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Glass transition temperature in hydrogen-bonded polymer mixtures

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A recent statistical thermodynamic theory of fluids interacting with strong specific intermolecular and intramolecular forces is extended in order to correlate and predict the glass transition temperatures in polymer mixtures. The Gibbs–DiMarzio approach of zero configurational entropy at the glass transition is adopted. The configurational entropy is composed of three distinct parts: a chain flexibility or internal part, an equation-of-state part and a hydrogen bonding part. The approach is tested against our own experimental data and literature data. The agreement between experimental and predicted glass transition temperatures is satisfactory.

(Keywords: glass transition; polymer mixtures; Gibbs–DiMarzio theory; hydrogen bonding)

INTRODUCTION

Experimental information or techniques for the estimation of the glass transition temperatures (T_gs) in polymer mixtures are of much practical and academic 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 the 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[1–3].

Polymers are, as a rule, not miscible[4]. Miscibility is often achieved by modifying one of the component polymers through incorporation along its chain of appropriate functional groups which may interact with strong specific forces with complementary groups in the other component polymers[5]. A typical example is the incorporation of hydroxyl groups in one type of polymer which interact with the carbonyl, ether or amine groups of the other polymer component.

The glass transition temperatures of polymer mixtures of the above type very often exhibit positive deviations from linearity with composition[6]. Existing treatments of the composition dependence of T_g in these polymer mixtures are mainly empirical in character and do not take explicitly into account the extent of hydrogen bonding and its orientational character[7].

The objective of this work is to develop a statistical thermodynamic model for the description of glass transition temperatures in polymer mixtures interacting with strong specific intermolecular forces. It is based on our recent equation-of-state theory of hydrogen bonding in fluids[8,9] which is now extended to the glassy state. The theory is tested against our own experimental data and data from the literature[6].

In the next section we present the experimental procedure for the polymer sample preparation and the calorimetric measurement of the glass transition temperatures. Subsequently we present the theoretical development and its application to the experimental T_g data.

EXPERIMENTAL

Poly(isobutyl methacrylate) (PIBMA) is not miscible with polystyrene or with poly(vinyl phenol). However, random copolymers of styrene (St) and vinyl phenol (VPh) exhibit miscibility with PIBMA over the full composition range[10]. The system studied in this work is the mixture of PIBMA with the copolymer St-*co*-VPh with 60 mol% vinyl phenol content, hereafter referred to as SVPh60. The copolymer was synthesized by copolymerizing freshly distilled styrene and acetoxystyrene in toluene solution. 2,2′-Azobis(isobutyronitrile) (AIBN) was used as initiator. The acetoxy groups of the copolymer were subsequently hydrolysed quantitatively to hydroxyl groups using hydrazine hydrate. Copolymer composition was determined using ^1H n.m.r. G.p.c. analysis gave $M_w = 32\,960$ and $M_w/M_n = 1.63$ for the copolymer.

Appropriate amounts of copolymer and PIBMA were weighed and dissolved in methyl ethyl ketone to produce a 10% w/v polymer solution. The solutions were cast on aluminium plates. The solvent was slowly removed overnight at ambient temperature. Complete removal of the solvent was done in a vacuum oven at 110°C, where the samples remained for up to 7 days. During measurements the samples were kept in a desiccator to prevent them from absorbing any moisture.

The glass transition temperatures were determined using a Shimadzu fast quenching differential scanning calorimeter, model DSC-50Q. Approximately 10 mg of

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each blend was weighed and sealed in aluminium pans. Each sample was initially heated to 40°C above T_g and held at that temperature for 10 min. It was subsequently quenched with liquid nitrogen and rescanned again at a rate of 10°C min^{-1} up to a final temperature that was 40°C above the T_g of the blend. A second rescanning was conducted for verification.

In *Figure 1* are shown the experimental glass transition temperatures of the blends. As observed, the blend is miscible over the full composition range. It is also observed that the T_gs exhibit a positive deviation from linearity over the full composition range. A rationalization of this behaviour is undertaken in the next section.

