum_j \Delta H_{cal_j}} \Delta C_{p_{overall}} \quad (4)$$

where $\Delta C_{p_{overall}}$ is the overall heat capacity change for the system.¹¹

Uncertainties exist in both the experimental data and the parameters obtained in the model fitting exercise. Typically the expected experimental uncertainties lie between ± 3 and 5% for ΔH_{cal} , ± 8 to 10% for ΔH_{vH} , and $\pm 1\%$ for $T_{1/2}$. Typically

uncertainties in the fitted parameters are as follows: ± 1 to 4% for ΔH_{cal} and ΔH_{vH} ; ± 2 to 3% for ΔC_p ; $\pm 0.2\%$ for $T_{1/2}$ and between ± 5 and 10% for n .

Finally, the number of parameters obtained in the model fitting exercise is large. Scientist provides information on cross correlation between the parameters. In general ΔH_{vH} and n were correlated with each other as were ΔH_{cal} and $T_{1/2}$. For the first pair of parameters, this is very likely due to the relationship between the two parameters shown in eq 4 below. For the latter pair this presumably arises from the temperature dependence of ΔH_{cal} . $\Delta H_{\text{cal},1}$ and $\Delta H_{\text{cal},2}$, the calorimetric enthalpies of the two deconvoluted peaks, are unsurprisingly negatively correlated with each other. It would be expected that as one is increased in size the other decreases in order for the total integral area to remain constant. Such correlations clearly indicate that the model parameters are not necessarily unique though they do represent the best estimates based upon the minimization of the squares of the residuals.

Results and Discussion

The temperature dependence of the stability of the single phase POP solutions has been attributed to the changing enthalpic and entropic contributions to the overall free energy of mixing of the systems.^{2,4,7} It is clear that the enthalpy of mixing is invariably exothermic and is related to the formation of an extensive hydrogen bonded structure in water, the result of hydrophobic hydration.¹² Such an extensive structure gives rise to a negative entropy. The balance between the enthalpic and entropic contributions to the excess partial molar free energy of mixing controls the stability of the system.² The phase boundary of a temperature–composition phase diagram presents the boundary between the single phase and two phase systems. The area between phase boundary and the spinodal is the metastable region. Within this region there is no spontaneous liquid–liquid phase separation.¹³ The region is stable to small concentration fluctuations. However, phase separation does occur where there are large concentration fluctuations¹³ normally referred to as nuclei.⁹ Phase separation proceeds by growth of these nuclei.^{9,13} This two-stage process is referred to as nucleation and growth. The latter stage is expected to be subject to some kinetic limitation since growth is a diffusive process.¹³ Phase separation is normally noted as the onset of clouding in the aqueous system and cloud points normally lie between the coexistence and spinodal decomposition curves for the system.¹⁴ Moreover it should be emphasized that the cloud point does not represent an equilibrium state.¹⁴

The data shown in Figure 1 were superimposed upon each other using the data analysis package Origin. Each scan was treated in the following way. The pretransitional portion of the scan was delineated by eye. A base line was then drawn, using the “Cursor Draw Baseline” option, through this portion of the signal and subsequently subtracted from the whole signal. The resultant signals, obtained at the various scan rates employed, are superimposable. The very slight divergence at the high temperature end of the signals may be a real effect though it is as likely to be due to the data treatment. Of course the data treatment steps may also have obfuscated a real divergence. Any divergences at the high-temperature end of the signals due to scan rate variations could be evidence of a kinetic limitations in this region. However, the superimposability of the main body of the signals provides strong evidence that the calorimetric signals show no scan rate dependence and thus indicates that the transitions are not subject to any kinetic limitation.^{10,15} The shape of the signals also point to a process that is not subject to kinetic constraint. Friere *et al.*¹⁵ have shown that the signals

