Freezing and glass transition phenomena in polymer–diluent mixtures

Michael A. Masse, Erdoğan Kiran and Arthur L. Fricke*
Department of Chemical Engineering, University of Maine at Orono, Orono, ME 04469, USA

(Received 24 June 1985)

The freezing and glass transition phenomena in a binary system of polystyrene–benzene and in a multicomponent system (known as kraft black liquor) containing ionic species and polymeric lignin derivatives have been examined using differential scanning calorimetry. The experimental observations indicate that in these binary and multicomponent systems there exist a particular concentration (~50%) at which the phenomenon occurring changes from freezing to glass transition. Using the existing theories of freezing and glass transition, the significance of this particular concentration where the change-over occurs and its dependence on the polymer–solvent interaction parameter and other characteristics of the components have been examined. Depending on the particular values used the change-over concentration for the polystyrene–benzene system has been predicted to be in the concentration range of 50–70% polymer, which is in accord with experimental observations. Comparisons of the freezing behaviour of the kraft black liquor with that of other aqueous solutions indicate that the overall effect on the freezing point results from the combined influence of the polymeric and ionic constituents of the solute.

(Keywords: polymer–diluent systems; freezing; glass transition; polystyrene–benzene; kraft black liquor; differential scanning calorimetry; interaction parameter)

INTRODUCTION

This paper is concerned with the freezing and glass transition phenomena in polymer–diluent systems. Of particular interest is the concentration range where the change-over from one type of behaviour to the other occurs. The theories describing the phenomena of freezing and glass transition are well developed. It is well known that in solutions the presence of the solute results in a lowered freezing point of the diluent. In binary polymer solutions this effect may be accounted for using the Flory lattice theory[1]. Flory's development described the concentration dependence of the freezing point of a polymer solution through the relationship:

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}=-\frac{R}{\Delta H_1^f}[\ln\phi_1+(1-1/x)\phi_2+\chi_1\phi_2^2] \tag{1}$$

where ϕ_i is the volume fraction of component i, and x represents the number of lattice volume elements per polymer chain, commonly expressed as the ratio of polymer and solvent molar volumes. Subscripts 1 and 2 indicate the diluent and polymer, respectively. When the molecular weight of the polymeric solute is high, $1/x$ approaches 0 and as a result the relationship is simplified to:

$$\frac{1}{T_m}-\frac{1}{T_m^\circ}=-\frac{R}{\Delta H_1^f}[\ln\phi_1+\phi_2+\chi_1\phi_2^2] \tag{2}$$

Like the freezing point the glass transition temperature, T_g, of a mixture is also composition dependent. Couchman and Karasz[2] have described the effect of composition on T_g of binary mixtures using classical thermodynamics. The result of their development is expressed in the following relationship:

$$\ln\frac{T_g}{T_{g_1}}=\frac{x_2\Delta C_{p_2}\ln(T_{g_2}/T_{g_1})}{x_1\Delta C_{p_1}+x_2\Delta C_{p_2}} \tag{3}$$

where T_{g_i}, ΔC_{p_i} and x_i are the glass transition temperature, the heat capacity increment occurring at T_{g_i} and the mass fraction of component i. Using these equations the freezing and glass transition temperatures can be predicted theoretically. Further, if these relationships are extrapolated over the entire concentration range they would be expected to intersect at some intermediate concentration. Indeed, experimental data on compositionally simple binary solutions such as polystyrene–benzene, and complex multicomponent solutions such as kraft black liquor show the existence of such a change-over range.

Kraft black liquor is generated from the chemical pulping of wood. In the kraft pulping process wood is chemically delignified using alkaline, aqueous solution containing sodium hydroxide and sodium sulphide. The products of the delignification process are cellulose fibres in the form of wood pulp and a dilute liquid stream (black liquor) containing inorganic salts, extracted light organic compounds, carbohydrates and derivatives of polymeric lignin that are solubilized. Among the constituents, polymeric lignin fragments make up the single largest fraction[3]. Even though compositionally complex, the representation becomes simplified if black liquor is considered to be a pseudo-binary solution of a diluent (i.e., water) and a compositionally complex solute which is

---

* Present address: Department of Chemical Engineering, University of Florida, Gainsville, FL, USA.

