

# The Influence of Thermal Properties on the Glass Transition Temperature in Styrene/Divinylbenzene Network-Diluent Systems

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## Synopsis

The depression of glass transition temperature in polystyrene and styrene/divinylbenzene networks, by the addition of ethylbenzene, ethyl acetate, and *m*-diethylbenzene, respectively, has been investigated by differential scanning calorimetry. The predictive quality of the Couchman-Karasz treatment for the composition dependence of  $T_g$  in compatible systems was found to provide excellent agreement with experimental results for the depression of  $T_g$  by ethylbenzene, provided certain modifications were made. Qualitatively, the theory predicts that for a given diluent, the depression of  $T_g$  is particularly sensitive to the incremental change in heat capacity of the pure polymer or network. The behavior of ethylbenzene provided good quantitative agreement with the theory, provided that the incremental change in heat capacity of the diluent at its  $T_g$  was approximated by  $\Delta C_p = \text{constant}/T$  and that the incremental change in heat capacity of the network at  $T_g$  represents only those units capable of thermal activation. The anomalous behavior observed on plasticization by ethyl acetate and *m*-diethylbenzene could in part be explained by a reduction in solvent quality or syneresis of diluent in the highly crosslinked samples.

## INTRODUCTION

The compositional dependence of glass transition temperature ( $T_g$ ) in polymer-polymer and polymer-diluent mixtures has provided considerable research interest over recent years. While several empirical approaches<sup>1,2</sup> have been made to interpret experimental data, these have also been complemented by more exacting fundamental treatments relying on configurational entropy theories<sup>3</sup> and a classical thermodynamic interpretation of the glass transition in polymers.<sup>4-6</sup> The compositional dependence of  $T_g$  can also be equated<sup>7</sup> in terms of the free-volume theory of the glass transition. However, we do not wish to present a critique of the various views of the glass transition and their application to polymer-solvent compositional dependence; therefore, we will concentrate only on extending the classical thermodynamic interpretation to these systems.

Recent work by Moy and Karasz<sup>8,9</sup> has shown that the enhanced sensitivity of  $T_g$  in highly crosslinked epoxy resins to small amounts of absorbed water can be explained qualitatively by applying a limiting condition to the Couchman treatment<sup>6</sup> of the composition dependence of  $T_g$  in compatible polymer mixtures. The expression derived predicts that the depression of  $T_g$  in a polymer-diluent mixture is particularly sensitive to the incremental change in heat capacity ( $\Delta C_p$ ) of the pure polymer. It is well established<sup>10,11</sup> that an increase in the degree of

crosslinking in a network polymer results in an increase in  $T_g$ , provided copolymerization effects are relatively small. Experimental studies in agreement with theory have also indicated that the incremental thermal properties at  $T_g$  such as  $\Delta C_p$  decrease as the degree of crosslinking increases. At very high degrees of crosslinking,  $\Delta C_p$  becomes practically unobservable. The implications of these observations when placed in the context of the preceding discussion are clearly consistent with the experimental data. Moy<sup>8</sup> has shown that for an epoxy network, where  $\Delta C_p$  at  $T_g$  was approximately one-third that of a less crosslinked polymer of similar chemical composition, the addition of 1% by weight of water resulted in an approximate threefold greater decrease in  $T_g$  than that of the less crosslinked material with an equivalent quantity of plasticizer. Theory predicts that the depression of  $T_g$  in a network system by a given compatible diluent should increase as the degree of crosslinking increases. It was the intention of this study to examine the  $T_g$  behavior using a network-diluent system divorced from the strong interactions that exist in the epoxy-water system. The styrene/divinylbenzene network was chosen as well suited to fulfill this requirement.

## EXPERIMENTAL

### Materials

All monomers and reagents were purified and distilled prior to use.