THEORETICAL

The general thermodynamic theory of hydrogen-bonded systems and the detailed derivations are presented in the original paper[8]. Here we will present the formalism for the case of a binary system consisting of a polymer (component 1) with d_1 proton-donor groups and a_1 $(=d_1)$ proton-acceptor groups, and a polymer (component 2) with a_2 proton-acceptor groups.

Consider a mixture of N_1 and N_2 molecules of type 1 and 2, respectively, at temperature T and external pressure P. Each molecule of type 1 or 2 consists of r_1 or r_2 segments, respectively. The molecules are assumed to be arranged on a quasi-lattice of N_r sites, N_0 of which are empty. Following the nomenclature of ref. 8, let molecules of type 1 and 2 be characterized by v_1^* and v_2^* hard-core volumes per segment and ε_1^* and ε_2^* average intermolecular interaction energies per segment, respectively. The N_r sites of the quasi-lattice are given by

$$N_r = N_0 + r_1N_1 + r_2N_2 \tag{1}$$

In the following one should distinguish between segment fractions and site fractions in the mixture. Segment fractions are defined by

$$\phi_i = \frac{r_iN_i}{r_1N_1 + r_2N_2} = \frac{r_iN_i}{rN} = \frac{x_ir_i}{r} \tag{2}$$

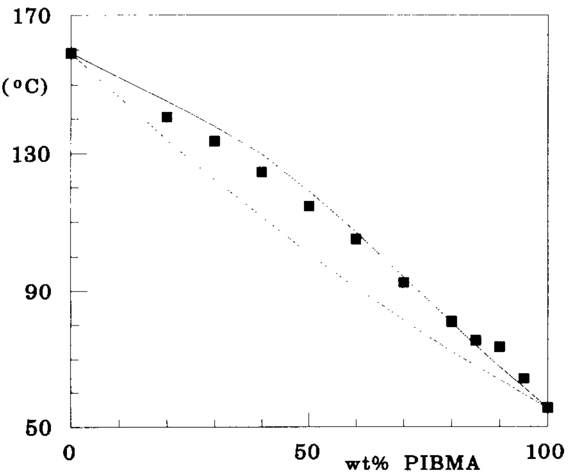

Figure 1 Glass transition temperatures of the mixture SVPh60/PIBMA. Filled squares are experimental data. Solid line was calculated with the present model. Dashed line is the non-hydrogen-bonding contribution to T_g

while site fractions are defined by

$$f_i = \frac{r_iN_i}{N_r} = \frac{r_iN_i}{rN}\frac{rN}{N_r} = \phi_i\tilde{\rho} \qquad i = 1, 2 \tag{3}$$

where x_i is the mole fraction of component i in the mixture. The fraction of empty sites is analogously defined by

$$f_0 = \frac{N_0}{N_r} = \frac{N_r - rN}{N_r} = 1 - \tilde{\rho} \tag{4}$$

where $\tilde{\rho} = (1/\tilde{v})$ is the reduced density ($\tilde{v}$ being the reduced volume) which can be obtained from the equation of state given later.

The crucial assumption of the equation-of-state theory of hydrogen bonding[8,9] is the division of intermolecular interactions into physical (or van der Waals') and chemical (or specific, e.g. hydrogen bonding) interactions. A direct consequence of this is the factorization of the canonical partition function of our system (in its maximum term approximation) into two factors, one physical Q_P and one chemical Q_H, or

$$Q = Q_PQ_H \tag{5}$$

Following our previous practice[8,9,11], we approximate the physical factor Q_P by the lattice–fluid partition function[12,13]

$$Q_P = \left(\frac{1}{f_0}\right)^{N_0} \prod_{i=1}^{2} \left(\frac{\omega_i}{f_i}\right)^{N_i} \exp\left(-\frac{E_{LF}}{RT}\right) \tag{6}$$

E_{LF} is the physical contribution to the lattice (intermolecular potential) energy of the system and is given by

$$-E_{LF} = rN\tilde{\rho}\varepsilon^* \tag{7}$$

For simplicity we will not differentiate here surface fractions from segment fractions. The full surface fraction formalism has been presented previously[8]. In the one fluid approximation the average interaction energy per segment in the mixture is assumed to be given by the following combining and mixing rules

$$\varepsilon^* = \sum_i \sum_j \phi_i\phi_j\varepsilon_{ij}^*$$
$$\varepsilon_{12}^* = \xi_{12}\sqrt{\varepsilon_1^*\varepsilon_2^*} \tag{8}$$

$(\varepsilon_{ii}^* = \varepsilon_i^*)$. ξ_{ij} in equation (8) is a dimensionless binary parameter expected to have values close to unity (Berthelot's rule). For simplicity, this parameter was set equal to unity throughout this work.

