

A Lattice-Fluid, Group-Contribution Treatment of the Glass Transition of Homopolymers, Copolymers, and Polymer Solutions

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ABSTRACT: The glass transition temperature of polymers and polymer solutions was approached through a combination of the group-contribution, lattice-fluid equation of state and the Gibbs–DiMarzio criterion. The model assumes zero entropy at the glass transition temperature and treats molecules as semiflexible chains. This stiffness is associated with a flex energy obtained from the glass transition temperature at atmospheric pressure. Whereas the application of the model is straightforward for homopolymers and polymer solutions, a new formalism using the dyad concept was developed for copolymers. It takes into account the copoly-

mer composition as well as the sequencing of the monomers. The results obtained are consistent with experimental data. For polymer solutions, the model predictions are semiquantitative depending on the system. The interaction parameter required for binary systems was found to have little effect on the glass transition temperature predictions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 697–705, 2003

Key words: glass transition; lattice models; modeling; equation of state; copolymer; polymer solutions

INTRODUCTION

Polymers are characterized by a distinct transition from an amorphous state to a glassy state. Although this phenomenon has been studied extensively, its nature, kinetic or thermodynamic, is still not known. It is often referred to as a second-order transition because the density changes continuously along the transition, whereas a discontinuity is observed for the thermal expansion coefficient. The glassy state is not an equilibrium state in the thermodynamic sense. Thus, several criteria have been proposed for the occurrence of the glass transition. The earliest were based on the free-volume concept and on the conformational entropy.

Williams et al.¹ proposed that the glass transition temperature occurred at a specific value of the free volume as determined from the viscoelastic behavior of polymers. Kelly and Bueche² later applied this concept to polymer solutions. They proposed that the polymer solution free volume was equal to the volume fraction average of the pure polymer and solvent-free volumes. The model accurately predicted the solution glass transition temperature. However, below a certain temperature (52°C in the case of polystyrene and diethyl benzene), the contribution of the polymer free

volume becomes negative, which is physically incorrect.

The most successful thermodynamic criterion of the occurrence of the glass transition was proposed by Gibbs and DiMarzio,³ who introduced an entropic interpretation based on the configurational entropy. In their original work, the true glass transition temperature (T_g) is associated with a second-order transition that occurs at T_2 , about 50°C below the measured T_g . As the transition occurs, the molecular configurational entropy was assumed to be equal to zero. This criterion has been widely used in combination with different lattice models for pure polymers, polymer solutions, and polymer blends.^{4–6}

The objective of this work was not to support either of these theories. Rather, we endeavored to propose a simple and effective thermodynamic-based approach requiring the least *a priori* information to predict the glass transition of homopolymers, copolymers, and polymer solutions.

To have a predictive model applicable to copolymers, the pure component parameters were obtained by using the group contribution method developed by Lee and Danner⁷ as applied to the equation of state of Panayiotou and Vera.⁸ The combination of the equation of state (EoS) of Panayiotou and Vera and the group contribution method are referred to as the group-contribution lattice-fluid (GCLF) EoS. The number of configurations available to the system is a contribution of the intra- and intermolecular configu-

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rations. In the Panayiotou–Vera model, these contributions are expressed in two separate terms. The intramolecular configuration term was assumed not to contribute to the equation of state. An estimation of the entropy, however, requires an explicit expression for the number of intramolecular configurations. In this work, the intramolecular configuration term was treated by assuming that each bond can be described by two energetic configurations. The transition from one configuration to another is characterized by a flex energy.

The treatment of copolymers by use of an EoS generally requires input information such as densities and/or other thermodynamic data. If a group contribution approach is used, only the molecular structure of the monomers and their proportion in the copolymer are required. Lee and Danner⁹ have shown that with the GCLF-EoS only the molecular structure was needed to successfully predict the sorption of vapors in copolymers. In the case of the T_g , the sequencing drastically affects the glass transition. In the following, the formalism based on the GCLF-EoS and the Gibbs–DiMarzio criteria is extended to copolymers for which the sequencing is treated by using the dyad concept.

THEORY

The general form of the canonical partition function (as given by Panayiotou and Vera⁸) for N_1, N_2, \dots, N_p semiflexible molecules having a configurational energy, E , was expressed as

$$Q = \Omega \exp\left(-\frac{E}{RT}\right) \quad (1a)$$

$$Q = \prod_{i=1}^p \left(\frac{\delta_i}{\sigma_i}\right)^{N_i} g_c g_{nr} \exp\left(-\frac{E}{RT}\right) \quad (1b)$$

Here Ω is the number of configurations available to the system. It expands into g_c , the combinatorial term assuming a random distribution of the molecules, g_{nr} , the nonrandom correction for the combinatorial term, and δ_i/σ_i , which account for the flexibility and the symmetry of a molecule. The lattice-fluid theory as used in this model approximates the molecule by its equivalent made of r identical segments occupying consecutive lattice sites. The symmetry parameter is thus equal to 2. The flexibility parameter accounts for the number of internal configurations available to a semiflexible molecule i occupying r_i sites. Each lattice site is assumed to have a constant volume ($v_h = 9.75 \times 10^{-6} \text{ m}^3/\text{mol}$) and a fixed coordination number ($z = 10$). The lattice cells may be occupied (by molecules) or vacant (holes).

