The Effect of Sequence Distribution on Glass Transition in the Theory of the Cooperative Behaviour of Random Copolymers

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Summary

The description of the cooperative behaviour of polymers in the glass transition region according to ADAM and GIBBS (1965) has been extended to comprise the dependence of glass transition temperature, T_g, on the chemical composition of random copolymers if the distribution of dyads of comonomer units is included. The compositional dependence of T_g is expressed in terms of (i) differences between the isobaric heat capacities in the liquid and glassy states, and of (ii) the equilibrium T_2 temperatures of the parent homopolymers and of the alternating copolymer. Validity of this theory was verified by comparison with data on styrene/methyl methacrylate and styrene/n-octyl methacrylate copolymers; the results indicate that the relations derived agree quantitatively with the experiment similarly to the equations suggested earlier by JOHNSTON (1976) and BARTON (1970). Moreover, these relations are based on a physically better justified approach to the glass transition phenomenon.

Introduction

The shape of the compositional dependence of the copolymer glass transition temperature, T_g, cannot in many cases be predicted only from the T_g's of both parent homopolymers. The curvatures or even the extremes sometimes observed in the dependences of T_g of random copolymers on their overall chemical composition have been explained by the effect of sequence distribution (BARTON 1970, JOHNSTON 1976). In the dyad approximation, equations can be constructed for these dependences containing the T_g's of both parent homopolymers and of the alternating copolymer. (Similarly, equations can be constructed in the triad or higher approximation, which, unfortunately, contain experimentally inaccessible parameters.)

Several relations have been suggested for the

description of the sequence distribution effect. By
extending FOX's equation (1956), JOHNSTON (1976) ar-
rived at a relation in which the reciprocal copolymer
T_g equals the sum of the reciprocal T_g's of both parent
homopolymers and of the alternating copolymer, all the
three contributions being weighted by the weight frac-
tions of the respective dyads. The BARTON's approxi-
mation (1970) is based on the Gibbs-DiMarzio theory
(DiMARZIO and GIBBS 1959) and holds, strictly speaking,
only for the equilibrium transition temperature, T_2,
as introduced in their theory; here, the copolymer T_2
(or T_g) is assumed to equal the sum of the T_2's (or T_g's)
of both parent homopolymers and of the alternating
copolymer, all the three terms being weighted by the
mole fractions of rotatable bonds pertaining to the
respective dyads. Although both approaches are phenom-
enological, Johnston's equation can be regarded rather
as an isochoric one, while Barton's equation is isen-
tropic with respect to T_g. UEMATSU and HONDA (1965,
1966) suggested another isentropic approach, using
contributions of stiffness energy. Barton, and Uematsu
and Honda consider the configurational entropy at T_g
to vanish. Although the equations thus obtained ad-
equately describe some experimental dependences, it
has been shown that the glass transition is neither an
isochoric nor an isentropic phenomenon (HAVLÍČEK et al.
1980 b).

All experimental procedures used in the determi-
nation of T_g examine the glass transition in the range
of approximately the same relaxation times. Hence, a
comparison between the theory and experimental data is
feasible by regarding the glass transition as an iso-
chronic phenomenon. In a preceding paper (HAVLÍČEK et
al. 1980 a), the theory of the cooperative behaviour
of polymers (ADAM and GIBBS, 1965) was employed to
describe the compositional dependence of the random
copolymer glass transition temperature without taking
into account the effect of sequence distribution. In
this paper, the effect of sequence distribution in the
dyad approximation is involved.

Theory
A model of the cooperative rearrangement of polymer
molecules and their parts was suggested by ADAM and
GIBBS (1965). For the probability of a cooperative con-
figurational change, they derived the relation

$$W(T) = A \exp[-m/TS_c(T)] \qquad (1)$$

in which S_c is the configurational entropy, m is a

quantity related to the topological and energetical features of the cooperative transition, and A is a frequency factor (its temperature and compositional dependence need not be taken into account). The configurational entropy may be approximated by

$$S_c(T) = \Delta C_p \ln(T/T_2) \tag{2}$$

where ΔC_p is a difference between the isobaric heat capacities below and above the glass transition. At a hypothetical T_2 temperature which lies approx. 50 K below T_g, the number of configurations attainable by the material drops to unities, whence the configurational entropy $S_c = 0$.

