

Glass Transition Temperatures in Polymer Mixtures

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ABSTRACT: A fluid-lattice theory of fluid mixtures is combined with the Gibbs–DiMarzio approach of zero configurational entropy at glass transition in order to correlate and predict the composition dependence of glass transition temperature, T_g , in one-phase polymer mixtures. Such a combination allows an independent quantitative estimation of the significance to T_g of both equation-of-state terms and chain flexibility terms. The model is tested against experimental data on T_g 's for three polymer mixtures known to be compatible in the complete range of composition. The effect of the various binary parameters on glass transition is discussed along with the effect of chain flexibility change upon mixing. It is shown that chain flexibility terms are predominant in determining T_g . Two possible ways of taking into account chain flexibility change are proposed.

KEY WORDS Glass Transition / Polymer Mixtures / Statistical Thermodynamics / Gibbs–DiMarzio Theory / Fluid Lattice /

Prediction and correlation of the composition dependence of glass transition temperature in compatible polymer mixtures is a subject of, both, practical and theoretical interest. From the practical point of view a knowledge of T_g is of considerable importance in connection with the processing conditions and the in-service properties of polymer mixtures. From the theoretical point of view the thermodynamic as well as the kinetic character of liquid-glass transition have to be taken into account in fundamental treatments of the phenomenon. Existing treatments are only approximate ones and such a fundamental treatment still remains a challenge to theoreticians.

The rapid accumulation of information on compatible and semicompatible polymer mixtures, especially in the last decade, justifies efforts towards extensions of traditional treatments of glass transition for pure polymers to polymer mixtures. Polymer solution thermodynamics is of great value in these extensions. For engineering calculations,

of course, one may resort to simple empirical or semiempirical equations such as the simple Fox equation¹ or the Couchman equations.² Although the thermodynamic basis of Couchman's equations has been seriously disputed recently,³ they have been proved quite successful in a number of cases.² Deviations from linearity with composition of T_g in polymer mixtures may be negative, zero or positive and it is rather too much to expect from these simple equations to be successful in all these diverse cases. Nevertheless, molecular theories are more appropriate if we, also, wish to gain some physical insight of the liquid-glass transition phenomenon.

Fluid-Lattice models of polymer solutions^{4–9} is a promising class of models for their thermodynamic properties. A variety of properties of polymer mixtures have been correlated, so far, with these models such as the basic thermodynamic quantities of mixing, upper and lower critical solution temperatures and gas solubilities at various external conditions. On the other hand, in spite of its

shortcomings,^{10,11} the Gibbs–DiMarzio theory^{12,13} may be considered as one of the best available thermodynamic treatments of the glass transition today. The links between the fluid-lattice models and the Gibbs–DiMarzio theory have been recently discussed for the case of pure polymers.¹⁴

In the present work we combine an improved fluid-lattice model for polymer solutions⁹ with Flory's approximate rotational isomeric state model for chain conformations¹⁵ and with the Gibbs–DiMarzio approach^{12,13} of zero configurational entropy at glass transition in order to estimate the composition dependence of T_g in one-phase polymer mixtures. The fluid-lattice model is used for a separate estimation of the equation-of-state terms from independent information on other thermodynamic properties of the polymer mixtures.

THEORY

Consider a mixture of N_1 molecules of type 1 each consisting of r_1 segments and N_2 molecules of type 2 each consisting of r_2 segments at temperature T , external pressure P , and total volume V . Both types of molecules are considered semiflexible. In order to formulate the partition function of the system, we consider that the molecules are arranged on a quasi-lattice of N_r sites, N_o of which are empty. In other words, we consider that the void volume between the chain molecules is evenly divided in N_o holes.