obtained for kinetically constrained processes show a long leading edge at low temperatures and a sharp decrease at high temperatures. This results from the way in which the rate constant for the process increases as the temperature is raised, as expected from the Arrhenius relationship.¹⁵ Our signals show no such features. It would of course be reasonable to anticipate that if higher scan rates were employed then kinetic limitations may become apparent. However, for the time scales employed in this investigation it is concluded that the growth stage of the phase separation process, which should be kinetically controlled, is calorimetrically silent. It is surmised that the calorimetric signal therefore arises from nucleus formation. The model of Kjellander and Florin² suggests that phase separation in aqueous PEO systems requires, as a preliminary step, the overlap of the hydration spheres of adjacent PEO chains, with the attendant loss of water to the bulk. Since water in the hydration sphere is, according to the model, “structured” this loss must be endothermic. It is therefore suggested that the nucleation step comprises the aggregation of POP chains in those parts of the homogeneous phase where there is a sufficient concentration of chains to produce a stable nucleus. It is this aggregation step which provides the enthalpic activity underpinning the calorimetric signal.

Figure 2 demonstrates the similarity between the signals obtained from up scanning and down scanning. The two signals are in fact very nearly mirror images of each other giving rise to the suggestion that the down scan represents the separation and subsequent hydration of the POP chains, i.e., the reversal of the up-scan process. The down-scan signal does not require, for its explanation, any reference to the diffusive transport of chains moving apart from each other. Indeed it is difficult to see how such transport could have any enthalpic component. Thus, given that the down-scan represents the separation of aggregates to form near neighbors, we are forced to conclude that the upscan represents the aggregation of near neighbors. This has important repercussions for our understanding of the impact of polydispersity upon the thermal transitions. We have no information on the polydispersity of the POP samples used in this study though there is little doubt that the samples are polydisperse. It is further clear that the longer the chain length, the lower the temperature at which the transition begins.⁸ It is consequently anticipated that as the temperature of the system rises the longer chains, that is, the more hydrophobic chains, tend to drive the aggregation/phase separation process. However since there is no reason to suppose that mixing does not give rise to a completely random distribution of chains in solution, these chains will aggregate with near neighbors regardless of their size. Changes in polydispersity, however, may well affect the onset temperature of the thermal transition as has been noted for the EO–PO–EO block copolymers.¹⁶

It has in fact been suggested that the polydispersity of the system is the reason the phase transition observed by DSC is gradual and occurs over a relatively large temperature range.¹ This however loses sight of the fact that molecular size is also likely to be pivotal.⁵ Essentially the enthalpy change per molecule accompanying the desolvation of small molecules is smaller than that obtained for larger molecules. Since it is the enthalpy change that controls the temperature dependence of the equilibrium constant and thus the composition of the system, a small enthalpy results in a gradual change in composition with temperature. This can however be counterbalanced by a large van't Hoff enthalpy. A large value for the ratio, $\Delta H_{\text{vH}}/\Delta H_{\text{cal}}$ is indicative of a highly cooperative system.

Phase separation in polymer systems produces a solvent phase which contains a small amount of polymer and a polymer phase

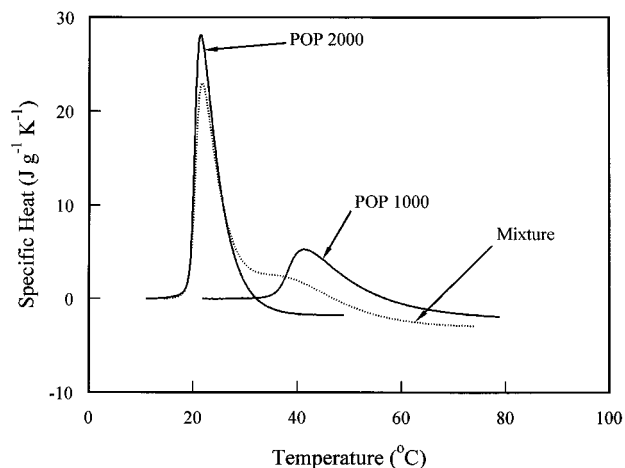


Figure 3. Superposition of data obtained for an aqueous mixture of POP 2000 and POP 1000 (—) and single component aqueous solutions of POP 1000 and POP 2000 (---).