In equation (6) ω_i is given by

$$\omega_i = \delta_i \frac{r_i}{\sigma_i} \exp(1 - r_i) \tag{9}$$

where σ_i is a symmetry number (taken equal to unity here) and δ_i is given by[9]

$$\delta_i^{N_i} = \frac{Z_i^{N_i}(Z_i - 2)^{f_iN_i(r_i-2)}[(r_i - 2)N_i]!}{[f_iN_i(r_i - 2)]![(1 - f_i)N_i(r_i - 2)]!} \exp\left[\frac{-f_iN_i(r_i - 2)\varepsilon_i}{RT}\right] \tag{10}$$

Z_i is the bond (lattice) coordination number (bond conformations) for bond of type i. For simplicity we set $Z_1 = Z_2 = Z$. ε_i is the flex energy for bonds of type i, that is the potential energy of the $Z - 1$ bend conformations over the favoured conformation. The equilibrium fraction f_i of bonds i in bent conformations is given by

$$f_i=\frac{(Z-2)\exp(-\varepsilon_i/RT)}{1+(Z-2)\exp(-\varepsilon_i/RT)} \tag{11}$$

The chemical or hydrogen bonding factor in equation (5) is given by[8]

$$Q_{\mathrm{H}}=\left(\frac{\tilde{\rho}}{rN}\right)^{N_{\mathrm{H}}}\frac{(\mathrm{N}_1\mathrm{d}_1)!}{\mathrm{N}_{10}!}\prod_{j=1}^{2}\frac{(\mathrm{N}_j\alpha_j)!}{\mathrm{N}_{0j}!\mathrm{N}_{1j}!}\exp\left(-\frac{N_{1j}F^0_{1j}}{RT}\right) \tag{12}$$

where

$$N_{\mathrm{H}}=N_{11}+N_{12} \tag{13}$$

is the total number of hydrogen bonds in the system and

$$F^0_{1j}=E^0_{1j}-TS^0_{1j} \tag{14}$$

is the free energy change upon formation of the hydrogen bond of type $1-j$. In addition

$$N_{10}=N_1d_1-N_{11}-N_{12} \tag{15}$$

is the number of donors of type 1 that are not hydrogen bonded. Similarly

$$N_{0j}=N_j\alpha_j-N_{1j} \qquad j=1,2 \tag{16}$$

is the number of acceptors of type j that are not hydrogen bonded.

On the basis of equation (5) we may write for the Gibbs partition function (N, P, T ensemble) of the system

$$\Psi=Q_{\mathrm{P}}Q_{\mathrm{H}}\exp\left(-\frac{PV}{RT}\right) \tag{17}$$

The total volume V of the system is given by

$$V=rN\tilde{v}v^*+N_{11}V^0_{11}+N_{12}V^0_{12} \tag{18}$$

The V^0_{1j}s are the volume changes accompanying hydrogen bond formation between an (1, j) pair. The hard-core volume per segment in the mixture is assumed, for simplicity, to be given by

$$v^*=\phi_1v^*_1+\phi_2v^*_2 \tag{19}$$

On the basis of equation (17) we may write for the Gibbs free energy of the system and in its maximum term approximation

$$G=-RT\ln\Psi=G_{\mathrm{LF}}+G_{\mathrm{H}} \tag{20}$$

A direct consequence of this approximation are the following minimization conditions

$$\left(\frac{\delta G}{\delta\tilde{v}}\right)_{T,P,\{N_k\},\{N_{ij}\}}=0 \tag{21}$$

$$\left(\frac{\delta G}{\delta N_{1j}}\right)_{T,P,\tilde{v},\{N_k\},\{N_{1s}\}_{s\neq j}}=0 \tag{22}$$