Following Flory,¹⁵ Gibbs and DiMarzio^{12,13,16} and our previous work⁹ we may write for the system configurational partition function in the T, P ensemble and in its maximum term approximation

$$Q_N = \delta_1^{N_1} \delta_2^{N_2} \left(\frac{N_r}{N_o} \right)^{N_o} \left(\frac{N_r}{\omega_1 N_1 r_1} \right)^{N_1} \left(\frac{N_r}{\omega_2 N_2 r_2} \right)^{N_2} \times \exp \left[\frac{-(E_o + PV)}{RT} \right] \quad (1)$$

where

$$\omega_i = \frac{\sigma_i}{r_i} \exp(r_i - 1) \quad (2)$$

and¹⁵

$$\delta_i^{N_i} = \frac{Z_i^{N_i} (Z_i - 2)^{f_i N_i (r_i - 2)} [(r_i - 2) N_i]!}{[f_i N_i (r_i - 2)]! [(1 - f_i) N_i (r_i - 2)]!} \times \exp \left[\frac{-f_i N_i (r_i - 2) \varepsilon_i}{RT} \right] \quad (3)$$

– E_o is the lattice (intermolecular potential) energy of the system, Z_i is the bond (lattice) coordination number (bond conformations) for bond of type i ; For simplicity we set $Z_1 = Z_2 = Z$. σ_i is a symmetry number and ε_i is the flex energy for bonds of type i , that is the potential energy of the $Z - 1$ bent conformations over the favoured conformation. The equilibrium fraction f_i of bonds i in bent conformations is given by¹⁵

$$f_i = \frac{(Z - 2) \exp \left(-\frac{\varepsilon_i}{RT} \right)}{1 + (Z - 2) \exp \left(-\frac{\varepsilon_i}{RT} \right)} \quad (4)$$

For convenience we will call the first two terms in eq 1 flexibility terms and all other terms equation-of-state terms. For the evaluation of the equation-of-state terms we will adopt the fluid-lattice approach.^{4,9} In this approach, each pure r_i -mer is characterized by three scaling constants or equation-of-state parameters: A characteristic pressure, P_i^* ; a characteristic temperature, T_i^* ; and a characteristic density, ρ_i^* . An equivalent set of scaling constants is the interaction energy, η_i^* ; the number of segments per molecule, r_i , and the characteristic volume per segment, v_i^* . The basic relation between the scaling constants is

$$\eta_i^* = RT_i^* = P_i^* v_i^* \quad (5)$$

For our mixture and in the one-fluid approximation the total volume of the system is

$$V = N_r v^* \quad (6)$$

where v^* is the average close-packed volume per segments in the mixture, assumed to be given by the common quadratic mixing rule⁹

$$v^* \phi_1^2 v_1^* + 2\phi_1 \phi_2 v_{12}^* + \phi_2^2 v_2^* \quad (7)$$

The segment fraction ϕ_i is given by

$$\phi_i = \frac{r_i N_i}{N_1 r_1 + N_2 r_2} = \frac{r_i N_i}{r N} = \frac{x_i r_i}{r} \quad (8)$$

where x_i is the mole fraction of component i . v_{12}^* is assumed to be given by

$$v_{12}^* = \left(\frac{v_1^{*1/3} + v_2^{*1/3}}{2} \right)^3 \quad (9)$$

as for hard spheres. Notice that with the mixing rule of eq 7 the close-packed volume is not, generally, conserved during mixing.

The reduced volume is

$$\tilde{v} = \frac{N_r v^*}{r N v^*} = \frac{\rho^*}{\rho} = \frac{1}{\tilde{\rho}} \quad (10)$$

where ρ is the density of the mixture.

The intermolecular potential energy of the system is given by⁹

$$\begin{aligned} -E_o &= \frac{r N \eta^*}{\tilde{v}} \\ &= \frac{r N}{\tilde{v}} (\phi_1 \eta_1^* + \phi_2 \eta_2^* - \phi_1 \phi_2 R T X_{12}) \end{aligned} \quad (11)$$

where

$$X_{12} = \frac{\eta_1^* + \eta_2^* - 2\zeta_{12} \sqrt{\eta_1^* \eta_2^*}}{R T} \quad (12)$$

The binary parameter ζ_{12} is expected to have values close to unity and can be estimated from experimental data for various thermodynamic properties of the mixture.