which contains a large amount of solvent.¹⁷ If we focus upon the system at the temperature at which phase separation begins, it is apparent that at some temperature infinitesimally lower than the phase separation temperature the system comprises a single-phase system characterized by some particular heat capacity value. At some temperature infinitesimally larger than the phase separation temperature two phases coexist both having, it is presumed, altered heat capacities. The phase separation event should therefore be characterized by a discontinuity in the heat capacity of the system.⁸ Schild and Tirrell⁵ in their microcalorimetric investigation of phase separation behavior in a variety of aqueous polymer solutions have produced a number of scans in which the leading edge of the calorimetric signal is very sharp if not very nearly perpendicular to the temperature axis. However such data is only obtained for high molecular weight polymers. Their scan for an oligomeric POP sample is much the same as those reported in this study.

The combination of eqs 2 and 9 along with the condition that $\phi C_{p,xs} = C_{p,1/2}$ when $T = T_{1/2}$ provides the following equation for ΔH_{vH} :

$$\Delta H_{vH} = \frac{2(n+1)C_{p,1/2}RT_{1/2}^2}{\Delta H_{cal}} + 0.5\Delta C_p \quad (4)$$

It is readily apparent that a large aggregation number n , will provide a large ΔH_{vH} value. Indeed it is easily demonstrated that a large n value (≥ 50) will yield a very nearly discontinuous signal. This is not that surprising; it has been pointed out that systems composed of such large aggregation numbers approach phase separation behavior.^{18,19} On the other hand, it is possible that a large value for ΔH_{vH} may be produced by some other form of intermolecular cooperativity. For instance, some form of preaggregation association may create cooperative units for which the aggregation enthalpy change is large. It therefore seems probable that the molecular mass of POP determines the calorimetric enthalpy while a combination of aggregation number value and the extent of preaggregation association affects the van't Hoff enthalpy and polydispersity affects the onset temperature.

Examples and a comparison of HSDSC output obtained for single-component aqueous solutions of POP 1000 and POP 2000 and an aqueous mixture of the two are shown in Figure 3. The most striking feature of the diagram is the observation that the signal for the lower temperature transition (POP 2000) occurs, apparently, independently of the other component (POP 1000).

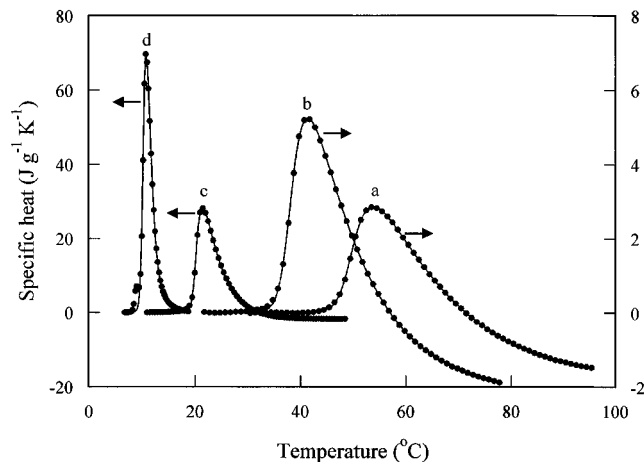


Figure 4. Model fitting results obtained for (a) POP 725, (b) POP 1000, (c) POP 2000, and (d) POP 4000. The diagrams show the best fit line (—) and the obtained data (●).

Indeed the transition for POP 2000 in a single-component aqueous solution and in the aqueous mixture are barely distinguishable and suggests that the phase transition for POP 2000 is unaffected by the presence of POP 1000. The sharp leading edge of the POP 2000 transition clearly points to an aggregation process.¹⁰ In Figure 3 the POP 1000 transition is clearly distinguishable from the POP 2000 transition but appears to be affected in terms of size and shape and suggests that the details of phase separation are altered in some way. Schild and Tirrell⁵ have produced similar looking output for a poly(*N*-isopropylacrylamide) sample which has a bimodal molecular mass distribution.