　　If the constant relaxation time of the configurational change τ $(\tau \sim 1/W)$ is taken as the criterion of the glass transition, we can write:

$$W^c(T_g^c) = W^{AA}(T_g^{AA}) = W^{BB}(T_g^{BB}) = W^{AB}(T_g^{AB}) =$$

$$= W^{ij}(T_g^{ij}) \tag{3}$$

Here, as well as in the following equations, the quantities with the superscripts c, AA, BB and AB relate to any random copolymer, the parent homopolymers A and B, and the alternating copolymer, respectively.

　　For the quantities m and ΔC_p, molar additivity in the dyad approximation is assumed:

$$m^c = \sum_{ij} x^{ij} m^{ij} \tag{4}$$

$$\Delta C_p^c = \sum_{ij} x^{ij} \Delta C_p^{ij} \tag{5}$$

In the Eqs (4) and (5), and also in the following ones, summations are performed for ij = AA, BB, and AB; x^{ij} are mole fractions of the respective dyads. Since T_2^c is the temperature of zero configurational entropy, it obeys Barton's equation (BARTON 1970), which is additive in mole fractions of rotatable bonds y^{ij} corresponding to the dyad ij, i.e.

$$T_2^c = \sum_{ij} y^{ij} T_2^{ij} \tag{6}$$

here, $y^{ij} = x^{ij}(n^i + n^j)/2(x^A n^A + x^B n^B)$, where n^A and n^B respectively are the numbers of rotatable bonds in the monomeric units A and B; x^A and x^B are mole fractions of these units. By combining equations (1) - (6),

we obtain for the glass transition temperature of a random copolymer in the dyad approximation

$$T_g^c \Delta C_p^c \ln(T_g^c/T_2^c) = \sum_{ij} x^{ij} T_g^{ij} \Delta C_p^{ij} \ln(T_g^{ij}/T_2^{ij}) \qquad (7)$$

If we assume the molar additivity of configurational entropy at $T = T_g$, viz.

$$S_c^c(T_g^c) = \sum_{ij} x^{ij} S_c^{ij}(T_g^{ij}) \qquad (8)$$

instead of the isochronic criterion discussed above, we obtain a similar relation for the copolymer glass transition:

$$\Delta C_p^c \ln(T_g^c/T_2^c) = \sum_{ij} x^{ij} \Delta C_p^{ij} \ln(T_g^{ij}/T_2^{ij}) \qquad (9)$$

Comparison with Experiment and Discussion

Two copolymer systems were chosen in order to verify the theory, namely, styrene/methyl methacrylate (S/MMA) and styrene/n-octyl methacrylate (S/OMA). The ΔC_p values were determined for all samples by the DSC method. The samples were first cooled at a rate of 10 K/min and then heated at the same rate. Heating run was used in the evaluation. Syntheses of copolymers, experimental procedure and evaluation of T_gs are given elsewhere (PODEŠVA and BIROŠ 1980). The data support the suitability of Eq.(5) as shown in Fig.1. Extrapolation based on Eq.(5) was used for the determination of the experimentally inaccessible ΔC_p value for POMA. Mole fractions of dyads were calculated from the relations (HARWOOD and RITCHEY 1964)

$$x^{AB} = 4x^A x^B / \left\{ 1 + [1 + 4x^A x^B (r^A r^B - 1)]^{+1/2} \right\} \qquad (10)$$

where r^A and r^B are monomer reactivity ratios, and

$$x^{AA} = x^A - x^{AB}/2 \qquad (11)$$

Input data used in equations (7) and (9) are given in Table I.