In terms of the reduced quantities of the mixture the equation of state obtained from eq 1 is⁹

$$\frac{\tilde{P} \tilde{v}}{T} = \frac{1}{r} - 1 - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - \frac{\tilde{\rho}}{\tilde{T}} \quad (13)$$

where

$$\tilde{P} = \frac{P}{P^*} \quad \text{and} \quad \tilde{T} = \frac{T}{T^*} \quad (14)$$

An equation analogous to eq 5 is valid between η^* , P^* , v^* , and T^* for the mixture.

The total configurational entropy of the system obtained from eq 1 is

$$\begin{aligned} \frac{S}{r N} &= (\tilde{v}-1) \ln \frac{\tilde{v}}{\tilde{v}-1} + \frac{\ln \tilde{v}}{r} \\ &+ \frac{\ln Z}{r} + \frac{1}{r} \ln \frac{r}{2} + \frac{1}{r} - 1 \\ &- \frac{x_1 \ln x_1 + x_2 \ln x_2}{r} \\ &+ \frac{x_1(r_1-2)}{r} \left[\frac{f_1 \varepsilon_1}{R T} - \ln(1-f_1) \right] \\ &+ \frac{x_2(r_2-2)}{r} \left[\frac{f_2 \varepsilon_2}{R T} - \ln(1-f_2) \right] \end{aligned} \quad (15)$$

In the case of high polymers this equation simplifies to the equation

Table I. Characteristic parameters for pure polymers

Polymer	T^* K	P^* mN m ⁻²	ρ^* kg m ⁻³	T_g K	ε/R K
Poly(dimethyl siloxane)	476	302	1104	150	177.2
Poly(ε -caprolactone) (PCL)	570	500	1189	202	258.8
Polyisobutylene	643	354	974	243	321.5
Poly(vinyl methyl ether) (PVME)	639	679	1115	244	325.8
Poly(vinyl chloride) (PVC)	661	754	1485	355	597.2
Polystyrene (PS)	735	357	1105	373	602.4
Poly(methyl methacrylate)	696	503	1269	395	689.3
Poly(2,6-dimethylphenylene oxide) (PPO)	739		1186	485	936.9

$$\begin{aligned} \frac{S}{rRN} = & (\bar{v}-1) \ln \frac{\bar{v}}{\bar{v}-1} \\ & - 1 + \varphi_1 \left[\frac{f_1 \varepsilon_1}{RT} - \ln(1-f_1) \right] \\ & + \varphi_2 \left[\frac{f_2 \varepsilon_2}{RT} - \ln(1-f_2) \right] \quad (15a) \end{aligned}$$

The suggestion of Gibbs and DiMarzio is that the entropy S is becoming zero at the glass transition temperature. By adopting this suggestion, one can use eq 15 for the case of pure polymers and evaluate the flex energies ε_i . Values of ε_i along with equation-of-state parameters for some common polymers are shown in Table I.

It is worth observing in this table, that the quantity ε/RT_g varies, to a good approximation, linearly with T_g . The least squares line is

$$\frac{\varepsilon}{RT_g} = 0.797 + 2.34 \times 10^{-3} T_g$$

with a correlation coefficient equal to 0.990.

If ε_1 , ε_2 , and ξ_{12} are known, eq 15 or 15a may be used for an estimation of the composition dependence of glass transitions in one phase polymer mixtures. It would be more appropriate to say that, at T_g , $S/rRN = s_g/r$, where s_g is of the order of $-(\varphi_1 \ln \varphi_1 + \varphi_2 \ln \varphi_2)$. In our case ($r \rightarrow \infty$), on inspection of eq 15, s_g/r is essentially zero.