The first of these two minimization conditions leads to the equation of state

$$\tilde{P}+\tilde{\rho}^2+\tilde{T}\left[\ln(1-\tilde{\rho})+\tilde{\rho}\left(1-\frac{1}{\bar{r}}\right)\right]=0 \tag{23}$$

where the reduced pressure, $\tilde{P}$, is defined by

$$\tilde{P}=\frac{P}{P^*}=\frac{P\varepsilon^*}{v^*} \tag{24}$$

the reduced temperature, $\tilde{T}$, by

$$\tilde{T}=\frac{T}{T^*}=\frac{RT}{\varepsilon^*} \tag{25}$$

and the modified average chain length, $\bar{r}$, by

$$\frac{1}{\bar{r}}=\frac{1}{r}-\sum_{j=1}^{2}\frac{N_{1j}}{rN}=\frac{1}{r}-\nu_{\mathrm{H}} \tag{26}$$

where ν_{H} is a measure of the fraction of hydrogen bonds in the system.

The second minimization condition, equation (22), yields

$$\frac{\nu_{1j}}{\nu_{10}\nu_{0j}}=\tilde{\rho}\exp(G^0_{1j}/RT) \qquad j=1,2 \tag{27}$$

where

$$\nu_{1j}=\frac{N_{1j}}{rN} \quad \nu_{10}=\frac{N_{10}}{rN} \quad \nu_{0j}=\frac{N_{0j}}{rN} \tag{28}$$

and the free enthalpy change accompanying formation of one (1, j) hydrogen bond is given by

$$G^0_{1j}=E^0_{1j}+PV^0_{1j}-TS^0_{1j} \tag{29}$$

Equations (27) is a set of two simultaneous quadratic equations in ν_{1j}. They may easily be solved by a trial-and-error procedure as described in ref. 8.

On the basis of equation (20) we may now write for the entropy of the system

$$S=-\frac{\partial G}{\partial T}=S_{\mathrm{LF}}+S_{\mathrm{H}} \tag{30}$$

The first physical term may be written, for convenience, as follows

$$\frac{S_{\mathrm{LF}}}{RrN}=\frac{S^{\mathrm{c}}_{\mathrm{LF}}}{RrN}+\frac{\phi_1}{r_1}\ln\delta_1+\frac{\phi_2}{r_2}\ln\delta_2 \tag{31}$$

The first term on the right-hand side is the 'configurational' contribution and the remaining terms are the 'internal' or 'flexibility' contributions to the entropy. The first term may be written as[14]

$$\frac{S^{\mathrm{c}}_{\mathrm{LF}}}{RrN}=(1-\tilde{v})\ln(1-\tilde{\rho})+\frac{\ln\tilde{v}}{r}-\frac{x_1\ln x_1+x_2\ln x_2}{r}+\frac{\ln r}{r}+\frac{1}{r}-1 \tag{32}$$

From equation (10) we may write

$$\ln\delta_i=\ln Z_i+f_ir_i\ln(Z_i-Z)-f_ir_i\ln f_i-r_i(1-f_i)\ln(1-f_i)-\frac{f_ir_i\varepsilon_i}{RT} \tag{33}$$

and by combining equations (12), (17), (20) and (30) we obtain

$$\frac{S_{\mathrm{H}}}{RrN}=-\nu_{\mathrm{H}}+\frac{\phi_1d_1}{r_1}\ln\frac{\phi_1d_1}{\phi_1d_1-r_1\nu_{\mathrm{H}}}+\frac{\phi_1a_1}{r_1}\ln\frac{\phi_1a_1}{\phi_1a_1-r_1\nu_{11}}+\frac{\phi_2a_2}{r_2}\ln\frac{\phi_2a_2}{\phi_2a_2-r_2\nu_{12}} \tag{34}$$