A series of styrene/divinylbenzene (S/DVB) network polymers was prepared by free-radical polymerization in the bulk phase at 60°C using 0.05% by weight recrystallized azobisisobutyronitrile as initiator. After 24 h, the solid rods of polymer were removed, sliced into discs approximately 1–2 mm thick, washed with distilled methanol, and dried under vacuum at approximately 195°C for a minimum of 48 h. A polystyrene homopolymer (PS) was also produced using the same procedure.

### Calorimetry

Glass transition temperatures and incremental changes in heat capacity at  $T_g$  were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, DSC-2, programmed at a heating rate of 20°C/min. Large-volume stainless steel sample pans<sup>12</sup> capable of containing up to 35 mg of sample were used instead of the standard aluminum pans. Typical DSC traces of the polymers are shown in Figure 1. All glass transition temperatures were determined by the midpoint method. Values of  $\Delta C_p$  were determined using a sapphire disc of known specific heat<sup>13</sup> for reference.

### Network Characterization

Determination of the degree of crosslinking was effected by swelling in toluene over a period of two months until constant weight uptake was attained. Calculation of the average molecular weight between crosslinks ( $M_c$ ) was performed using known methods.<sup>14,15</sup>

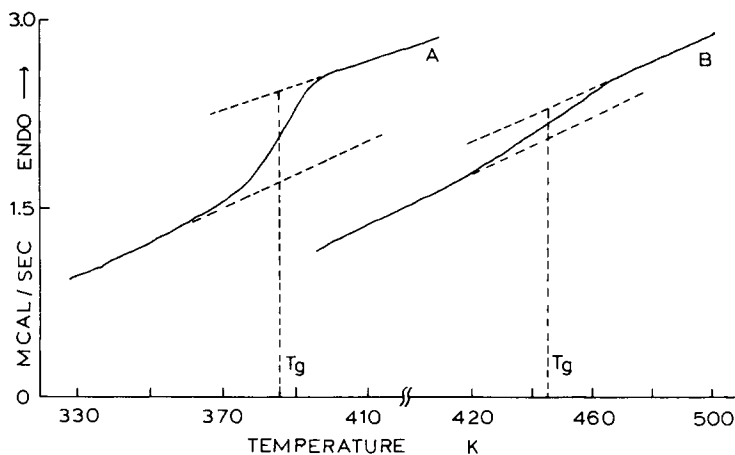


Fig. 1. Typical DSC traces of the prepared polymers: A, PS; B, PST5.

### Sample Preparation

Addition of diluent to samples of polymer was performed in a sealed glass tube, at a temperature slightly greater than or equivalent to the  $T_g$  of the “dry” polymer. Weighed samples of polymer were placed in the glass tube together with a small ampoule of diluent. After the tube had been evacuated and sealed, the ampoule of diluent was broken by shaking and the whole assembly placed in an oven for 48 h at the desired temperature. The quantity of diluent added to the polymer could only be arbitrarily controlled by modulating the quantity of diluent placed in the ampoule, but the diluent uptake was determined accurately by microbalance ( $\pm 0.01$  mg).

Properties of the polymers and diluents are shown in Table I.

TABLE I  
Properties of the Polymers and Diluents

Sample code	% DVB w/w	Polymers		$\Delta C_{p1}$ , J/g·K	$M_c$
		Onset, $T_{g1}$ , K	Midpoint		
PS	0	378.0	385.0	0.283	—
PST1	5.0	384.7	390.3	0.252	1091
PST4	21.0	403.3	415.6	0.200	224
PST5	35.7	418.0	444.9	0.095	113
		Diluents			
		$T_{g2}$ , K	$\Delta C_{p2}$ , J/g·K	BP, °C/760 mm	
Ethylbenzene		113 <sup>a</sup>	0.70 <sup>d</sup>	136.2	
Ethyl acetate		119 <sup>b</sup>	—	77.1	
<i>m</i> -Diethylbenzene		163 <sup>c</sup>	—	181.0	

<sup>a</sup> Reference 16.

<sup>b</sup> Reference 1.

<sup>c</sup> Reference 7.

