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## Thermodynamics of formation of high impact polystyrene

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The manufacture of high impact polystyrene by the polymerization of an initially binary solution of polybutadiene in styrene, has been extensively described in the literature in terms of general concepts of nucleation and phase inversion<sup>1</sup>. This note seeks to describe the process in terms of the nucleation of an equilibrium phase and spinodal decomposition occurring under isothermal conditions in a ternary system.

The dynamic system can be represented by a vector crossing the ternary polystyrene, polybutadiene, styrene phase diagram. This vector successively intersects the binodal curve which defines the miscibility gap and the spinodal curve which defines the limit of diffusional stability in the system. On a weight fraction basis this vector will be straight line.

The total Gibbs free energy of mixing of the components passes through a turning point with respect to composition at the binodal<sup>2</sup>. The coupled partial molal Gibbs free energies of mixing pass through a turning point with respect to composition at the spinodal. These two conditions coincide at the plait point which has the status of a multicomponent critical point<sup>3</sup>.

A particular initial concentration,  $C_p$ , of polybutadiene will correspond to a vector which passes through the plait point. Initial concentrations of polybutadiene lower than  $C_p$  will give rise to vectors which intersect the miscibility gap on the polystyrene rich side of the plait point. This causes the polybutadiene rich phase at the opposite end of the tie line to nucleate<sup>4</sup>. Initial concentrations of polybutadiene higher than  $C_p$  will conversely result in the nucleation of a disperse polystyrene rich phase.

The miscibility gap is a section of a surface in composition-temperature space. If the miscibility gap shrinks with increasing temperature the value of  $C_p$  will increase. This means that it will be possible for a single initial concentration to give rise to disperse polystyrene at a low temperature of polymerization and disperse polybutadiene at a higher temperature. Such an effect has been observed by Moore<sup>5</sup>, and indicates that the miscibility gap slowly converges towards an upper consolute point. This shows that the system has a small positive value for both the enthalpy and entropy of mixing. This is in marked contrast to the behaviour of the polystyrene-poly(methyl methacrylate)-benzene system<sup>6</sup> which shows evidence of having fairly high negative values for the enthalpy and entropy of mixing. Polyacrylate rubbers have never found favour as reinforcing agents for polystyrene and this may be the reason.

As the polystyrene rich phase undergoes growth it rejects a shell of polybutadiene. The initial solution process and the dissolution of initiator involves the formation of high molecular weight polystyrene, which facilitates the nucleation process.

The reaction proceeds, increasing the polystyrene concentration and bringing the composition of the metastable ternary mixture up to the spinodal. A corollary of the concentration independence of the partial molal Gibbs free energy of mixing is that the surface excess Gibbs free energy with respect to liquid-liquid separation becomes zero. This results in the polymers present undergoing a severe expansive conformational transition. This is the cause of the viscosity peak known as phase inversion<sup>7</sup>.

Once within the spinodal the sys-

tem encounters a condition where the coupled partial molal Gibbs free energies of mixing assume an inverse dependence on concentration. The mixing volume shows a large excess value, causing anomalous dilatometric measurements of the reaction rate to be obtained<sup>8</sup>. The spinodal condition occurs in a miscibility gap tending to show an upper consolute point and the system rapidly undergoes spinodal decomposition<sup>4</sup>. This tends to give two continuous interdigitated networks. The necessity to continue stirring despite the viscosity increase may be due to the need to disrupt a continuous polybutadiene matrix.

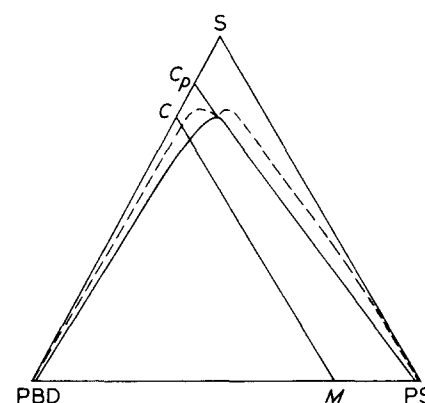


Figure 1 Schematic diagram of the styrene (S), polystyrene (PS), polybutadiene (PBD) system based on the data of Welygan and Burns (ref 2).  $C_p$ , the binary composition corresponding to an intersection of the reaction vector and the critical point.  $CM$ , a reaction vector corresponding to the normal manufacturing process