Table 1 Parameters for pure polymers

Polymer	T^* (K)	P^* (MPa)	ρ^* (kg m^{-3})	T_g (K)	ε (J mol^{-1})
Poly(dimethyl siloxane)	476	302	1104	150	338
Poly(ε-caprolactone)	708	388	1127	202	406
Poly(vinyl methyl ether)	657	353	1100	244	675
Poly(n-butyl methacrylate)	627	431	1125	300	1245
Poly(isobutyl methacrylate)	621	395	1164	329	1451
Poly(methyl methacrylate)	696	503	1269	395	1914
Polystyrene (atactic)	735	357	1105	373	1560
Poly(vinyl chloride)	721	413	1464	355	1427
Poly(2,6-dimethyl phenylene oxide)	739	517	1161	489	2900
MPS9.7	735	357	1105	383	1672
MPS16.7	735	357	1105	386	1688
SVPh60	735	357	1105	432	2211
Polyisobutylene	643	354	974	243	687

APPLICATION TO THE GLASS TRANSITION

As before[14,15] we adopt here the Gibbs–DiMarzio argument[16,17] that at a transition temperature T_2, the entropy S of the system is becoming zero. This transition temperature has been found to be proportional to the glass transition temperature T_g of the system, the proportionality constant[18,19] being about 0.77. Using this argument for pure polymers one can determine the flex energy ε by zeroing the entropy at T_2. For all practical purposes, however, one may follow this process directly at the glass transition temperature and determine the pure polymer flex energy ε by zeroing the entropy at the T_g. We have adopted for convenience this latter process and determined the flex energies of a number of polymers, which are reported in *Table 1*. In the same table are also reported the lattice–fluid scaling constants for the same polymers. The scaling constants for poly(isobutyl methacrylate) have been determined on the basis of *PVT* measurements kindly provided by Professor I. C. Sanchez from the University of Texas at Austin.

Once the flex energies ε for pure polymers are known, one may use Gibbs–DiMarzio's argument for the mixture and find the temperature at which the entropy is becoming zero. By identifying this temperature with the glass transition temperature one has a predictive scheme for the glass transition temperatures of the polymer mixtures. This is the calculation scheme that we have adopted in this work.

In order to use this scheme in our systems, we need an estimate of the hydrogen bonding parameters for the OH- - -OH and OH- - -O=CO interactions. These parameters have been estimated previously[9] from phase equilibrium and *PVT* data for the mixture poly(vinyl phenol) + poly(vinyl acetate). For the OH- - -OH interaction they are: $E^0_{11} = -21.8$ kJ mol^{-1}, $S^0_{11} = -26.5$ J K^{-1} mol^{-1} and $V^0_{11} = 0.0$ cm^3 mol^{-1}, and for the OH- - -O=CO interaction they are: $E^0_{12} = -18.4$ kJ mol^{-1}, $S^0_{12} = -12.8$ J K^{-1} mol^{-1} and $V^0_{12} = 0.0$ cm^3 mol^{-1}. With these parameters, and following the above calculation scheme, we have calculated the glass transition temperatures for the mixture SVPh60 + PIBMA, which are compared with the experimental ones in *Figure 1*. Notice that we have not made any new binary parameter adjustment in this work. The theory seems to be in qualitative agreement with the experiment. It predicts correctly the positive deviation of the glass transition temperature of the mixture from the straight line between the T_gs of the pure components ($w_1T_{g1} + w_2T_{g2}$). In the same figure is also shown the prediction of the theory by disregarding the hydrogen bonding contribution. As observed, the hydrogen bonding contribution is a major contribution to the T_g of the mixture.

