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Approach to the Glass Transition Temperature of Random Copolymers Using the Gibbs-DiMarzio Theory

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Summary

It is supposed that the molecular parameters of the Gibbs-DiMarzio (GD) theory (hole energy, flex energy and coordination number) of random copolymer vary linearly with the molar composition from the molecular parameters of one parent homopolymer to those of the other. This assumption enables us to calculate,according to the GD theory, the configurational entropy of a random copolymer $S_{c,cop}$ and thus (if $S_{c,cop}$ at the glass transition temperature of the random copolymer, $T_{g,cop}$, is again a linear function of the composition) also $T_{g,cop}$. The theoretical prediction has been compared with the experimental data obtained on the system butyl methacrylate - methyl methacrylate, and a good agreement between the theory and experiment has been found.

Introduction

Theories based on configurational properties dealing with the composition dependence of the glass transition temperature, T_g, of copolymers can be divided into two groups. The first group is outlined from the Gibbs-DiMarzio (GD) theory of glass formation (1-4) while the second one originates from the Adam-Gibbs (AG) theory of cooperative relaxation properties of glass-forming liquids (5).

The first group started with the theoretical arguments of DiMarzio and Gibbs (6) who derived T_g of the copolymer only from the properties of parent homopolymers. This approach was further extended to include properties of an alternating copolymer by Uematsu and Honda (7) and by Barton (8) who incorporated the dyad approximation. In these approaches it is supposed that the configurational entropy, S_c, vanishes at T_g. This should be true for the equilibrium transition which can be reached only by an infinitely slow cooling rate. S_c corresponding to the glassy state obtained by a finite cooling rate is frozen-in at some non-zero value.

The non-zero value of S_c at T_g is taken into account by theories of the second group. It has been assumed that the configurational entropy at T_g changes linearly with composition for random copolymers (9) as well as for sequence distribution (10). This assumption has been found practically identical with the hypothesis of a compositionally independent relaxation time, if the height of the rotational potential

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barrier varies linearly with composition.

Recently, it has been shown (11,12) that the molecular parameters of the GD theory for a homopolymer can be calculated from experimentally determined values of T_g, T_2, ΔC_p and $\Delta\alpha$, where ΔC_p and $\Delta\alpha$ are respectively changes in the isobaric heat capacity and thermal expansion coefficient at T_g, and T_2 means the temperature of equilibrium transition. Using the calculated molecular parameters, a good agreement between the GD theory and the molecular weight dependence of T_g has been obtained (12). Moreover, the knowledge of molecular parameters can be useful for a further theoretical comparison of the GD theory with other properties of polymers. A theoretical modification of the GD theory to random copolymers would lead to mathematical difficulties connected with the determination of the number of ways of possible accommodations of copolymer molecules onto the lattice. It is, therefore, worthwhile to try to find some simplifying procedure for the determination of the GD molecular parameters of random copolymers.

In this paper a simple method for the calculation of the glass transition temperature of random copolymers is suggested and the theory is compared with experimental data obtained for the system butyl methacrylate - methyl methacrylate.

Theory

The Gibbs-DiMarzio lattice theory outlines configurational properties of high-molecular weight polymers on the basis of three molecular parameters: (i) the hole energy E_h which characterizes the interaction between chemically non-bonded polymer segments, (ii) the flex energy ε representing the difference between the higher and the lower minima of the rotational potential (i.e. the difference between the energy of gauche and trans conformations) and (iii) the coordination number z which is the number of the nearest-neighbouring segments. The molar configurational entropy, S_c, of a homopolymer at T_g has the form

$$S_c/n_rR = \ln S_o + E_h(1-S_o)^2/(1-V_o)kT_g + f\varepsilon/kT_g - \ln(1-f) \qquad (1)$$

where n_r is the number of rotatable groups per monomer unit, R is the ideal gas constant, $S_o = zV_o/[z-2(1-V_o)]$, and V_o, i.e. the fractional free volume at T_g is expressed as follows

$$E_h(1-S_o)^2/kT_g = \ln (V_o^{z/2-1}/S_o^{z/2}) \qquad (2)$$

The fraction of bonds which are in the position gauche, f, is given by

$$f = (z-2)\exp(-\varepsilon/kT_g)/[1 + (z-2)\exp(-\varepsilon/kT_g)] \qquad (3)$$

The application of the GD theory to random copolymers composed from monomer units A and B meets with considerable complications connected with increasing number of molecular parameters. In fact, already in the simple dyad approximation we have different hole energies corresponding to contacts of A-A, B-B and A-B chemically non-bonded units respectively; the same regards the flex energies for chemically bonded neighbouring monomer units. Also, the coordination number of the copolymer depends on its local or average composition. Since not always sufficient experimental data for obtaining all above mentioned molecular parameters are at disposal, let us assume a linear change of the molecular parameters of homopolymers with composition of the random copolymer

$$E_{h,cop} = x_A E_{h,A} + (1-x_A) E_{h,B} \tag{4a}$$

$$\varepsilon_{cop} = x_A \varepsilon_A + (1-x_A) \varepsilon_B \tag{4b}$$

$$z_{cop} = x_A z_A + (1-x_A) z_B \tag{4c}$$

where the indices cop, A and B relate to the random copolymer, homopolymer A and homopolymer B respectively, and x_A is the molar fraction of the monomer A.

It has been found (9) that for the random copolymer the configurational entropy at T_g depends linearly on composition

$$S_{c,cop}(T_{g,cop}) = x_A S_{c,A}(T_{g,A}) + (1-x_A) S_{c,B}(T_{g,B}) \tag{5}$$

If E_h, ε and z for both homopolymers are known, the compositional dependence of the glass transition temperature of the random copolymer can be calculated using eqs (1)-(5).