APPLICATIONS

In this section we will compare theoretical estimations of glass transition temperatures with experimental data for pairs of high polymers known to be compatible in the complete range of compositions. Such a comparison requires the following experimental information:

a) PVT data over extended range of external conditions for each pure polymer in order to evaluate the pure component equation-of-state parameters.

b) Experimental data for any (in principle)

basic thermodynamic quantity of mixing of the polymer pair in order to evaluate their binary(ies) parameter(s).

c) Data for the chain flexibility change on mixing the two polymers. In addition one must, of course, have:

d) Experimental data on glass transition temperatures for various compositions of the polymer mixture. Unfortunately the available experimental information for any compatible pair of polymers is, by no means, complete.

The first polymer mixture in which we will apply the above theory is poly(vinyl chloride)–poly(ε -caprolactone). This pair of polymers is known to be compatible in the complete range of compositions.¹⁷ Glass transition temperatures for various compositions have been measured by Koleske and Lundberg.¹⁸ Estimations of Flory–Huggins χ interaction parameter at various compositions are also available.^{19,20} Unfortunately, good quality PVT data over extended range of external conditions for both PVC and PCL are not available and their equation-of-state parameters reported in the Table have been estimated from a very limited set of data.¹⁹ On the basis of the available experimental information^{19,20} the maximum value of the binary interaction parameter ξ_{12} is 1.065 and the minimum value is 0.957.

In Figure 1 we present various theoretical estimations of glass transition temperatures for this polymer mixture along with the experimental data.¹⁸ Curves 1, 2, and 3 show the effect of varying ξ_{12} on glass transition temperatures (ξ_{12} is equal to 1.0, 0.957, and 1.065 for curves 1, 2, and 3 respectively). Curve 3 indicates that stronger intermolecular interactions (higher values of ξ_{12}) between the constituents of the mixture lead to maximum deviations of T_g -composition data from linearity and this is in accordance with physical intuition. Curve 3 seems to indicate that for an adequate representation of experimental data a lower value of ξ_{12} is needed. However

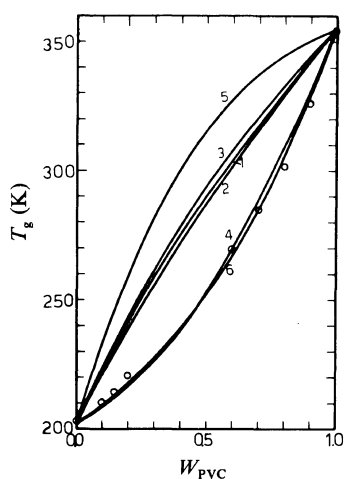


Figure 1. Glass transition temperatures for the mixture PVC–PCL vs. the weight fraction of PVC. \circ , experimental points.¹⁸ Curves 1 to 6 are theoretical estimations of T_g for the mixture and have been obtained as described in the text.

lower values of ζ_{12} violate the phase stability (spinodal) condition⁹ for the mixture. Consideration of v_{12}^* in eq 9 as an adjustable binary parameter does not improve significantly the model. Curves 1, 2, and 3 were calculated by assuming that the chain flexibilities of the two polymers remained unchanged upon mixing. Relaxation of this later assumption can lead to agreement with experiment. Curve 4 was calculated by assuming a simple linear decrease of the flex energy of the less flexible PVC with composition:

$$\frac{\varepsilon_{\text{PVC}}}{R} = 597.2 - 325x_{\text{PCL}} \quad (16)$$

while ε_{PCL} was considered constant. x_{PCL} is the mole fraction of PCL in the mixture. An increase of the flex energy of the more flexible PCL as

$$\frac{\varepsilon_{\text{PCL}}}{R} = 258.8 + 325x_{\text{PVC}} \quad (17)$$

while keeping ε_{PVC} constant gives curve 5. Both curves 4 and 5 were calculated with $\zeta_{12} = 1$. A simultaneous consideration of chain flexibility change for both polymers can

lead, also, to a better agreement with experiment.