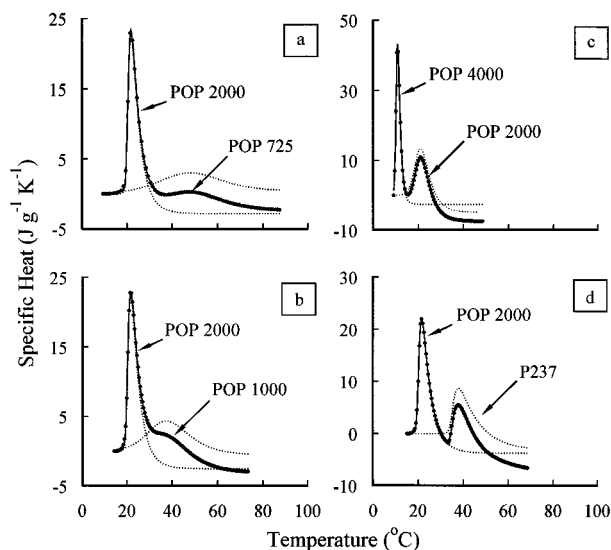
Figure 4 provides a visual indication of the excellent fits obtained for the single polymer component solutions using the model fitting software. The coefficient of determination, a measure of the amount of variance about the mean explained by the model, for all the HSDSC scans was greater than 99.9%. Additionally the model selection criterion determined by the software, a measure of the amount of information contained by the model, was high in all cases. It has been noted that the breadth of the transition is dependent upon the molecular mass of the polymer.⁵ This is confirmed by the output shown in Figure 4.

The model parameters for the single-component solutions show interesting variations with molecular mass. It is clear that both ΔH_{cal} and ΔH_{vH} increase with increasing molecular mass. This presumably is related to the increasing quantities of water that the larger molecules interact with. $T_{1/2}$ decreases with molecular size and is presumably an indication of increasing hydrophobicity. n , too, decreases with molecular size. Finally, ΔC_p appears to become increasingly negative as the molecular mass increases though this trend is not observed for POP 4000. The signal for this polymer shows the presence of a small peak ahead of the large transition. This may indicate the presence of an impurity and thus possibly explains the apparently anomalous value for ΔC_p .

The success of model fitting exercise requires some comment, since its success has a number of implications. The model is capable of fitting the data over the entire temperature range implying that over this range the initial molecular assemblies are in thermodynamic equilibrium with the final molecular aggregates. The model implies that increasing the temperature merely results in an increase in the number of aggregates rather than their size—the model assumes that the aggregation number is constant. Clearly these aggregates must change size since their growth is a necessary mechanistic aspect of phase

TABLE 1: Thermodynamic Data Obtained for Various Aqueous Solutions of Single- and Two-Component Mixtures of Poly(oxypropylene) Oligomers^a

	P237	POP 725	POP 1000	POP 2000	POP 4000
ΔH_{cal} (kJ mol ⁻¹)	254	49.3	108	334	584
ΔH_{vH} (kJ mol ⁻¹)	795	307	556	1949	2670
n	7.8	19.1	13.3	9.3	3.6
$T_{1/2}$ (K)	319.9	353.5	326.0	296.4	284.3
ΔC_{p} (kJ mol ⁻¹ K ⁻¹)	-10.2	-12.1	-15.5	-21.9	15.9
	POP 2000-POP 725	POP 2000-POP 1000	POP 2000-POP 4000	POP 2000-P 237	
		POP 2000			
ΔH_{cal} (kJ mol ⁻¹)	292	300	272	302	
ΔH_{vH} (kJ mol ⁻¹)	1536	1721	427	1588	
n	7.7	9.6	2.0	9.1	
$T_{1/2}$ (K)	296.9	297.0	296.0	296.9	
ΔC_{p} (kJ mol ⁻¹ K ⁻¹)	-29.6	-39.7	-15.3	-39.8	
		Other Component			
ΔH_{cal} (kJ mol ⁻¹)	74	132	428	1078	
ΔH_{vH} (kJ mol ⁻¹)	95	159	2188	912	
n	1.0	1.8	3.4	15.4	
$T_{1/2}$ (K)	320.4	315.2	284.3	318.8	
ΔC_{p} (kJ mol ⁻¹ K ⁻¹)	0.4	-1.3	-52.6	-23.6	