0032-3861/86/040619-04$03.00

mainly polymeric in character[4]. The interest in the thermal characterization and properties of black liquor stems primarily from the fact that in the pulp and paper industry this liquor is concentrated and burned to reclaim the inorganic chemicals as well as energy from the combustion of the organic compounds. Black liquor is also the primary source of commercial lignins, which have the potential of being used as chemical feedstocks.

The existence of a particular concentration at which a polymer–diluent system displays a change-over from a diluent to a polymer dominated behaviour has industrial implications with respect to, for example, rheological behaviour of polymer solutions, and also with respect to the ease or limitations of solvent removal from solutions by freezing or other cryogenic procedures.

This paper discusses the experimental behaviour of polystyrene–benzene and kraft black liquor systems and the associated theoretical predictions.

EXPERIMENTAL

The benzene was of reagent grade quality and was used as received. The polystyrene was a molecular weight standard obtained from Arro Laboratories (Joliet, IL) with $M_n = 92\,600$ and $M_w = 93\,050$.

The black liquor sample (obtained from the kraft pulping of southern slash pine) was kindly provided by St. Regis Paper Co. Polymeric lignin fragments composed 34.3% of this black liquor on a dry basis. The number and weight average molecular weights of the lignin isolated from this liquor were $M_n = 2250$ and $M_w = 38\,000$, respectively[5]. The liquor was treated as a pseudo-binary mixture consisting of water (diluent) and the total solutes.

The freezing points and glass transition temperatures were measured using differential scanning calorimetry (Perkin–Elmer DSC-2). The samples were prepared by evaporation of a relatively dilute stock solution ($\sim 10\%$ solute). Concentrations were then measured gravimetrically. Large volume d.s.c. capsules were used. All samples, with the exception of pure polystyrene, were initially held at 350 K and then cooled through the transition region at a rate of $10\,\mathrm{K\,min^{-1}}$. The T_g of polystyrene was determined by heating from 350 K through the transition at $10\,\mathrm{K\,min^{-1}}$.

RESULTS

D.s.c. scans of polystyrene–benzene solutions of two different concentrations are shown in *Figure 1*. In the case of the dilute sample (15.0%), the observed phenomenon is freezing. The associated latent heat is evident as a peak in the d.s.c. scan. With the concentrated sample (57.5%) the observed phenomenon is that of glass transition, which reflects itself as a step change in the heat capacity. Using this ability of d.s.c. to differentiate the freezing and glass transition phenomena, the transition temperatures were measured at different solute concentrations. The results for the polystyrene–benzene system are shown in *Figure 2*, where the temperature of transition has been plotted as a function of polymer concentration. *Figure 3* shows a similar plot for the black liquor system. In both systems freezing of the diluent occurs up to a concentration of approximately 50% solute. The temperature at which the systems freeze decreases with increasing solute concentration. For systems concentrated to greater than