The other possibility is to consider the effect of temperature on chain flexibility. Flex energies may be considered flex free energies in analogy with free energies of interaction⁸ as a consequence of the averaging procedures over microstates involved in formulating the partition function. In other words, we may write

$$\varepsilon = \varepsilon_h - T_{\varepsilon_s} \quad (18)$$

Notice that segments of the polymers in the present treatment are fictitious and that “bond” conformations are considered independent of the conformations of previous bonds.

Once a value for ε_s (or ε_h) is assumed, ε_h (or ε_s) is obtained from the T_g of the polymer. Use of eq 18 leaves unaltered eq 4. However in eq 15 and 15a the flex energies must be replaced by the “enthalpic” parts, ε_h .

In the case of the mixture PVC–PCL and for simplicity, we considered the effect of temperature on the flexibility of the more flexible component, PCL. Curve 6 in Figure 1 was obtained by setting for the flex energy of PCL:

$$\frac{\varepsilon_{\text{PCL}}}{R} = 586 - 0.962T \quad (19)$$

while keeping ε_{PVC} constant and $\zeta_{12} = 1.0$.

The second polymer mixture in which we apply the theory is polystyrene–poly(2,6-dimethylphenylene oxide), also, known to be compatible in the complete range of compositions.¹⁷ Glass transition temperatures for various compositions have been measured by Kwei and Frish.²² PVT data over extended range of external conditions are available for polystyrene. However for PPO the available PVT data are very limited and in fact they allow an estimation of only T^* and ρ^* .⁴ Variation of P^* from 200 to 500 mN m^{-2} does not affect significantly the estimated flex energy for PPO.

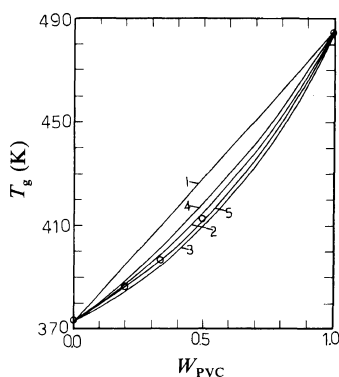


Figure 2. Glass transition temperatures for the mixture PS-PPO vs. the weight fraction of PVC. \circ , experimental points.²² Curves 1 to 5 are theoretical estimations of T_g for the mixture and have been obtained as described in the text.

In Figure 2 we present various theoretical estimations of T_g for this polymer mixture along with the experimental data.²¹ Curve 1 was calculated with $\xi_{12}=1.0$ and $P_{\text{PPO}}^*=359 \text{ mN m}^{-2}$ so that P^*/T^* is the same for both PS and PPO. Agreement with experimental data is reached by a much lower value of P_{PPO}^* . Curve 2 is calculated with $\xi_{12}=1.0$ and $P_{\text{PPO}}^*=210 \text{ mN m}^{-2}$. Curves 3 and 4 are, also, calculated with this value of P_{PPO}^* but with ξ_{12} equal to 0.95 and 1.05 respectively. Such a value for P_{PPO}^* is, rather, too low. The characteristic volume per segment for PPO corresponding to this value of P^* is $29.3 \text{ cm}^3 \text{ mol}^{-1}$ which is significantly larger than $17.1 \text{ cm}^3 \text{ mol}^{-1}$ which is the largest reported value of v^* for polymers⁴ and still larger than $20.9 \text{ cm}^3 \text{ mol}^{-1}$ which is the largest reported value of v^* for r -mers.²³ Adoption of higher values for P_{PPO}^* necessitate as in the previous case consideration of chain flexibility change upon mixing in order to correlate satisfactorily the experimental T_g 's.