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## Mechanism of formation of asymmetric membranes used in reverse osmosis

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The distinction between segregation of compositions due to spinodal decomposition and separation of phases due to nucleation and growth has been drawn by Smolders *et al.*<sup>1</sup>. The mechanism of formation of the asymmetric membrane used in reverse osmosis has been considered by Strathmann and Scheible<sup>2</sup> in terms only of nucleation and growth. This Note seeks to describe the membrane formation in terms of both mechanisms.

The membrane consists of cellulose diacetate arranged in a continuous thin top layer 0.2  $\mu\text{m}$  thick which gives way to a porous supporting layer 2 mm thick. The preparation starts with a 25% homogeneous solution in an acetone/formamide mixture. This viscous syrup is spread evenly on a glass plate and evaporation is allowed to proceed for some minutes. It is then plunged into ice water for some hours. The membrane may then be peeled from the glass and is finally warmed to approximately 100°C for some minutes. The temperature and duration of this final step is vital in controlling the characteristics of the membrane.

Strathmann and Scheible have made the valuable contribution of providing a phase diagram showing the miscibility gap in the quaternary system, polydisperse cellulose diacetate, acetone, formamide, water, in the plane acetone:formamide equals 3:1. It is clear that this miscibility gap will shrink with decreasing temperature, i.e. it is subtended by a lower consolute point due to the predominant specific interaction in the system<sup>3</sup>.

It is also clear that the initial evaporation step is responsible for the generation of the thin top layer. During this

step the polymer content of the surface film will rise to about 50%. This yields a high viscosity gel in which nucleation is inhibited. Rapid diffusion of water into the gel gives rise to the process which has become known as spinodal decomposition. This mechanism was first proposed by Smolders *et al.*<sup>1</sup>.

At the plait point and along the spinodal curve, the chemical potentials of the species present become independent of concentration. The chemical potential *versus* concentration relationships are similar to the *pV* isotherms given by the Van der Waals equation of state. The components of homogeneous mixtures lying within the spinodal region undergo a condition in which their chemical potentials assume an inverse dependence on concentration. Two important corollaries of this inverse behaviour are that the surface excess free energy will be negative and polymers present under these conditions will have consequently undergone a severe expansive conformational transition not related to that treated by Edwards<sup>4</sup>.

The use of ice water lowers the temperature further, increasing the viscosity and the predominance of the specific interaction. The concentration fluctuations which are the subject of the standard treatment of spinodal decomposition are damped by the specific interaction. The segregation of the system into polymer rich and water rich regions is arrested at a very early stage. The conformational transition is acting on the cellulose diacetate molecule which is inherently fairly stiff and the process provides a continuous assembly of rod-like molecules, randomly oriented. This hydrogen bonded polymer matrix is inherently amor-

phous with a high free volume. It survives the loss of acetone/formamide and is only altered on heating.

Water percolates slowly through the thin top layer entering the more dilute cellulose acetate solution below. To some extent the system may undergo counter diffusion of water and acetone/formamide. The changing composition can be represented by a vector crossing the single phase region to intersect the miscibility gap on the polymer rich side of the plait point. This results in the nucleation of the water rich phase at the opposite end of the tie line, initially giving a water rich disperse phase.

As water progressively diffuses into the lower layer, phase growth occurs in the direction of most rapidly increasing water supersaturation. This yields a porous textured system with the pores directed to the back surface of the membrane. The glass plate forms a boundary in the counter diffusion system and the separation becomes coarser in proximity to it.

The primary effect of heating the system is the decomposition of the metastable non-equilibrium arrangement of the thin top layer. The free volume decreases as conformational relaxation occurs. This progressively limits the flow of water and hydrated sodium and chloride ions through the top layer. The flow of the ions decreases more rapidly than that of water until their passage is virtually completely barred. This will be accompanied by a decrease in the thickness of the thin top layer.

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