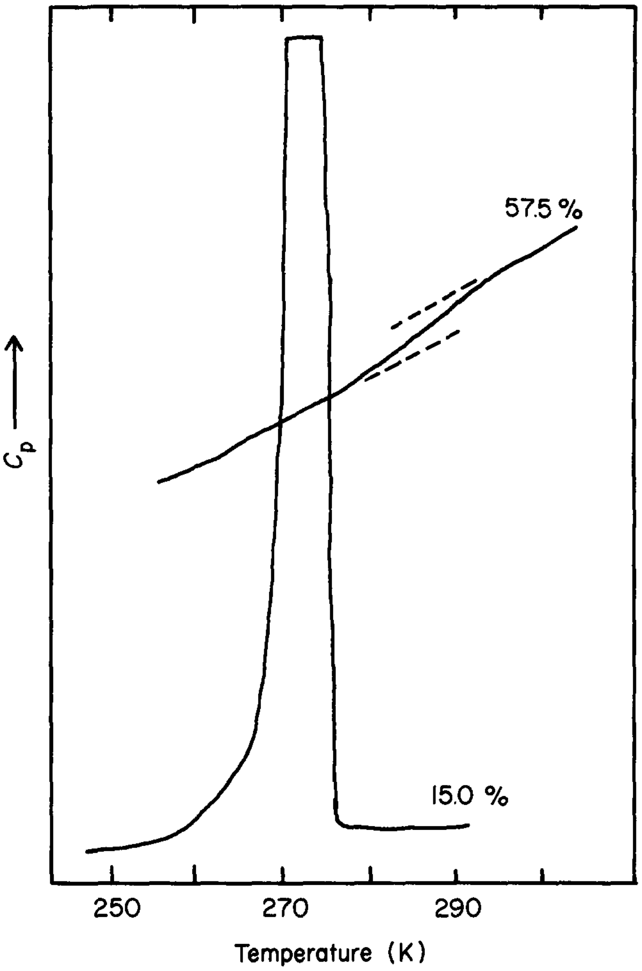

Figure 1 D.s.c. scans of polystyrene–benzene solutions. Numerals indicate the concentration

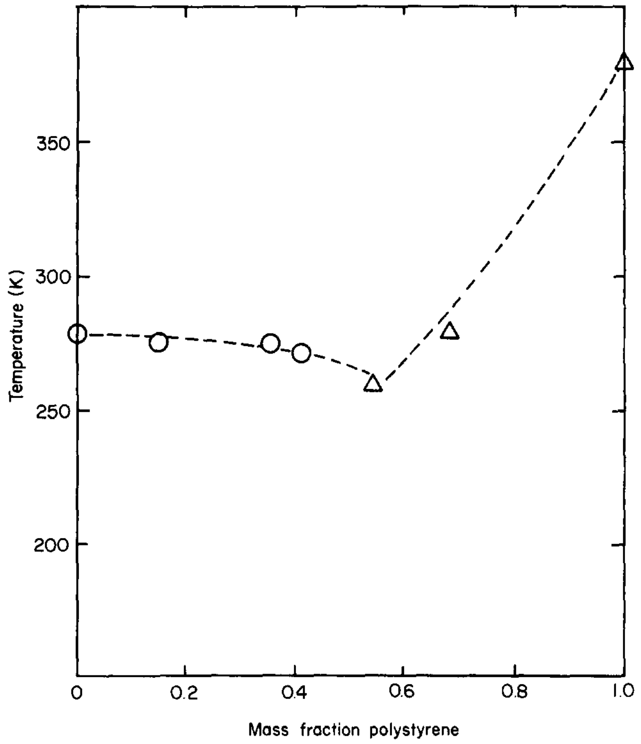

Figure 2 Freezing (○) and glass transition (△) temperatures of the polystyrene–benzene system

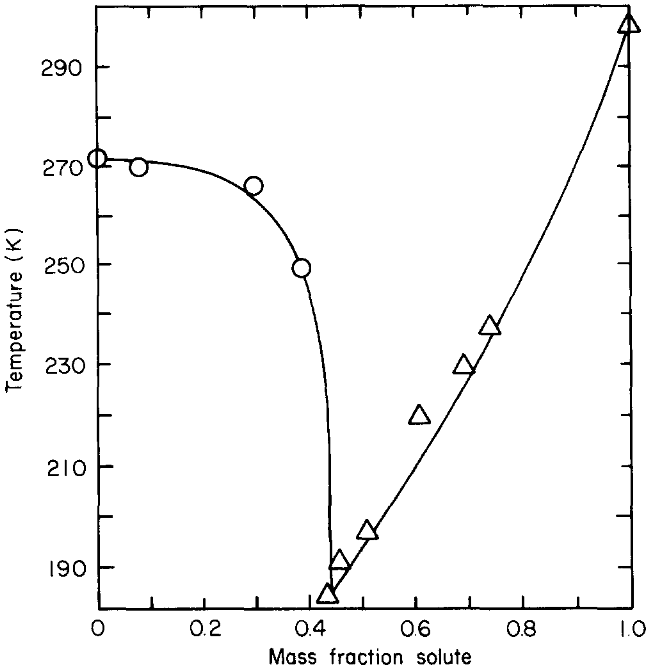

Figure 3 Freezing (○) and glass transition (△) temperatures of the kraft black liquor system