For this mixture we may, also, use eq 18 to describe the flex energy for the more flexible polystyrene. Curve 5 in Figure 2 was obtained by setting

$$\frac{\epsilon_{\text{PS}}}{R} = 1101 - 0.842T \quad (20)$$

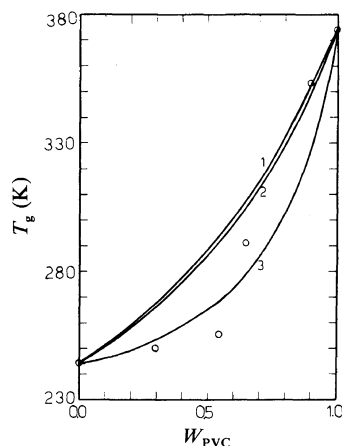


Figure 3. Glass transition temperatures for the mixture PS-PVME vs. the weight fraction of PS. \circ , experimental points.²⁴ Curves 1 to 3 are theoretical estimations of T_g for the mixture and have been obtained as described in the text.

while keeping ϵ_{PPO} constant, $\xi_{12}=1.0$ and $P_{\text{PPO}}^*=359 \text{ mN m}^{-2}$.

As a third example we apply the theory to the mixture polystyrene-poly(vinyl methyl ether), also, known to be compatible in the complete range of compositions.¹⁷ Flory-Huggins χ interaction parameters for this mixture are available.²⁰ Glass transition temperatures for various compositions have been measured by Kwei, Nishi, and Roberts.²⁴ PVT data for PVME are very limited²⁵ and the estimation of the scaling constants of the Table are based on this set.

In Figure 3 we present various theoretical estimations of T_g 's for this polymer mixture along with the experimental data.²³ Curve 1 was calculated with $\xi_{12}=1.0$ while curve 2 with $\xi_{12}=0.95$. Once again the theory and the experiment cannot be reconciled by considering chain flexibilities unaffected upon mixing. Considerably lower values of ξ_{12} will violate the phase stability condition⁹ for the mixture.

Consideration of the effect of temperature on the chain flexibility of the more flexible PVME leads to curve 3 in Figure 3 which was obtained by setting $\xi_{12}=1.0$ and

$$\frac{\epsilon_{\text{PVME}}}{R} = 758.2 - 1.083T \quad (21)$$

while keeping constant ϵ_{PS} .

DISCUSSION AND CONCLUSIONS

In this work we have combined a recent fluid lattice model⁹ of r -mer fluid mixtures with the Gibbs–DiMarzio^{12,13} theory of glass transition in order to estimate the composition dependence of T_g 's in one-phase polymer mixtures. The fluid lattice model has allowed a separate estimation of the equation-of-state terms consistent with the thermodynamic behavior of the polymer at higher temperatures. It was, then, possible to estimate the significance of the chain flexibility terms to T_g . In addition it was possible to test the validity of the assumption of no change of flex energies upon mixing.

The theory has been applied to three polymer mixtures, known to be compatible in the complete range of composition, for which the information needed for calculations was available. From this comparison it has been shown that the assumption of no change of chain flexibilities upon mixing cannot lead to agreement of theory and experiment without violating the phase stability condition. In fact, theoretical estimations of T_g 's even with the lowest permissible value of the interactional binary parameter ξ_{12} are significantly higher than the experimental T_g 's.

Agreement between experimental T_g 's and theoretical estimations with the present model can be reached by allowing for a chain flexibility change to take place either upon mixing or upon changing the temperature. We have not attempted, in this work, to present and justify a detailed model for this change. However, such a change upon mixing, besides being rather, drastic (see eq 16)), would, also, impose serious questions on the validity of traditional thermodynamic models for polymer mixtures since chemical potential is af-

ected by this change.^{25,26,27} This problem can be alleviated by considering a temperature dependence of flex energies for pure polymers. Equation 18 requires, however, further justification and in a more consistent approach it must be applied to both components for all mixtures and for any value of r .

The above mentioned problems point to the limitations of, both, the fluid lattice models and the Gibbs–DiMarzio approach to glass transition. Polydispersity has not been taken into account in the present work and the segments of the polymers in the fluid-lattice treatment^{4,9} are fictitious. These approximations may, in part, be responsible for the observed discrepancy between theory and experiment. The otherwise required, change of chain flexibilities may be due to a combined effect of the change in temperature and a change in mixture composition. How much contribute each of these changes to the flex energies? It is hoped that the present work will stimulate, both, theoretical and experimental work towards clarifying this question.

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