Following the treatment of Gibbs and DiMarzio, a r_i -mer is assumed to have two energetic states ($z' - 1$

of high energy and 1 of low energy). The flexibility parameter is expressed as a function of f_i , the fraction of r_i -mers in the higher energy state^{10,11}:

$$\delta_i = z' \left(\frac{z' - 2}{f_i}\right)^{(r_i-2)f_i} \left(\frac{1}{1 - f_i}\right)^{(r_i-2)(1-f_i)} \quad (2)$$

Havlicek et al.¹² found a z' value between 4 and 6 for several polymers from a fit of thermodynamic properties of polymers. For the current study, z' was set equal to 4, as suggested by Gibbs and DiMarzio.³

In the treatment of both pure fluids and mixtures, the holes are assumed to have a random distribution in the lattice. For pure fluids, the molecules are also assumed to have a random distribution. The canonical partition function of pure fluids does not involve the nonrandomness term that is used for mixtures where molecules of different species are allowed to have a nonrandom distribution. Because of this difference, different treatments are required for pure fluids and mixtures.

The random combinatorial term adopted was that proposed by Guggenheim–Huggins–Miller,¹³

$$g_c = \frac{N_r!}{N_h! \prod_{i=1}^p N_i!} \left(\frac{N_q!}{N_r!}\right)^{z/2} \quad (3)$$

Here, N_r and N_h are, respectively, the total number of cells and the number of holes in the lattice, and zN_q is the number of external contacts displayed by the system,

$$N_r = N_h + \sum r_i N_i \quad (4)$$

$$zN_q = zN_h + zq_i N_i \quad (5)$$

$$zq_i = r_i(z - 2) + 2 \quad (6)$$

The number of external contacts is expressed in eq. (5) as a function of the product zq_i , which is the number of interacting sites per molecule.

The system energy E is calculated by using the mean field approximation. It is a contribution of the intermolecular interactions and the intramolecular configurational energies accounting for the flexed bonds. A r_i -mer has $(r_i - 2)$ bonds that may be flexed, each having an energy $\Delta\varepsilon_i$. The total energy of the system is written as

$$E = \sum_{i=1}^p \sum_{j=1}^p P_{ij} \varepsilon_{ij} + \sum_{i=1}^p N_i f_i (r_i - 2) \Delta\varepsilon_i \quad (7)$$

where P_{ij} is the probability of interaction between species i and j with an interaction potential energy ε_{ij} . A pure fluid i is defined by two specific parameters referred to as the scaling parameters ε_{ii} and r_i . In the present treatments, they are obtained by using the

group-contribution method implemented by Lee and Danner.⁷ The first term of eq. (7) refers to the intermolecular interactions. More details on that term could be found in the original article of Panayiotou and Vera.⁸

The equilibrium number of flexed bonds is obtained by finding the minimum of the canonical partition function with respect to f_i . An expression identical to that obtained by Gibbs and DiMarzio³ was derived as

$$f_i = \frac{(z' - 2)\exp(-\Delta\varepsilon_i/kT)}{1 + (z' - 2)\exp(-\Delta\varepsilon_i/kT)} \quad (8)$$

Following the standard treatment of the partition function, the equation of state of Panayiotou and Vera⁸ is obtained

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v} - 1}\right) + \frac{z}{2} \ln\left(\frac{\tilde{v} + q/r - 1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \quad (9)$$

where \tilde{P} , \tilde{T} , and \tilde{v} are the reduced pressure, temperature, and molar volume, respectively, and

$$\tilde{P} = P/P^* \quad \tilde{T} = T/T^* \quad \tilde{v} = v/v^* \quad \theta = \frac{q/r}{\tilde{v} + q/r - 1} \quad (10)$$

and

$$P^* = z\varepsilon^*/2\nu_h \quad T^* = z\varepsilon^*/2R \quad v^* = \nu_h r N \quad (11)$$

with the following mixing rules:

$$r = \sum_{i=1}^p x_i r_i \quad q = \sum_{i=1}^p x_i q_i \quad \varepsilon^* = F(\varepsilon_{ii}, \varepsilon_{ij})$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} (1 - k_{ij}) \quad (12)$$

The molecular interaction parameter ε^* is a function $[F(\varepsilon_{ii}, \varepsilon_{ij})]$ of the pure components interaction energy ε_{ii} and the cross interaction energy ε_{ij} . More details on this relationship may be obtained in the original article of Panayiotou and Vera.⁸ Furthermore, the binary interaction parameter k_{ij} is obtained by using the group-contribution method implemented by Lee and Danner.⁷