^a All concentrations in 5 g dm⁻³.**Figure 5.** Deconvolution results obtained for aqueous mixtures of (a) POP 725 and POP 2000, (b) POP 1000 and POP 2000, (c) POP 4000 and POP 2000, and (d) P 237 and POP 2000. The diagrams show the best fit line (—), the deconvoluted peaks (---) and the obtained data (●).

separation. However given that growth is a diffusive, kinetically controlled process and that the signals show no kinetic limitation, it is concluded that growth is calorimetrically silent.

Figure 5a–d show the results obtained for four deconvoluted HSDSC scans. All the scans were obtained for mixtures in which one component was POP 2000. The figures indicate the excellence of the fits which is likewise attested to by the goodness-of-fit statistics. Figure 5a,b show the results obtained when the other component is POP 725 and POP 1000, respectively. When viewed in combination with data in Table 1, a number of aspects relating to the data become apparent. In the first instance it appears that the peak assigned to POP 2000 is largely unaltered by the presence of the other component. There appear to be slight changes in the model derived parameters. For instance, values obtained for ΔH_{vH} and ΔH_{cal} appear slightly low, while the ΔC_p values appear slightly higher compared to the values obtained for the POP 2000 solution. Values for n and $T_{1/2}$ seem unaltered. On the other hand, there are clear changes in the POP 725 and POP 1000 peaks. The

transitions do not appear to involve aggregation. Indeed the visual and tabulated evidence suggests that these molecules are slowly desolvated—desolvation occurring at about the same point as the POP 2000 undergoes aggregation—and join the separated POP 2000 phase. The n values of 1 for POP 725 and 1.8 for POP 1000 certainly do not indicate the formation of large aggregates. The ratio $\Delta H_{\text{vH}}/\Delta H_{\text{cal}}$ is of interest since it provides an indication of the size of the molecular unit that participates in the thermal transition. If the ratio is greater than 1, it implies aggregation involving multimolecular cooperative units rather than single molecules. If the single-component solutions are examined, it is apparent that the molecular unit partaking in the transition has the following values: P237 (3.1), POP 725 (6.2), POP 1000 (5.1), POP 2000 (5.8), and POP 4000 (4.6). In those two-polymer component solutions where the two transitions are visually distinct, the lower temperature peak retains this degree of cooperativity. However, the higher temperature peak has, in all cases, a cooperativity of about 1, implying that the higher temperature transition simply involves single molecules. We are thus brought to the conclusion, which appears reasonable, that the POP 2000 molecules will undergo the thermal transition and form the separate concentrated polymer phase. As the temperature is raised still further, the second-polymer component will now begin to separate from aqueous solution and, since there is no substantial chemical difference between the POP molecules, the second component joins the separate concentrated polymer phase.

Figure 5c,d comprise the results obtained for mixtures of POP 2000 with POP 4000 and P237, respectively. In Figure 5c POP 2000 is identified as the higher temperature transition and as before this transition is altered. The transition for POP 4000 on the other hand is only slightly altered. Finally Figure 5d displays the results obtained for POP 2000 and P237. This is interesting in that both transitions appear to be quite independent of each other. P237 is identified as the higher temperature transition and is clearly an aggregation transition with a large n value. Interestingly, for the single-polymer component P237 solution, the transition involves the aggregation of multimolecular cooperative units. However, in the two polymer component solution the transition involves the aggregation of single molecules.