<sup>d</sup> Obtained as an approximation from Ref. 17.

## RESULTS AND DISCUSSION

Although  $T_g$  may be influenced by copolymerization effects, the strong chemical similarity between styrene and divinylbenzene would suggest that the observed increase in  $T_g$  as the divinylbenzene content is increased is predominantly the result of crosslinking. Table I shows that the onset  $T_g$  is less affected by crosslinking than the midpoint value. It is important to consider which constitutes the more accurate representation of  $T_g$  of the polymers. In view of the method of preparing these polymers, it is recognized that there will be a considerable range of molecular weights between crosslinks. In a DSC scan, the longer meshes will be activated at a lower temperature than the very short ones. The thermogram obtained therefore represents the glass transition of a spectrum of meshes which should produce a broadening of the  $T_g$  range. This is observed experimentally, as can be discerned in Figure 1 by comparing the thermograms obtained for PS and PST5. If but for this reason alone the midpoint determination was deemed the more realistic representation of  $T_g$ .

Although it is desirable to use small samples when determining  $T_g$  by DSC, in order to minimize errors due to thermal lag effects, relatively large samples (25–35 mg) were used because of the substantially reduced  $\Delta C_p$  at  $T_g$  in the highly crosslinked system.

While it is doubtful that the results from swelling are entirely accurate in glassy materials with such a high degree of crosslinking, the results do indicate a sensible trend, and the value of  $M_c$  for PST5 is in reasonable agreement with the stoichiometry of the polymerization composition.

The diluents chosen are all known to be good plasticizers and/or solvents for polystyrene, particularly ethylbenzene, with relatively high boiling points, except perhaps for ethyl acetate. Diluent volatility is obviously of some importance when plasticized samples are subjected to temperatures in excess of the boiling point of the diluent. However, successive determinations of the  $T_g$  of the plasticized samples produced no significant variation, indicating that the time scale of measurement was smaller than the time required for diluent to diffuse out of the sample.

Data showing the depression of  $T_g$  by ethylbenzene are shown in Figure 2, except for those of polystyrene, which were virtually coincident with those of PST1 and have been omitted to preserve clarity. Figure 2 also shows the curve generated by the Couchman–Karasz equation [Appendix, eq. (A-1)] using data for  $\Delta C_p$  and  $T_g$  presented in Table I for PS and ethylbenzene. Although this curve relies on an approximation for the incremental change in heat capacity ( $\Delta C_{p2}$ ) at  $T_{g2}$ , it can be seen that eq. (A-1) overestimates the plasticization effect. This is also true for the crosslinked polymers and is consistent with the observations of Moy.<sup>8</sup> Moy reconciled this behavior principally by considering the validity of the temperature independence of  $\Delta C_p$ . Couchman recognized this shortcoming in his arguments, but the simplicity of the relationship produced by his treatment, together with the excellent agreement in experimental polymer–polymer blends, outweighed the need to include additional parameters. In the polymer–polymer systems studied by Couchman,  $T_{g1}$  and  $T_{g2}$  were in relatively close proximity to each other; but in polymer–diluent systems,  $T_{g1}$  and  $T_{g2}$  are considerably further apart. Therefore, in polymer–diluent systems such as these,  $\Delta C_{p2}$  cannot be considered temperature independent but has to be