Experimental

The samples of random copolymers butyl methacrylate (BMA) - methyl methacrylate (MMA) were prepared in the following molar concentrations of BMA: 0, 0.2, 0.4, 0.6, 0.8 and 1, using monomers of commercial grade. The polymerization reaction initiated by dibenzoyl peroxide occurred at the temperature of 323 K for 24 hours; 5% by weight of ethylene dimethylacrylate as crosslinking agent was added. The samples were than cured at the temperature of 393 K for 2 hours; the DSC traces showed that after this curing procedure the reaction was completed.

Measurements of the glass transition temperature were performed on the DSC apparatus Mettler TA 3000 using a heating rate 10 K/min. The values of T_g and ΔC_p were determined by the standard procedure of the apparatus.

Results and Discussion

In order to compare the theory with the experimental data, the calculation of the molecular parameters of the GD theory corresponding to the PBMA and PMMA was necessary. Input data for this calculation as well as the resulting molecular parameters of both homopolymers are given in Table 1. The method of calculation has been published elsewhere (11,12). The present results slightly differ from those obtained for PMMA in refs (11) and (12) because of the slightly higher ΔC_p value obtained by us. Table 1 also contains the calculated values of the order parameters of the GD theory, i.e. the fractional free volume, V_o, and the fraction of bonds in the position possessing higher energy, f, for both homopolymers.

Table 1. Properties of pure homopolymers (References for other data than those measured or calculated in this paper are given in brackets.)

Property	Dimension	PBMA	PMMA
T_g	K	308	388
T_2	K	242(13)*	305(13)
ΔC_p	J/mol K	37.8	38.7
$\Delta\alpha$	10^4 K^{-1}	2.3(14)	3.1(14)
n_r**		7	4
E_h/k	K	847	910
ε/k	K	457	816
z		3.93	5.30
V_o		0.0205	0.0381
f		0.304	0.287

*Because of higher value of T_g for PBMA, a correspondingly higher value for T_2 is used.

**n_r denotes the number of chemical bonds around which a rotation is possible with exclusion of rotationally symmetrical bonds and bonds of end atoms.

The dependence of the glass transition temperature on the composition for BMA-MMA copolymers calculated according to eqs (1)-(5) together with experimentally determined data is shown in Figure 1. The coincidence between the theoretical and experimental points proves that the present simple approach is satisfactory for the system under investigation.

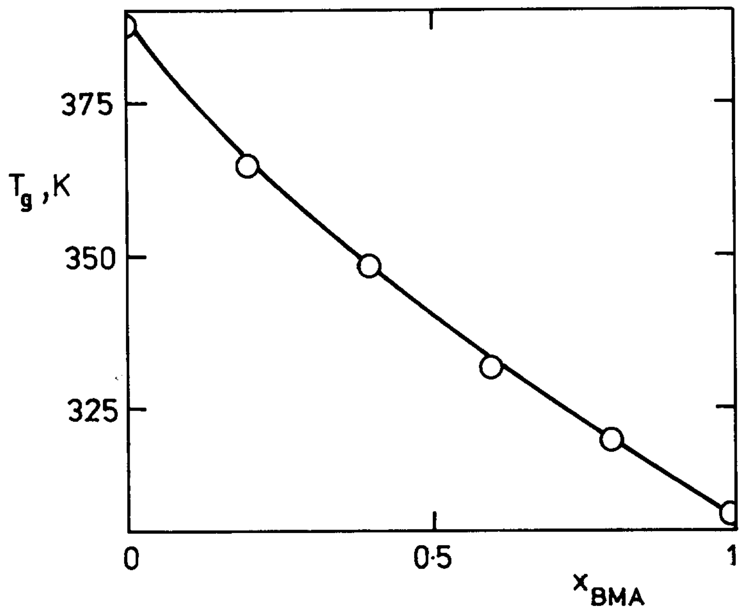

Fig.1. The glass transition temperature of BMA-MMA random copolymers as functions of composition. (o) Measured data of the glass transition temperature, the full line represents the theoretical dependence according to eqs (1)-(5).

It should be noted that there is no apriori reason why the configurational entropy itself should be key factor for the occurrence of T_g. It should be rather the relaxation time which is constant, if always the same method of the determination of T_g is applied. From the AG theory (5) we have that in this case the condition for the occurrence of T_g can be approximated by

$$T_{g,cop}S_{c,cop}(T_{g,cop}) = x_A T_{g,A} S_c(T_{g,A}) + x_B T_{g,B} S_c(T_{g,B}) \qquad (6)$$

The results obtained from eq.(6) and those according to eq.(5) differ very slightly (0.2 K at most) thus, eq.(5) can be used for the determination of $T_{g,cop}$.

The previous applications of the GD theory to random copolymers actually give not T_g but T_2. A comparison of the present results with those following the DiMarzio-Gibbs (6) equation shows that our theoretical values are higher, the maximal difference being 4 K.

Our calculation should also be compared numerically with the previous application of the AG theory. The calculated values of T_g (according to ref.9) are similar to those according to DiMarzio and Gibbs; the maximal difference is therefore again about 4 K.

It can be concluded that the glass transition temperature of the copolymer system BMA-MMA can be calculated by the suggested simple application of the GD theory. The advantage of this procedure lies in the possibility of the calculation of other properties of the random copolymer using the GD theory. It is, however, necessary to prove if also in this case it will be sufficient to assume a linear change of molecular parameters, or if also the properties of the alternating copolymer should be taken into account.

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