The HSDSC outputs obtained for the mixtures P237/POP1000 and POP725/POP1000 exhibit only one peak. These peaks have

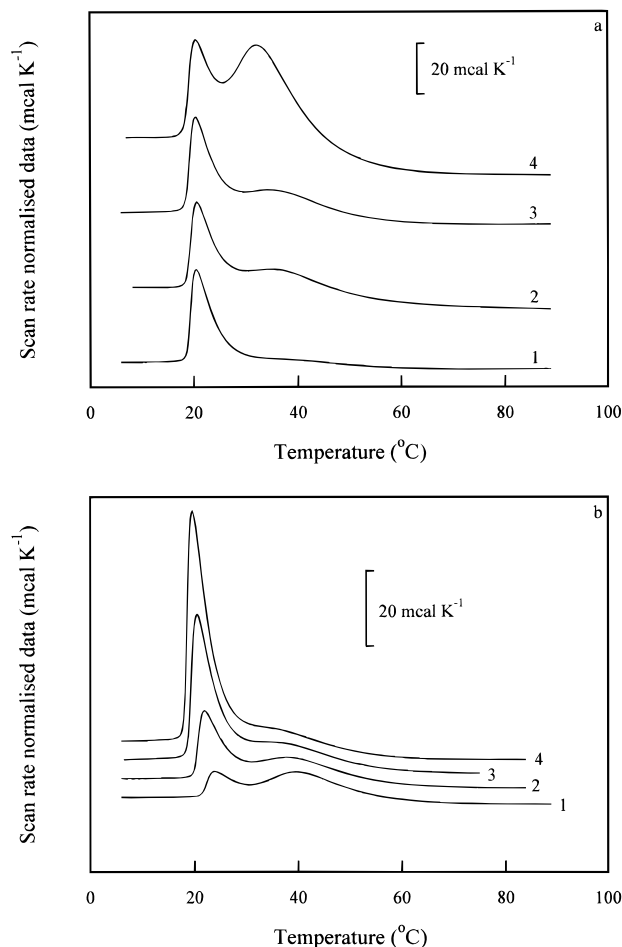


Figure 6. Data obtained for various mixtures POP 1000 and POP 2000 in aqueous solution. In (a) the concentration of POP 2000 is constant (5 g dm^{-3}) while the concentration of POP 1000 is changed giving aqueous solutions of various POP 1000/POP 2000 molar ratios (1) 1:1, (2) 2:1, (3) 3:1, and (4) 7.9:1. In diagram (b) the concentration of POP 1000 is constant (5 g dm^{-3}) and the concentration of POP 2000 is varied to give the following POP 1000/POP 2000 molar ratios (1) 10:1, (2) 4:1, (3) 2:1, and (4) 1.3:1.

been fitted to the aggregation model. The data of interest are, however, the $T_{1/2}$ and ΔH_{cal} values. For the aqueous mixture of P237/P1000, $T_{1/2}$ is 324.1 K and ΔH_{cal} is 154 J g^{-1} . For POP1000/POP725, $T_{1/2}$ is 330.1 K and ΔH_{cal} is 226 J g^{-1} .

Using the Kirchoff equation the ΔH_{cal} values obtained for the single-component solutions have been corrected to the $T_{1/2}$ values of the two-component solutions. If these adjusted values are then added, we obtain a ΔH_{cal} value of 145 J g^{-1} for the P237/POP1000 aqueous mixture and 226 J g^{-1} for the POP725/POP1000 aqueous mixture. Both values are very close to data obtained by model fitting and suggest that, despite the fact that the transitions overlap, the desolvation/aggregation behavior of the separate components is unaltered. This observation is actually unsurprising since it is understood that the major part of the enthalpic content of the transition involves the desolvation of the poly(propylene oxide) oligomers or blocks. In fact, if the enthalpies per repeat unit for P237, POP725, POP1000, and POP2000 are calculated and corrected to 298.15, we obtain an average value of $10.4 \pm 1.8 \text{ kJ (mol of repeat unit)}^{-1}$. This is about half the quoted value of 20 kJ mol^{-1} for a hydrogen bond.²⁰

A further series of experiments were performed using POP1000/POP2000 mixtures of varying composition. The calorimetric traces obtained for these mixtures are shown in Figure 6. The data shown in Figure 6a were obtained for a