approximately 50%, the diluent does not undergo freezing but the entire mixture behaves as an amorphous polymeric solid displaying glass transition. The glass transition temperature increases with increasing solute concentration.

DISCUSSION

The general trends in freezing and glass transition behaviour exhibited by both systems are as expected from theory. A remarkable feature of *Figures 2* and *3* is the change-over from freezing to glass transition at a particular concentration. Another interesting aspect is the deviation from linearity in the freezing point depression curves, which appears to be dependent on the nature of the solvent–solute pair. The existing theory of freezing point depression in polymer solutions as given in equation (2) involves the Flory interaction parameter, χ, which incorporates the influence of the polymer–solvent interactions on the freezing point depression. However, no theoretical predictions of the particular concentration at which the change-over from freezing to glass transition phenomena occurs has been reported. In order to put the experimental data in a quantitative frame and thereby develop an understanding of this particular concentration, a number of simulations were conducted for the polystyrene–benzene system using equations (2) and (3) and literature and experimental values for the physical properties (see Appendix). Using the χ parameter as a variable, the shape of the freezing curve was studied. The results of these simulations are shown in *Figure 4*, in which the experimental data are also included for comparative purposes. Even though the commonly accepted values of the χ parameter for this system are ~0.45 (ref. 6), better agreement of the experimental data and the simulation are observed if χ is considerably lower. Such low values as suggested from this analysis are in accord with the results of a previous study by Kawai[7], which was also based on the freezing point depression in polystyrene–benzene systems. Closer examination of *Figure 4* reveals that the proper value of χ that results in agreement with experimental data varies with the polymer concentration. Simulations could in principle be improved, if not unified, by first establishing the functional dependence of χ on polymer concentration and then using this functional form in equation (2). Such analyses, however, were not conducted at this time. It must be pointed out that for a given polymer–diluent system χ is in general a function of both concentration and temperature[8] and any rigorous analysis must consider both of these factors.

The theoretical expression for the glass transition temperature (i.e., equation (3)) required the knowledge of the glass transition temperature for benzene, for which unambiguous values are not available. (An estimated value of 131 K has been obtained by binary solution extrapolation using a solution of benzene–ethyl benzene[9].) Therefore the nature of the T_g curve for the polystyrene–benzene system was studied using different values for the T_g of benzene. The results of these simulations are also shown in *Figure 4*. These simulations indicate a reasonable fit with the experimental data for a glass transition temperature of benzene in the temperature range 140–170 K. It should be further noted that in these simulations ΔC_p of benzene has been estimated as being equal to that of distyrene[10] since the value for benzene is unavailable.

The simulation curves for freezing point and the glass transition temperature intersect at a particular composition, thus predicting a change-over concentration, the value of which depends upon the values used for χ and T_{g_1}. As shown in *Figure 4*, the predicted change-over concentration is in the range of 50–70%. The experimentally observed change-over concentration for polystyrene–benzene appears to be in agreement with the lower end of this predicted range.