Pure fluids

The criterion of the T_g as defined by Gibbs and DiMarzio is a value of 0 for the system entropy, which is a function only of the number of degeneracies. The system entropy is expressed as

$$S = k \ln \left[\left(\frac{\delta_i}{\sigma_i} \right)^{N_i} g_c \right] \quad (13a)$$

Substituting eqs. (2), (3), and (8) into eq. (13a) gives

$$\frac{S}{kr_i N_i} = (\tilde{v}_i - 1) \ln \left(\frac{\tilde{v}_i}{\tilde{v}_i - 1} \right) + \left(\frac{z\tilde{v}_i}{2} - 1 \right) \ln \left(\frac{\tilde{v}_i - 1 + q_i/r_i}{\tilde{v}_i} \right)$$

$$+ \frac{1}{r_i} \ln(\tilde{v}_i - 1 + q_i/r_i) + \frac{1}{r_i} \ln \left(\frac{z'r_i}{2} \right)$$

$$+ \left(\frac{r_i - 2}{r_i} \right) \left[f_i \frac{\Delta\varepsilon_i}{kT} - \ln(1 - f_i) \right] \quad (13b)$$

Here \tilde{v}_i is the reduced specific volume calculated from the equation of state for pure component i . For very large molecules where r approaches infinity, eq. (13b) becomes

$$\frac{S}{kr_i N_i} = (\tilde{v}_i - 1) \ln \left(\frac{\tilde{v}_i}{\tilde{v}_i - 1} \right) + \left(\frac{z\tilde{v}_i}{2} - 1 \right) \ln \left(\frac{\tilde{v}_i - 0.2}{\tilde{v}_i} \right)$$

$$+ \left[f_i \frac{\Delta\varepsilon_i}{kT} - \ln(1 - f_i) \right] \quad (13c)$$

Binary mixtures

For binaries, the nonrandomness term is taken into account

$$g_{nr} = \frac{\bar{N}_{11}^0! \bar{N}_{22}^0! \left(\frac{\bar{N}_{12}^0}{2} \right)!^2}{\bar{N}_{11}! \bar{N}_{22}! \left(\frac{\bar{N}_{12}}{2} \right)!^2} \quad \text{and} \quad \bar{N}_{ij} = \bar{N}_{ij}^0 \Gamma_{ij} \quad (14)$$

Here \bar{N}_{ij}^0 and \bar{N}_{ij} are the number of energetic external contacts for random and nonrandom distributions of species i and j . Panayiotou and Vera have followed the quasi-chemical treatment of Guggenheim¹³ to account for nonrandomness and to obtain the nonrandomness factor Γ_{ij} .

The system entropy is calculated as

$$S = k \ln \left[\left(\frac{\delta_1}{\sigma_1} \right)^{N_1} \left(\frac{\delta_2}{\sigma_2} \right)^{N_2} g_c g_{nr} \right] \quad (15a)$$

Substituting eqs. (2), (3), (8), and (14) in eq. (15a) gives

$$\frac{S}{krN} = (\tilde{v} - 1) \ln \left(\frac{\tilde{v}}{\tilde{v} - 1} \right) + \left(\frac{z\tilde{v}}{2} - 1 \right) \ln \left(\frac{\tilde{v} - 1 + q/r}{\tilde{v}} \right)$$

$$+ \frac{1}{r} \ln(\tilde{v} - 1 + q/r) + \frac{1}{r} \ln \left(\frac{zr}{2} \right) + \sum_{i=1}^2 x_i \left(\frac{r_i - 2}{r} \right) \left(f_i \frac{\Delta\varepsilon}{kT} \right.$$

$$\left. - \ln(1 - f_i) \right) + \frac{z}{2r} \left[(\Gamma_{12} \theta \dot{\varepsilon} / kT) \left(\prod_{i=1}^2 x_i q_i \right) - \sum_{i=1}^2 x_i q_i \ln(\Gamma_{ii}) \right] \quad (15b)$$

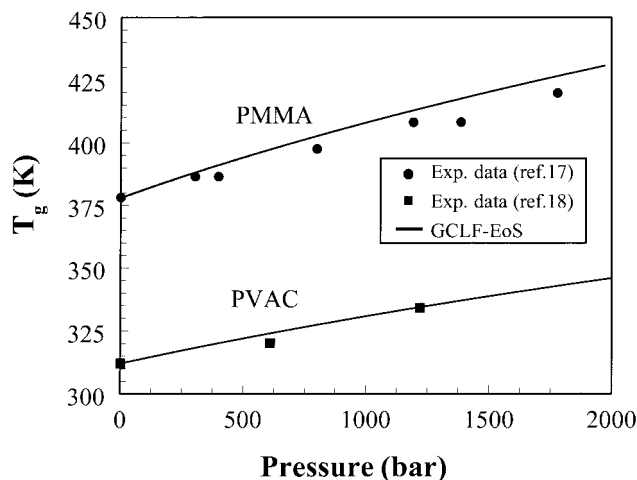


Figure 1 Effect of pressure on the glass transition temperature of poly(methyl methacrylate) and poly(vinyl acetate).