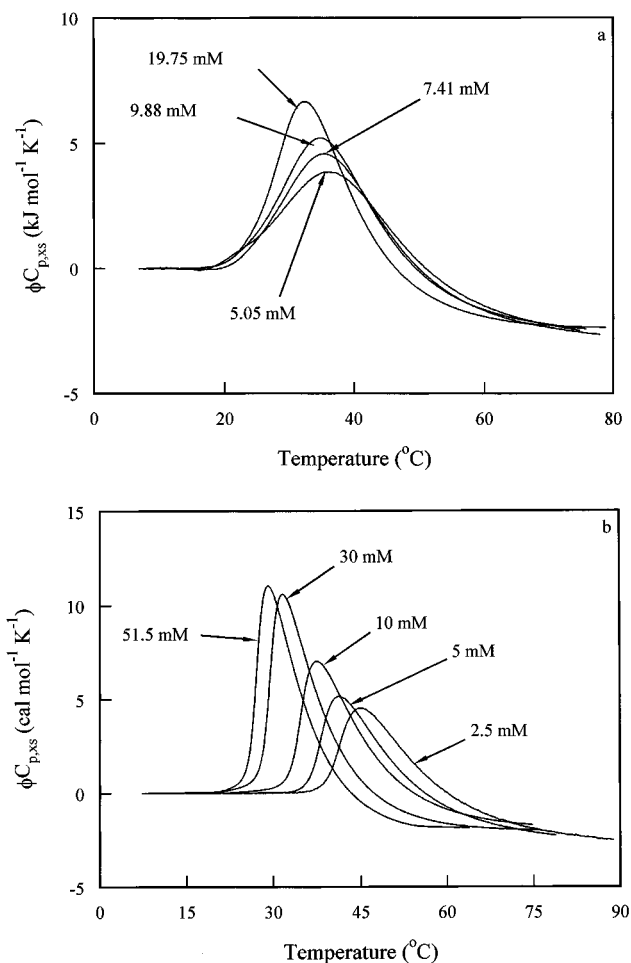


Figure 7. Comparison of scanning calorimetric data obtained for (a) POP 1000 solutions containing a fixed concentration of POP 2000 (5 g dm^{-3}) and (b) single-component POP 1000 solutions. Concentrations of POP 1000 are indicated on the plots. N.B. the signal for POP 2000 has been subtracted from the composite signals shown in diagram a.

range of aqueous mixtures in which the concentration of POP2000 remained constant and the concentration of POP1000 changed. A consideration of Figure 6a readily reveals that the signal for POP2000 is virtually unaffected by the varying concentration of POP1000. Indeed it is possible to subtract the data obtained for a single-polymer solution of POP2000, of the same concentration as the POP2000 in the mixtures, from the mixtures data. Very little residual signal is left. The resultant data, demonstrating how POP1000 is affected, are shown in Figure 7a. For comparison, data obtained for POP 1000 over a similar concentration range are shown in Figure 7b. These data have been previously reported.¹⁰ It is interesting to note that the POP1000 traces have altered. Essentially for the single-polymer solutions (Figure 7b), the calorimetric traces are characterized by a steep leading edge which is indicative of aggregation. The data in Figure 7a, on the other hand, are far more symmetrical indicating that the traces are far less representative of aggregation. The data in Figure 6b in which the concentration of POP1000 remains constant and the concentration of POP 2000 changes reveal a pattern of behavior in which the POP1000 signal becomes less independent as the POP2000 concentration rises.