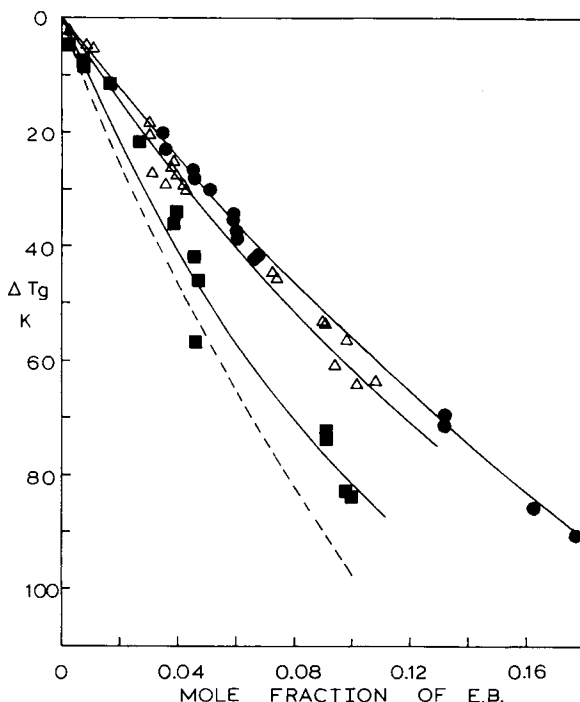


Fig. 2. Depression of glass transition temperature by ethylbenzene: (—●—) PST 1; (- -Δ- -) PST4; (—■—) PST5; (· · · · ·) depression of  $T_g$  in PS calculated using eq. (A-1) and parameters given in Table I.

extrapolated over a considerable range. From the Couchman treatment, it can be shown that

$$\left(\frac{dT_{g12}}{dx_2}\right)_{x_2=0} = \frac{-T_{g1}}{\Delta C_{p1}} \int_{T_{g2}}^{T_{g1}} \Delta C_{p2} d \ln T \quad (1)$$

where  $x_2$  refers to diluent.

If  $\Delta C_{p2}$  is assumed to be temperature independent, the equation above reduces to eq. (A-2) (see Appendix). A more accurate approximation is given by  $\Delta C_{p2} = \text{constant}/T$ , where the constant is determined by the value of  $\Delta C_{p2}$  at  $T_{g2}$ , and substitution into the equation above provides the expression shown below:

$$\left(\frac{dT_{g12}}{dx_2}\right)_{x_2=0} = \frac{-\Delta C_{p2}}{\Delta C_{p1}} (T_{g1} - T_{g2}) \quad (2)$$

This expression is identical to that obtained by applying the same limiting condition to the equation [eq. (A-3), Appendix] proposed by Gordon and co-workers. Such a result is not very surprising in view of the similar origins of the predictive treatments involved. However, it is important to stress that the former route makes no assumptions about the polymer.

If eq. (2) is used to calculate  $(dT_{g12}/dx_2)_{x_2=0}$  for the polymers using ethylbenzene as diluent, and compared to experimentally determined values, it can be seen, as shown in Table II, that although there is acceptable agreement with the data for polystyrene, there is still a discrepancy between theory and experiment which increases as crosslinking increases. Reasons for this can be found

TABLE II  
Comparison Between Experimental and Calculated Values of  $(dT_{g12}/dx_2)_{x_2=0}$  Using Ethylbenzene as Diluent<sup>a</sup>

Sample code	$\Delta C_{p1}$ , J/g-K	$\Delta C_{p1}^{\text{act}}$ , J/g-K	$(dT_{g12}/dx_2)_{x_2=0}$ , K/% diluent		
			Experimental	Calculated using eq. (2)	Calculated using eq. (4)
PS	0.283	0.283	6.5	6.7	6.7
PST1	0.252	0.279	6.5	7.7	7.0
PST4	0.200	0.262	8.0	10.6	8.1
PST5	0.095	0.245	10.0	24.5	9.5

<sup>a</sup> N.B.: Data presented in Figures 2-5 are in terms of mole fraction. For ethylbenzene mole fraction, weight fraction and weight % (weight fraction  $\times$  100%) are virtually identical:

$$\text{Mole fraction} = \frac{\frac{\text{wt diluent}}{\text{MW diluent}}}{(\text{wt diluent}/\text{MW diluent}) + (\text{wt polymer}/\text{average MW of repeat unit})}$$

by examining the validity of using the experimentally determined values of  $\Delta C_{p1}$ .