Here

$$\hat{\varepsilon} = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \quad (16)$$

Equation (15b) reduces to the pure equation fluid because the Γ_{ij} are equal to 1 for the pure components because of the random distribution assumption. The cross interaction energy ε_{12} is obtained from eq. (12).

RESULTS AND DISCUSSION

Pure polymers

In eq. (13b), the only unknown in the expression of the entropy is the polymer flex energy. A fit of the flex energy is obtained from the T_g at ambient pressure assuming a vanishing configurational entropy. The scatter in the reported values for the T_g is quite high. The generally accepted value for polystyrene is 100°C, although values as low as 90°C¹⁴ and as high as 107°C¹⁵ have been reported. In fact, the glass transition phenomenon spreads over a wide temperature range, inducing a significant measurement scatter as can be seen in dynamic scanning chromatography thermograms.¹⁶ The molecular weight may also play an important role. Equation (13c) could be used for high molecular weight polymers.

The effect of pressure on the T_g was predicted by using the GCLF-EoS and compared against experimental data for poly(methyl methacrylate)¹⁷ and poly(vinyl acetate).¹⁸ As shown in Figure 1, the model predictions and the experimental results are in good agreement. Furthermore, the model displays a curvature, indicating an asymptotic behavior of T_g with pressure, which is theoretically expected.¹⁹

Copolymers

Treatment of copolymers requires an average value for the molecular flex energy. A weighted average

value of the monomeric units is not satisfactory. Following such a procedure, the copolymer T_g cannot be lower than that of any of the homopolymers. Lower values have been found, however, for several cases such as poly(styrene-*co*-methyl methacrylate),^{20,21} poly(vinylidene chloride-*co*-methyl acrylate),²¹ and poly(phenyl acrylate-*co*-methyl methacrylate).²²

The glass transition temperature of copolymers has often been examined within the framework of several semiempirical equations.^{23,24} These approaches were in the form of an average between the homopolymers T_g 's and their weight fractions in the copolymer. Ellerstein²⁵ and later, Johnston,²⁶ pointed out that a copolymer [poly(A-*co*-B)] comprises three types of dyads: AA, BB, and AB. A more accurate prediction of the copolymer T_g must take into account its composition in terms of the dyads and the T_g of the alternating copolymer. Barton¹⁴ proposed the following equation for the copolymer T_g :

$$T_g = w_{AA}T_{gA} + w_{BB}T_{gB} + w_{AB}T_{gAB} \quad (17)$$

whereas Johnston^{26,27} suggested that

$$\frac{1}{T_g} = \frac{w_{AA}}{T_{gA}} + \frac{w_{BB}}{T_{gB}} + \frac{w_{AB}}{T_{gAB}} \quad (18)$$

Here w_{AA} , w_{BB} , and w_{AB} are the weight fractions or mole fractions of the AA, BB, and AB sequences, and T_{gAB} is the T_g of the alternating copolymer. The weight fraction of the dyads has been expressed as a function of the overall copolymer composition. These expressions have been extensively used with T_{gAB} as a fitting parameter.^{22,27}

We have combined the GCLF-EoS with the Gibbs and DiMarzio concept and applied it to copolymers. Although eqs. (17) and (18) are empirical, the dyad concept that they are based on is sound. The sequence distribution of a copolymer has a direct influence on the T_g . The T_g of an alternating poly(vinylidene-*co*-methyl acrylate) is about 15°C higher than that of the random copolymer with the same composition.²¹ The dyad concept can be used to derive the flex energy of the copolymer as a function of the flex energy relative to the homopolymers and the alternating copolymer $\Delta\varepsilon_{AB}$. A mixing rule involving the flex energies is required. The parameter in this mixing rule is neither the weight fraction nor the mole fraction of the monomers, but the fraction of segments in each type of dyad. The following relation was used:

$$\Delta\varepsilon = \bar{s}_{AA}\Delta\varepsilon_{AA} + \bar{s}_{BB}\Delta\varepsilon_{BB} + \bar{s}_{AB}\Delta\varepsilon_{AB} \quad (19)$$