All the data in Figure 6 have been deconvoluted and the model fitting data is reported in Table 2. It is useful to note that the model derived aggregation numbers do not alter overmuch and certainly not in a systematic way for POP2000. This would indicate that the transition is largely unaffected by

TABLE 2: Thermodynamic Data Obtained for Various Aqueous Mixtures of POP 1000 and POP 2000 of Varying Concentration

POP 2000					
concentration (g dm ⁻³)	1.01	2.525	5.05	7.5	10.1
ΔH_{cal} (kJ mol ⁻¹)	371	317	295	305	303
ΔH_{vH} (kJ mol ⁻¹)	1587	2144	2250	2848	2402
<i>n</i>	10.3	11.7	10.5	13.7	10.7
<i>T</i> _{1/2} (K)	299.6	297.1	295.4	294.5	293.8
ΔC_p (kJ mol ⁻¹ K ⁻¹)	-16.1	-21.9	-22.2	-30.5	-25.8
POP 1000					
concentration (g dm ⁻³)	5.05	5.05	5.05	5.05	5.05
ΔH_{cal} (kJ mol ⁻¹)	103	105	114	106	114
ΔH_{vH} (kJ mol ⁻¹)	256	190	128	133	121
<i>n</i>	2.5	1.8	1.0	1.0	1.0
<i>T</i> _{1/2} (K)	317.2	315.6	312.5	311.7	310.2
ΔC_p (kJ mol ⁻¹ K ⁻¹)	-2.6	-1.9	-1.3	-1.4	-1.3
POP 2000					
concentration (g dm ⁻³)	5	5	5	5	5
ΔH_{cal} (kJ mol ⁻¹)	289	293	327	372	372
ΔH_{vH} (kJ mol ⁻¹)	2393	2077	1627	1705	1705
<i>n</i>	11.4	9.6	8.1	10.0	10.0
<i>T</i> _{1/2} (K)	295.5	295.3	295.5	295.9	295.9
ΔC_p (kJ mol ⁻¹ K ⁻¹)	-24.5	-22.6	-24.2	-27.4	-27.4
POP 1000					
concentration (g dm ⁻³)	2.47	7.41	9.88	19.75	19.75
ΔH_{cal} (kJ mol ⁻¹)	116	121	129	125	125
ΔH_{vH} (kJ mol ⁻¹)	107	155	203	309	309
<i>n</i>	0.8	1.3	2.1	3.1	3.1
<i>T</i> _{1/2} (K)	313.2	311.8	312.6	310.0	310.0
ΔC_p (kJ mol ⁻¹ K ⁻¹)	-1.1	-1.7	-3.0	-5.0	-5.0

the presence of a polymer component that phase separates at a higher temperature. On the other hand, these numbers do seem to change in a consistent fashion. Essentially as the POP2000/POP1000 mole ratio increases the model derived aggregation numbers decrease, eventually approaching a value of about 1. This suggest the following hypothesis regarding the aqueous mixtures. When the POP2000/POP1000 mole ratio is high and the aqueous mixtures are randomly mixed, the number of POP2000 molecules forming near neighbors is large; however, it is likely that most of the POP1000 molecules are isolated and are more likely to be surrounded by POP2000 molecules. In these solutions as the temperature is raised the POP2000 molecules begin to nucleate, while the POP1000 molecules remain in solution. When the temperature is sufficiently high, these, too, begin to separate from the aqueous phase. However, it is likely that because of their isolation they will transfer to the separated POP2000 phase. However, as the POP2000/POP1000 mole ratio decreases the extent of the isolation of the POP1000 molecules also decreases. Thus when the temperature is high enough the POP1000 molecules begin to undergo phase separation. However, because other POP1000 molecules are more likely to be near neighbors the transitions for POP1000 increasingly take on an aggregative nature.

Conclusions

The enthalpic content of the phase separation of aqueous solutions of poly(oxypropylene) oligomers and aqueous mixtures

of these materials have been investigated. The calorimetric data has been satisfactorily fitted to an aggregation mass action model. It is suggested that this aggregation process is the nucleation event that characterizes phase separation in the region between the coexistence boundary and the spinodal boundary. It is concluded that the growth stage of phase separation, which is a kinetically limited process, is not seen by calorimetry because the calorimetric signals show no scan rate dependence. The signals obtained for the aqueous oligomeric mixtures have been successfully deconvoluted and suggest that the component of the mixture which phase separates first is unaffected by the presence of the second component. The phase separation parameters of the second component are, however, affected: the degree to which it is affected being determined by the mole ratio of the constituent polymers.

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