While a more exhaustive analysis can be found elsewhere,<sup>18</sup> it is more probable that the value obtained for  $\Delta C_{p1}$  is appropriate only to those units capable of being activated at the glass transition. These units are the only ones involved in the depression of the glass transition temperature by a diluent. Ueberreiter and Kanig<sup>10</sup> showed that in styrene/divinylbenzene networks, it is impossible for meshes of less than four carbon atoms to be thermally activated. These units are so restricted by crosslinking that they are unable to carry out the micro-Brownian wriggling movements associated with the glass transition and are therefore unable to contribute to the conformational component of  $\Delta C_p$ . As the divinylbenzene content increases, the fraction of chain units capable of being activated decreases. Therefore, the experimentally observed sharp decrease in  $\Delta C_{p1}$  with crosslinking is artificially exaggerated, and a more accurate value of  $\Delta C_{p1}$  is given by  $\Delta C_{p1}^{\text{act}}$ , the incremental change in heat capacity of the units capable of being activated. In order to obtain values of  $\Delta C_{p1}^{\text{act}}$  it can be shown that a reasonable approximation is given by equation (3), where  $X$  refers to the degree of crosslinking, such that  $X = 0$  represents polystyrene:

$$\Delta C_{p1}^{\text{act}}(X) T_{g1}(X) = \Delta C_{p1}(X = 0) T_{g1}(X = 0) \quad (3)$$

Substitution of this expression into eq. (2) yields eq. (4):

$$\left( \frac{dT_{g12}}{dx_2} \right)_{x_2=0} = \frac{-\Delta C_{p2}}{\Delta C_{p1}(X=0) T_{g1}(X=0)} \frac{T_{g1}(X)}{[T_{g1}(X) - T_{g2}]} \quad (4)$$

This has been utilized to calculate values of  $(dT_{g12}/dx_2)_{x_2=0}$ , the results of which are given in Table II. As can be seen, agreement between theory and experimental values is greatly improved.

Extending this theoretical manipulation of the Couchman treatment further, a new expression can be derived for the prediction of glass transition temperature in network polymer/diluent systems:

$$T_{g12} = \frac{x_1 \Delta C_{p1}^{\text{act}}(X) T_{g1}(X) + x_2 \Delta C_{p2} T_{g2}}{x_1 \Delta C_{p1}^{\text{act}}(X) + x_2 \Delta C_{p2}} \quad (5)$$

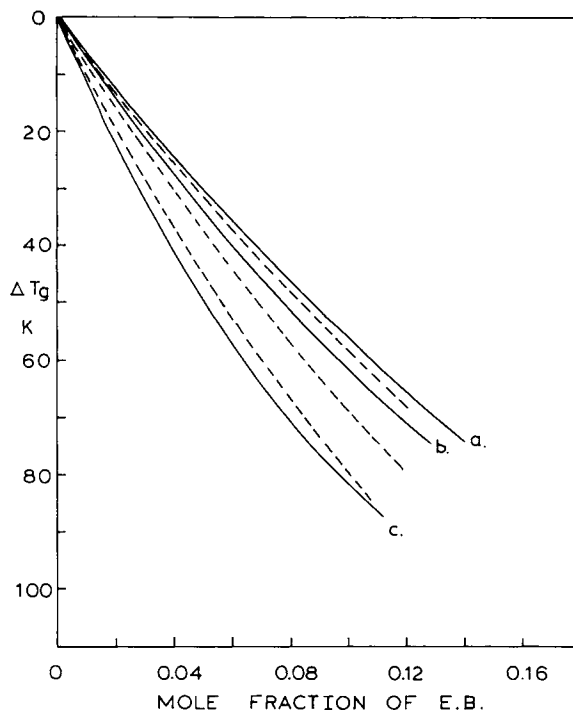


Fig. 3. Comparison of the depression of  $T_g$  by ethylbenzene determined experimentally with that predicted by eq. (5): (a) PS; (b) PST4; (c) PST5 [(—) experimental, (---) theory].