Here \bar{s}_{IJ} is the fraction of segments from the dyad IJ involved in the copolymer, $\Delta\varepsilon_{AA}$ and $\Delta\varepsilon_{BB}$ are the flex energies of the pure homopolymers, and $\Delta\varepsilon_{AB}$ is the

flex energy of the alternating copolymer. The monomers generally will occupy different numbers of lattice cells. DiMarzio and Gibbs²⁸ have treated this difference in terms of the number of bonds within each monomer. The fraction of segments found in the different dyads is not, therefore, a function of the copolymer composition only. The length of the monomer must be taken into account. Let r_A and r_B be the number of lattice sites occupied by monomers A and B. In this treatment, the number of lattice sites occupied by the monomers is obtained by using the group contribution method of Lee and Danner.⁷ The number of lattice sites occupied by the different dyads is obtained by simple additivity,

$$r_{AA} = 2r_A \quad (20)$$

$$r_{BB} = 2r_B \quad (21)$$

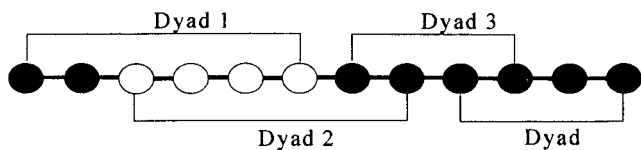
$$r_{AB} = r_A + r_B \quad (22)$$

If x_{AB} is the mole fraction of the AB dyad, the mole fraction of lattice sites it occupies is given by

$$\bar{r}_{AB} = \frac{x_{AB}r_{AB}}{x_{AA}r_{AA} + x_{BB}r_{BB} + x_{AB}r_{AB}} \quad (23)$$

The same equation applies to \bar{r}_{AA} and \bar{r}_{BB} . As a first approximation, the fraction of segments from dyad IJ , \bar{s}_{IJ} , is taken as equal to the fraction of lattice sites occupied by the dyad. Because a molecule occupies more than one lattice site, however, the contribution of these bonds to the overall flex energy of a molecule is averaged out by being counted twice, as shown below. Let monomer A occupy two lattice sites (solid circles) and monomer B occupy four lattice sites (open circles):

Let us consider the monomer A common to dyads 2 and 3. The bonds of this monomer contribute to an AB (dyad 2) and an AA (dyad 3) dyad. The overall mo-



lecular flex energy as expressed in eqs. (19) and (23) count the flex energy of monomer A in both dyads. In other words, the overall flex energy of monomer A will be given an average value of the flex energy for an AA dyad, $\Delta\epsilon_{AA}$, and an AB dyad, $\Delta\epsilon_{AB}$. The monomer common to dyads 3 and 4 is surrounded on both sides by an identical monomer and will contribute twice to the flex energy with a value equal to that of homopolymer A. On the other hand, the monomer common to dyads 1 and 2 will contribute twice to the flex energy with a value equal to that of the alternating copolymer

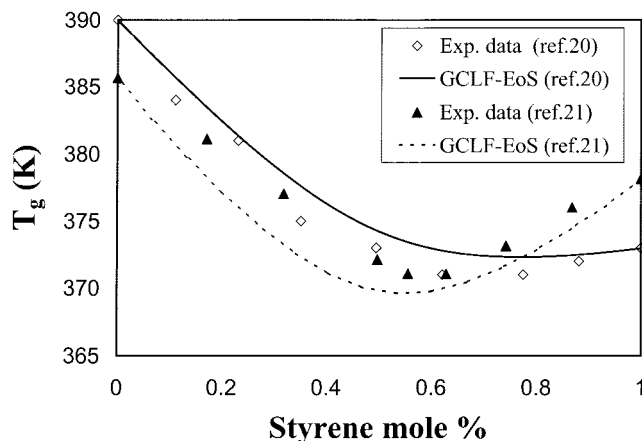


Figure 2 Glass transition temperature of styrene–methyl methacrylate copolymers.

AB. Thus, the dyad concept, as applied here, accounts for the first-order neighbors. It has the advantage over that of DiMarzio and Gibbs of implicitly incorporating some steric exclusion effects.

The distribution of dyads is a function of the monomer sequencing and may be calculated from the relation derived by Harwood and Richey,²⁹

$$x_{AB} = \frac{4x_Ax_B}{1 + [1 + 4x_Ax_B(\lambda_A\lambda_B - 1)^{1/2}]} \quad (24)$$

$$x_{AA} = x_A - \frac{x_{AB}}{2} \quad (25)$$

$$x_{BB} = x_B - \frac{x_{AB}}{2} \quad (26)$$

Here x_I and λ_I are the mole fraction and the reactivity ratio³⁰ of monomer I, and x_{IJ} is the mole fraction of dyad IJ .

For a given copolymer, the only needed information is the reactivity ratios and the T_g of the alternating copolymer. The T_g of the alternating copolymer is first used to obtain the flex energy of the dyad AB. The T_g of the copolymer along the whole composition range is then predicted by using the reactivity ratios generally available in the literature.