Similar simulations could not be conducted with the

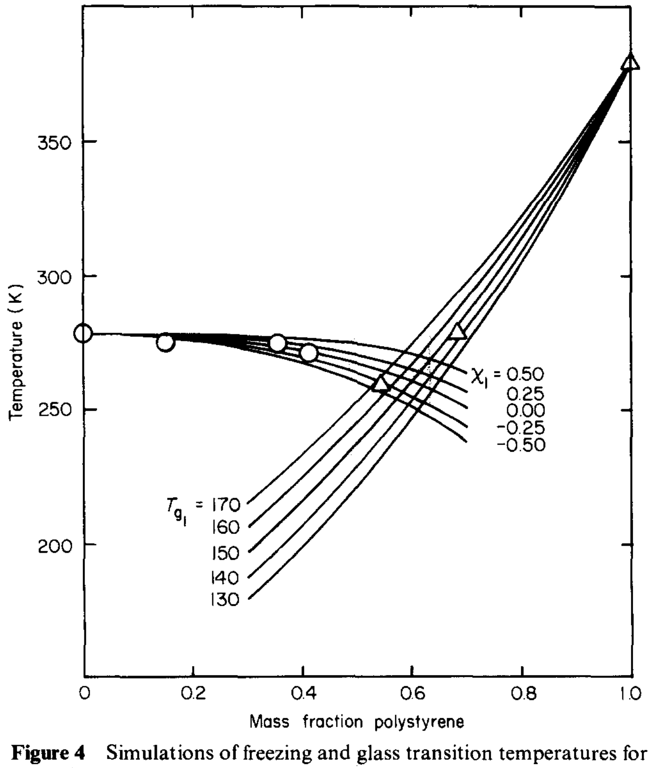

Figure 4 Simulations of freezing and glass transition temperatures for the polystyrene–benzene system

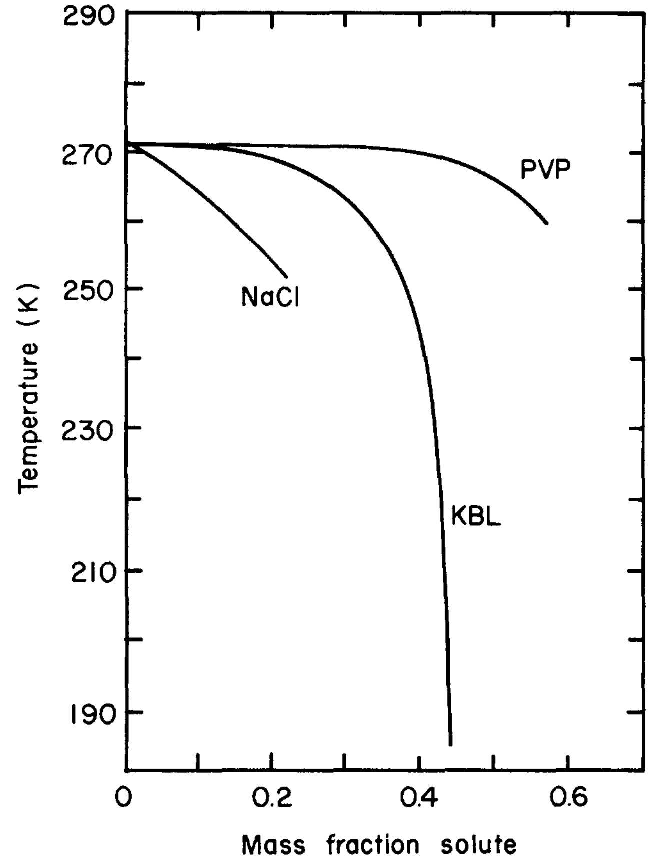

Figure 5 Freezing temperatures of kraft black liquor system (KBL), aqueous sodium chloride solutions (NaCl), and aqueous poly(vinyl pyrrolidone) solutions (PVP). The data for NaCl and PVP are from ref. 9