Using this new relationship and the calculated values of  $\Delta C_{p1}^{\text{act}}(X)$  provides quite good agreement in the ethylbenzene system, as shown in Figure 3. While this treatment is successful in accounting for plasticization by ethylbenzene, it does not account for the anomalous behavior of ethyl acetate and *m*-diethylbenzene, as shown in Figures 4 and 5.

The phase behavior of polymer network-diluent systems is considerably different from that of linear polymer-diluent systems. Networks can only assume a limited amount of solvent, which is dependent upon solvent quality. In general, the lower the interaction parameter  $\chi$ , the better the solvent quality. It is well known that the parameter  $\chi$  varies with temperature, such that a decrease in temperature may be accompanied by a decrease in solvent quality; hence, for networks, a reduction in equilibrium swelling will occur. If we have a particular network-solvent system where  $\chi$  decreases as the temperature increases, i.e., solvent quality improves at higher temperatures, and solvent is introduced at a high temperature, then if the quantity of solvent added is sufficiently large and cooling is very fast (minutes), instabilities will be created, giving rise to regions of alternately dense and dilute phases. A more detailed discussion concerning aspects of solvent quality may be found elsewhere.<sup>19</sup>

The highly crosslinked systems considered here can only take on small amounts of solvent at ambient conditions; and for a solvent concentration of 10%, they are already close to the completely swollen state. It is important to point out that sample preparation involved addition of diluent at elevated temperatures.

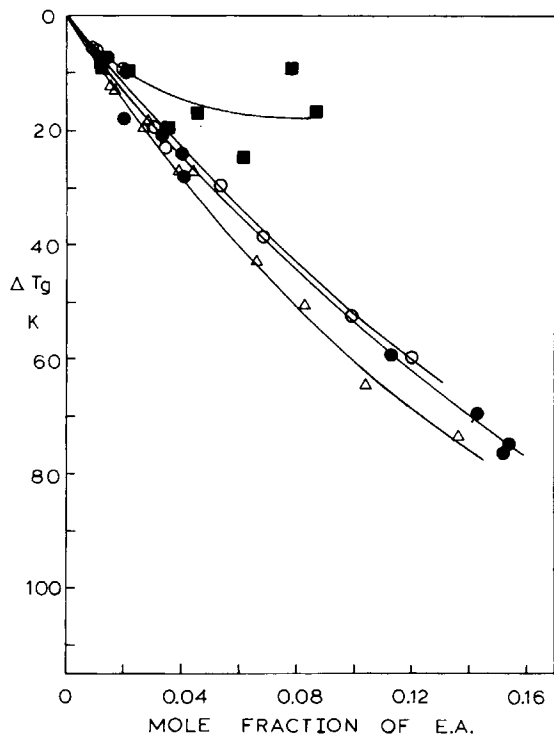


Fig. 4. Depression of glass transition temperature by ethyl acetate: (—○—) PS; (—△—), PST1, (—○—) PST4; (—■—) PST5.

It appears therefore that syneresis on cooling is a distinct possibility, particularly with the highly crosslinked systems.

The results presented here for the three different diluents suggest considerably different behavior. In particular, the highly crosslinked networks with ethyl acetate as diluent seem to have undergone severe syneresis. Hence, the interaction parameter  $\chi$  for this system is probably a decreasing function of temperature in the range of interest. Experimental data for polystyrene<sup>20</sup> do indeed imply that the solvent quality of ethyl acetate does in fact decrease as the temperature is reduced. The results with ethylbenzene indicate that  $\chi$  varies little or is a nondecreasing function of temperature, which is consistent with the findings of Hocker et al.<sup>21</sup> which show that ethylbenzene is a very good solvent for polystyrene, especially at relatively low temperatures.

The position with *m*-diethylbenzene is slightly different. Firstly, the quantities  $T_{g1}(X) - T_{g2}$  and  $\Delta C_{p2}$  will be smaller for this system, and any systematic variation in the depression of  $T_g$  with crosslinking by this diluent will consequently be smaller than for ethylbenzene. However, distinct differences should be observed, which is clearly not the case, as can be seen in Figure 5. While the arguments concerning solvent quality, as discussed previously for ethyl acetate, may also be applied to this system, the results themselves do not indicate any strong evidence of syneresis, and as yet we are unable to fully explain the behavior with this diluent.