Figures 2, 3, and 4 compare the experimental and predicted T_g of different copolymers with composition. Figure 2 addresses the case of poly(styrene-*co*-methyl methacrylate) as obtained from two different sources.^{20,21} Podesva and Biroš²⁰ attributed their high measured value of the T_g of PMMA to its tacticity and to the measuring technique. Fernandez-Martin et al.³¹ have reviewed the T_g of PMMA with different tacticity and found a range from almost 310 to 400 K. This wide temperature range illustrates the difficulties of any study related to the T_g . Figure 3 shows excellent agreement between the GCLF-EoS predictions and the data

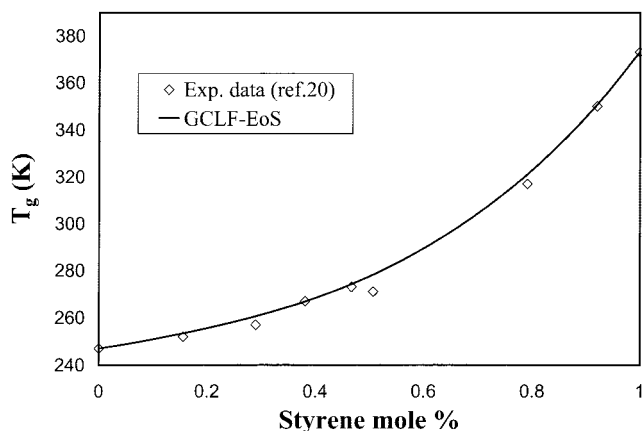


Figure 3 Glass transition temperature of styrene–octyl methacrylate copolymers.

of Podesva and Biroš²⁰ for the styrene–octyl methacrylate copolymer.

In the above cases, the flex energy of the homopolymers and alternating copolymer were obtained from the reference data. The model predictions are good with an average deviation of $<2^{\circ}\text{C}$. Also, the model successfully predicts the minima loci for the case of poly(styrene-*co*-methyl methacrylate), as shown in Figure 2. Figure 4 illustrates a case where the value of the flex energy of the alternating copolymer was obtained as an average of the homopolymers. The results are excellent. Such agreement can only be expected, however, in the case where neither steric hindrance nor specific interactions are involved.

The importance of the monomer distribution is illustrated in Figure 5. Three curves of poly(styrene-*co*-methyl methacrylate) were generated by using three different sets of reactivity ratios found in the literature. Table I gives the parameter values used for the pure polymers and alternating copolymer obtained from the measurements of Hirooka and Kato.²¹ Significant

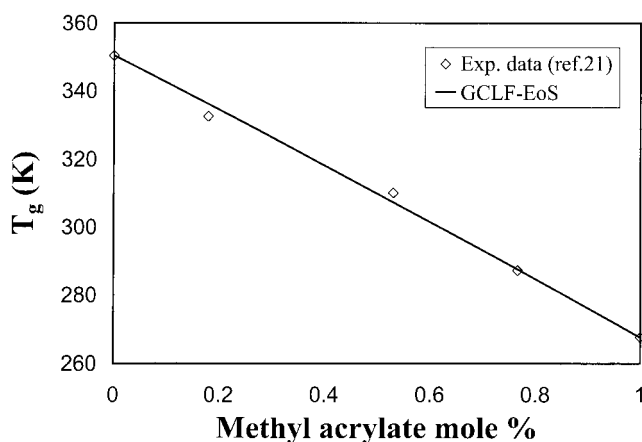


Figure 4 Glass transition temperature of methyl acrylate–vinyl chloride copolymers.

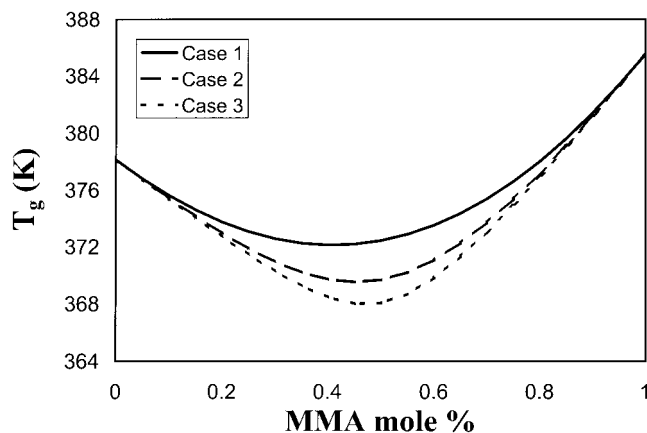


Figure 5 Effect of the copolymer sequencing and composition on the glass transition temperature of styrene–methyl methacrylate copolymers. The parameters used are given in Table I.

deviations are found particularly around the 50% composition area. The largest deviation is 4.4°C between case 1 and case 3. Much higher deviations can be obtained if the homopolymers differ more in their T_g 's. The locus of the minimum is shifted to higher MMA concentration as the comonomer sequencing changes from case 1 to case 3.

The success of the model shows that despite its simplistic background, the dyad approximation, combined with the mixing rule in eq. (19), can be applied for the prediction of copolymer T_g with composition for systems having a large deviation from linearity. The cases related to *n*-alkyl methacrylate copolymers are extreme because the alternating copolymer had a T_g below that of the homopolymers. In many cases, such as acrylate solvents and polystyrene,³² the copolymer glass transition is linear with composition. The alternating copolymer T_g is an arithmetic average of T_{gA} and T_{gB} , and the model predictions are accurate without any information on the alternating copolymer properties, as shown in Figure 4.