black liquor system due to lack of information on the physical properties of the black liquor solutes. The remarkable difference in the behaviour of the black liquor system as compared with the polystyrene–benzene system is in the sharp decrease in freezing point as the liquor solute concentration is increased. This sharp decrease is not predictable from theory (i.e., equation (2)) unless very large negative values of χ are used. Or else a highly concentration and temperature dependent function for χ may have to be used. It is nonetheless possible to gain some insight by comparing the freezing behaviour of this system with other aqueous systems. Since black liquor contains inorganic salt components as well as polymeric species, the influence of ionic species on the freezing point depression needs to be considered as well. Therefore, in *Figure 5*, the behaviour of black liquor has been compared with that reported for sodium chloride and poly(vinyl pyrrolidone) solutions[11]. In all these systems the diluent is water and thus the curves start at a common point, i.e., the freezing point of water, making the comparisons easier and meaningful. As shown in the Figure, NaCl as solute leads to a relatively steep decrease in the freezing point of water over the entire concentration range shown. The effect is significant even at low solute levels, whereas with PVP, the decrease in the freezing point becomes significant only at higher concentrations. This is understandable since at a given mass fraction of solute the number of particles will be less if the solute is a polymeric, high molecular weight compound, and the depression of freezing point will not be as high as would be observed with low molecular weight solutes. The freezing behaviour of black liquor lies between that of NaCl and PVP. This intermediate behaviour is suggestive of the combined effects of the ionic and polymeric character of the black liquor solution. Even though the effect of molecular weight of the polymeric constituents was not studied, the behaviour of the kraft black liquor is also in accord with the relatively low molecular weight of its polymeric lignin derivatives ($M_n \simeq 2250$).

CONCLUDING REMARKS

This study has shown that polymer–diluent systems display a change-over from freezing to glass transition in their behaviour at a particular concentration. Below this concentration the solution behaviour is dominated by the diluent, and above by the polymer. It has been shown that this change-over concentration can be predicted by theory and the experimental observations are in agreement with the predictions. Even in compositionally complex multicomponent solutions such as kraft black liquors, this change-over concentration is experimentally observed. The shape of the curves reflect the nature of constituents and their interactions.

REFERENCES

1 Flory, P. J., 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, NY, 1953, p. 568
2 Couchman, P. R. and Karasz, F. E. *Macromolecules* 1978, **11**, 117
3 Rydholm, S., 'Pulping Processes', Interscience Publishers, New York, 1965
4 Masse, M., Kiran, E. and Fricke, A. L. *ACS Polym. Prepr.* August 1985
5 Kim, H. K., 'Effect of Kraft Pulping Conditions on Molecular Weights of Kraft Lignins', *Ph.D. Thesis*, Department of Chemical Engineering, University of Maine, Orono, Maine 04469, 1985
6 Sheenan, C. J. and Bisio, A. L. *Rubber Chem. Technol.* 1966, **39**, 149
7 Kawai, T. *J. Polym. Sci.* 1958, **32**, 425
8 Schotsch, K. and Wolf, B. A. *Makromol. Chem.* 1984, **185**, 2169
9 Angell, C. A., Sare, J. M. and Sare, E. J. *J. Phys. Chem.* 1978, **82**, 2622
10 Wunderlich, B. *J. Phys. Chem.* 1960, **64**, 1052
11 MacKenzie, A. P. *Phil. Trans. Roy. Soc. Lond.* 1977, **B278**, 167
12 Weast, R. D. (Ed.), 'CRC Handbook of Chemistry and Physics', 60th Edn., Boca Raton, FL, 1979

APPENDIX

The following is a listing of the values of the physical properties used in the theoretical predictions of the freezing and glass transition temperatures of the polystyrene–benzene system.

Literature values

Heat of fusion of benzene, $\Delta H^{\mathrm{f}}_1 = 2375$ cal/mol[12].

Heat capacity increment of benzene at T_{g_1}, $\Delta C_{\mathrm{p}_1} = 0.0825 \, \mathrm{cal\,g^{-1}\,K^{-1}}$ (ref. 10) (estimated as equal to that of distyrene).

Experimental values determined in the present study

Glass transition temperature of polystyrene, $T_{g_2} = 380$ K.

Heat capacity increment of polystyrene at T_{g_2}, $\Delta C_{\mathrm{p}_2} = 0.0811 \, \mathrm{cal\,g^{-1}\,K^{-1}}$.

Melting point of benzene, $T^{\circ}_{\mathrm{m}} = 278.5$ K.