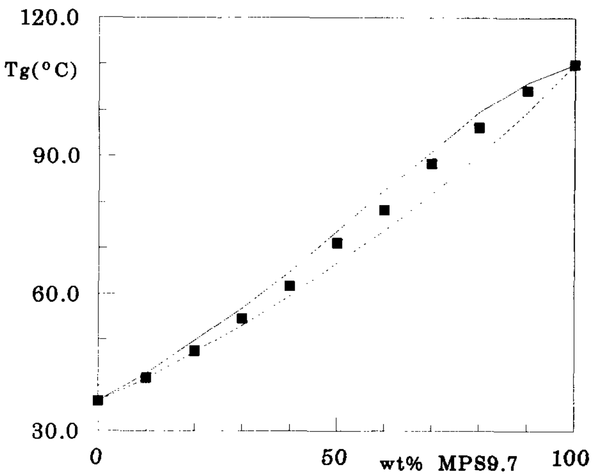

Figure 2 Glass transition temperatures of the mixture MPS9.7/PBMA. Filled squares are experimental data[6]. Solid line was calculated with the present model. Dashed line is the non-hydrogen-bonding contribution to T_g

To further test the model we have used relevant experimental data from the open literature. We have chosen data for mixtures with known lattice–fluid and hydrogen bonding parameters. Such systems are the mixtures of styrene-*co*-vinyl phenol hexafluorodimethyl carbinol (MPS) with poly(n-butyl methacrylate) (PBMA) studied by Pearce *et al.*[6]. The hydrogen bonding parameters for this system are[8]: $E^0_{11} = -25.1$ kJ mol^{-1}, $S^0_{11} = -26.5$ J K^{-1} mol^{-1}, $V^0_{11} = 0.0$ cm^3 mol^{-1}, $E^0_{12} = -18.4$ kJ mol^{-1}, $S^0_{12} = -12.8$ J K^{-1} mol^{-1} and $V^0_{12} = 0.0$ cm^3 mol^{-1}. For simplicity, the lattice–fluid scaling constants for the copolymers were set equal to those of

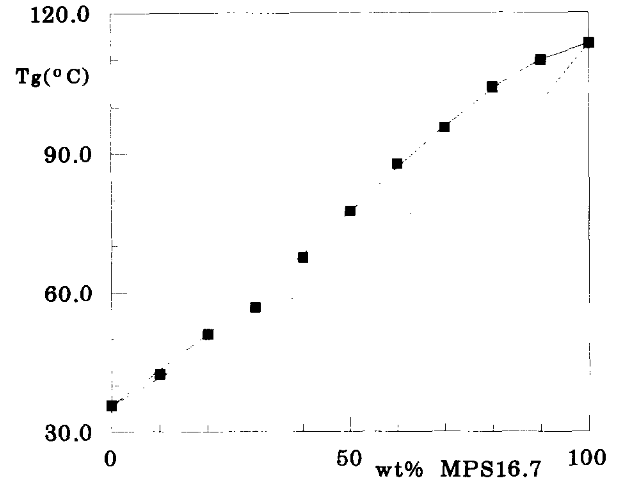

Figure 3 Glass transition temperatures of the mixture MPS16.7/PBMA. Symbols are as in *Figure 2*

polystyrene as before[8]. With these parameters we have calculated the T_gs of the mixtures MPS9.7 + PBMA and MPS16.7 + PBMA (the numbers after MPS indicate the vinyl phenol content of the copolymers), which are compared with the experimental ones in *Figures 2* and *3*. As can be seen, the theoretical predictions are in rather good agreement with the experiment over the full composition range. Once again, the model is able to predict the above-mentioned positive deviation of T_g from the weighted-average ones. In this case also the hydrogen bonding contribution to the T_g of the polymer mixture is an important contribution.

DISCUSSION AND CONCLUSIONS

In this work we have combined a recent equation-of-state theory of hydrogen bonding[8] with the Gibbs–DiMarzio[16,17] theory of glass transition in order to predict the composition dependence of the T_g in polymer mixtures which interact with strong specific intermolecular forces. It has been shown that the hydrogen bonding contribution to T_g is by no means negligible, at least in the studied systems. The limitations of both the lattice–fluid theory and the Gibbs–DiMarzio theory are well known[8,14,15]. The theoretical predictions, however, of their combination presented here are in rather satisfactory agreement with the experiment. The limiting factor for using the theory is the availability of the required hydrogen bonding parameters and the pure component scaling constants. It is hoped that in the near future there will be a larger set of these parameters available. Spectroscopic studies of such polymer mixtures will be particularly useful in this respect. Work is in progress in our laboratory towards this end.

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