In the case where no data are available for the alternating copolymer, only one measurement obtained from a copolymer of known sequencing is necessary to generate the whole composition range if the reactivity ratios are known. Indeed, the flex energy of

TABLE I
Parameters Used for the Cases Shown in Figure 5

	T_g (K)	$\Delta\varepsilon$ (J/mol)	r_i		
			Case 1	Case 2	Case 3
PMMA	385.65	6641.61	0.387	0.611	0.220
	378.15	6142.99	2.28	0.371	0.396
Alt.copol. ^a	364.15	5956.21	—	—	—

^a Alternating copolymer of methyl methacrylate and styrene.

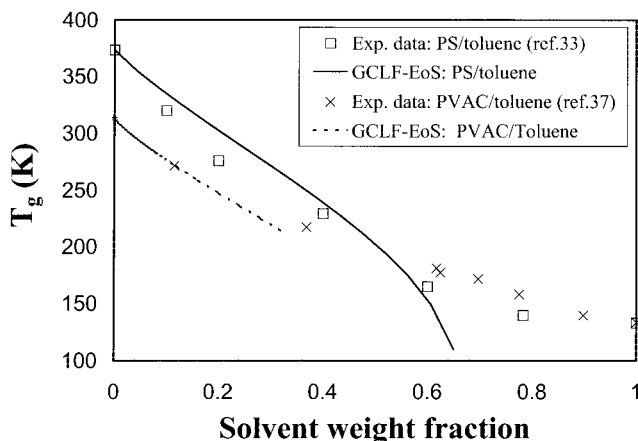


Figure 6 Glass transition temperature of polystyrene–toluene and poly(vinyl acetate)–toluene solutions.

the alternating copolymer can be obtained from a fit of the available T_g 's.

Polymer–solvent mixtures

The depression of the T_g with solvents can be calculated by using eq. (15b). In principle, one needs the T_g of the polymer and the solvent. Data for solvents, however, are scarce. As a first approximation, the solvent is assumed to have a zero value for the flex energy (i.e., the solvent molecule is totally flexible). Because the binary interaction parameter is calculated through the group contribution method, the approach is totally predictive.

Adachi et al.³³ measured the T_g of polystyrene/toluene solutions throughout the entire composition range. The flex energy of the solvents could be correlated in these cases. The GCLF-EoS parameters were obtained and are recommended for use in the range of 270 to 450 K, which is far above the T_g of most solvents. The calculations use only the polymer flex energy as input. Figure 6 illustrates such calculations for the polystyrene/toluene and poly(vinyl acetate)/toluene binary systems. Up to a composition of about 40 wt % of solvent, the model follows the experimental measurements trend. Above that composition, the model deviates significantly with the experimental results because of the assumed zero value of the solvent flex energy. At higher concentrations, the solvent flexibility cannot be neglected. Furthermore, these calculations were carried out at temperatures far below the recommended range of the GCLF-EoS model. Thus, it is not unexpected that the model predictions are only qualitative.

In an attempt to understand the causes of the model discrepancies, we compared the predicted solubility of toluene in polystyrene against experimental data at 25°C^{34,35} and 110°C.³⁶ The data used at 25°C were above the T_g of the mixture so that the GCLF-EoS

could be applied. The GCLF-EoS generates an interaction parameter independent of temperature equal to 0.0110 for a polymer molecular weight of 200,000 g/mol. The fit over the experimental data at 110 and 25°C yields a value of 0.0117 and 0.0066, respectively, indicating that the k_{ij} is temperature dependent. The fitted value was used to generate a similar plot to Figure 6 so as to investigate the importance of the k_{ij} in the glass temperature depression. The fitted value of the k_{ij} increased the T_g by only 0.2–0.3°C, which is insignificant. A more extended case is shown in Figure 7. The plot shows the T_g prediction for PS (2×10^5 g/mol) and toluene at 30% solvent weight fraction with changing values of the interaction parameter. In these calculations, the flex energy of toluene was taken equal to 3×10^3 J/mol. Obviously, the error made on the k_{ij} estimation has little influence on the T_g prediction. This was not the case for the work of Condo et al.¹¹ They studied the carbon dioxide–PMMA system by using a combination of the Sanchez–Lacombe EoS and the Gibbs–DiMarzio formalism. In their calculations, the T_g was calculated for a given pressure at the maximum solubility of CO₂. Changing the binary interaction parameter resulted in a variation of the pressure for the same CO₂ solubility and significantly affected the T_g .