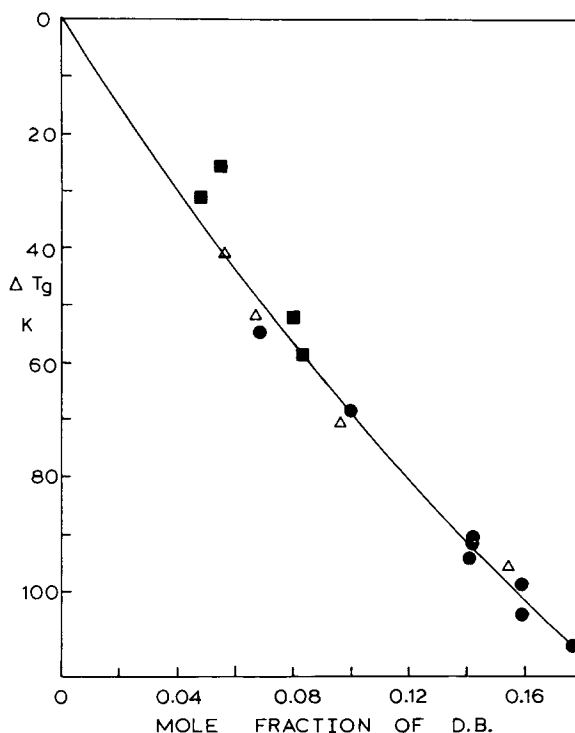


Fig. 5. Depression of glass transition temperature by *m*-diethylbenzene: (—●—) PS; (—△—) PST4; (—■—) PST5.

## CONCLUSIONS

The Couchman-Karasz approach to the temperature dependence of  $T_g$  in compatible mixtures has been found to successfully account for the  $T_g$  behavior of styrene/divinylbenzene networks plasticized by ethylenbenzene, provided certain corrections are applied. The inconsistencies in the data produced with plasticization by ethyl acetate and *m*-diethylbenzene has in part been explained by considering aspects of solvent quality and possible syneresis in the highly crosslinked systems. We recognize that the types of networks used here are difficult to characterize and will have a considerable range of molecular weights between crosslinks. Although model polystyrene networks with very uniform molecular weights between crosslinks are readily available through ionic polymerization methods, this route is unlikely as yet to give polymers with a sufficiently large enough range of  $\Delta C_p$  to merit investigation. While the composition dependence of  $T_g$  in network-diluent systems certainly warrants greater experimental attention, a more fruitful avenue of exploration may be found by focusing on the careful design of well-characterized model networks with a more uniform structure.

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## APPENDIX

The equations below are for two-component systems, where  $T_{g12}$  is the glass transition temperature of the mixture.  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the pure components, and  $\Delta C_{p1}$  and  $\Delta C_{p2}$  are the incremental changes in heat capacity at  $T_{g1}$  and  $T_{g2}$ , respectively, of the pure components:

$$\ln \frac{T_{g12}}{T_{g1}} = \frac{x_2 \Delta C_{p2} \ln (T_{g2}/T_{g1})}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}} \quad (\text{A-1})$$

where  $x_1$  and  $x_2$  are the mole or mass fractions of the pure components.

$$\left( \frac{dT_{g12}}{dx_2} \right)_{x_2 \rightarrow 0} = \frac{-T_{g1}}{\Delta C_{p1}} \Delta C_{p2} \ln (T_{g1}/T_{g2}) \quad (\text{A-2})$$

$$T_{g12} = \frac{x_1 T_{g1} + (1 - x_1) T_{g2} K}{x_1 + (1 - x_1) K} \quad (\text{A-3})$$

where  $K = \Delta C_{p2}/\Delta C_{p1}$ .

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