Figures 6, 8, and 9 plot the T_g depression of four different binaries. The model predictions are satisfactory considering the experimental errors involved in such measurements. Although the data of poly(vinyl acetate) and toluene³⁷ expand over a wider temperature range, the model prediction was limited to the temperature range of the pure component parameters. Satisfactory predictions are also obtained with polystyrene–benzene solutions.^{38,39} For polystyrene–pentane solutions,⁴⁰ the results are more qualitative.

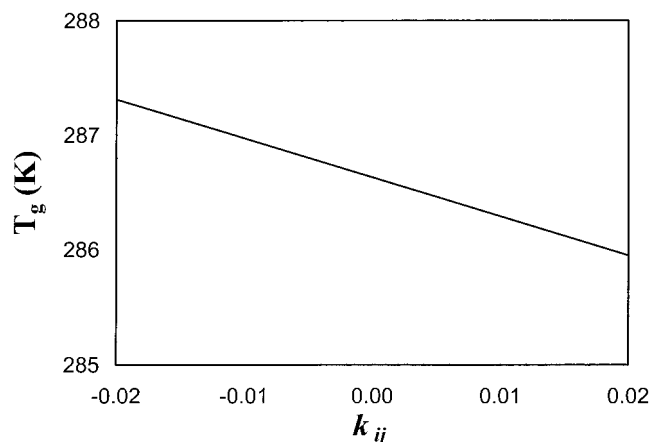


Figure 7 Effect of the binary interaction parameter on the glass transition temperature of a polystyrene–toluene solution (30 wt % toluene).

All the curves obtained from the model show a decreasing slope as the solvent concentration increases, that is, the general trend observed for polymers with liquids^{5,41} or compressed gases.^{42,43}

CONCLUSION

In this work, a group contribution equation of state was combined for the first time with the Gibbs and DiMarzio formalism to predict the glass transition temperature. The expression of the entropy was derived for pure fluids and binaries. Extension to multicomponent systems is straightforward. Also, the concept of dyads was applied to copolymers and a new approach for the calculation of the copolymer flex energy was developed.

The model predictions were quantitative for homo- and copolymers. For the latter, the proposed formalism has direct engineering applications thanks to the group contribution method because the only required information is the alternating copolymer T_g . Although the equation of state provides the volumetric properties or interaction with solvents, the combination with the Gibbs–DiMarzio formalism and the dyad concept gives access to the T_g .

The treatment of polymer solutions was found to be qualitative but satisfactory considering the experimental error. The binary interaction parameter was found to have a minor influence on the T_g predictions. The model can be applied to solvent concentrations below approximately 40% in solvent weight fraction if the solvent flex energy is taken equal to zero. At higher compositions, the solvent flexibility cannot be neglected in the overall entropy of the solutions.

A limitation in the use of the model comes from the pure components parameters, which are restricted to the range of 270 to 450 K.⁹ If the pure polymer and pure solvent PVT are known, the pure component parameters and k_{ij} could be regressed from literature

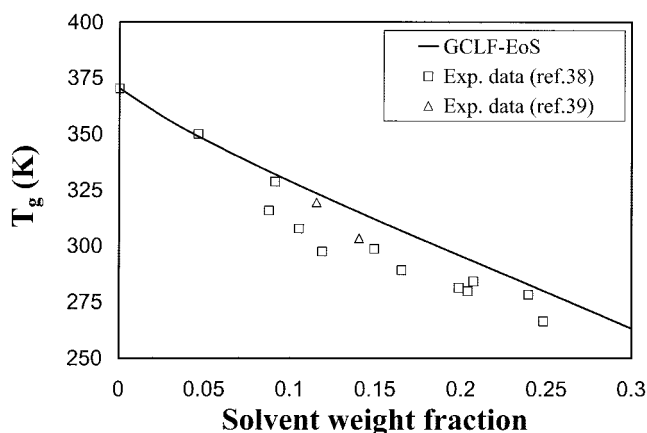


Figure 8 Glass transition temperature of polystyrene–toluene solutions.

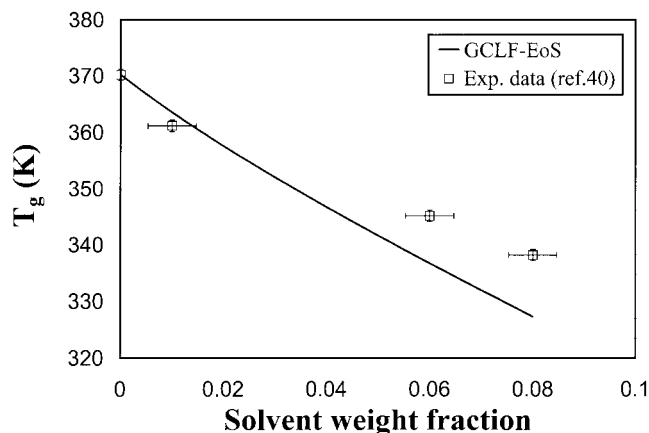


Figure 9 Glass transition temperature of polystyrene–pentane solutions.

data and the model could be used over a wider temperature range.

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