TABLE I

Input data for the calculation of the compositional
dependences of the random copolymer glass transition
temperatures

polymer	T_g[b], K	T_2, K	ΔC_p, J/mol K	n[g]
PS	373	324.5[c]	32.5	3
PMMA	390	305.1[c]	20.1	4
S/MMA[a]	371	321[d]	28.0	–
POMA	245	195[d]	20[f]	11
S/OMA[a]	270	250[e]	30.1	–

a) alternating copolymer; b) PODEŠVA and BIROŠ 1980;
c) HAVLÍČEK et al. 1978; d) $T_2 = T_g - 50$ K; e) adjusted
for a better fit between Eq.(7) and experimental data;
f) adjusted using Eq.(5); g) number of rotatable bonds.

Since neither homopolymers nor alternating copoly-
mers were studied by viscoelastic methods, the T_2
values for PS and PMMA were taken from a paper by HAV-
LÍČEK et al. (1978). For the alternating S/MMA and
S/OMA copolymers and for poly(n-octyl methacrylate)
(POMA), it was assumed that $T_2 = T_g - 50$ K, where for
T_g of POMA the extrapolated value 245 K was employed
(PODEŠVA and BIROŠ 1980). It appeared that if we used
somewhat higher values of T_2 for the alternating S/OMA
copolymer, a better agreement was achieved between ex-
periment and theory; for this reason, $T_2 = T_g - 20$ K
was adjusted for this copolymer.

Compositional dependences of the glass transition
temperatures of both random copolymer systems are com-
pared in Fig.2. It can be seen that the fit of exper-
imental points with the curves predicted by Eq.(7) is
satisfactory. This holds mainly for the S/MMA system,
for which in Eq.(7) reliable input parameters were
available (with the exception of T_2 of the alternating
copolymer). For this system, the fit with Eq.(7) is
better than with Johnston's and Barton's equations: the
arithmetic mean from absolute deviations of experim-
ental copolymer T_g's from theory, d, equals 0.9, 1.5,
and 2.3 K, respectively. A poorer fit is observed for
the S/OMA system: for Eq.(7), Johnston's and Barton's
equations, d = 5.6, 2.7, and 5.3 K, respectively.
Though the physical quantities ΔC_p and T_2 which appear
in Eqs (7) and (9) may be subjected to a considerable
error, numerical calculation shows that these errors
are not substantially reflected in the compositional

dependence of T_g: e.g., with the S/MMA system changes in ΔC_p by 10% or in T_2 by 10 K lead to changes in T_g^C in the range $\pm$ 1 K.
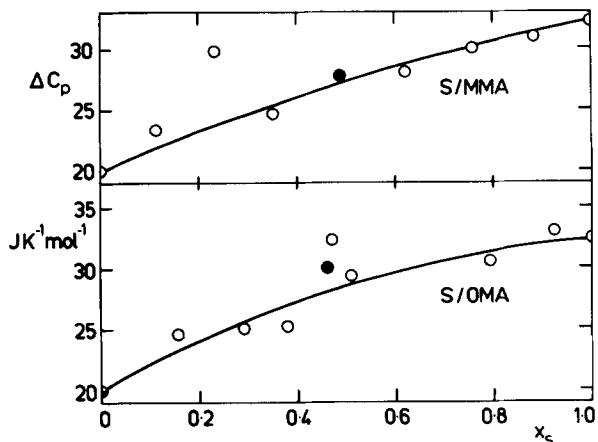

Figure 1. Dependence of a difference between the iso-
baric heat capacities below and above glass
transition, ΔC_p, of random styrene/methyl
methacrylate (S/MMA) and styrene/n-octyl meth-
acrylate (S/OMA) copolymers on the mole frac-
tion of styrene, x_s.
Solid lines correspond to Eq.(5); ○ - homo-
polymers and random copolymers;● -alternating
copolymers; ◕ - extrapolated value

The results suggest that, with the systems under
study, Eq.(7) may be considered equally adequate in a
quantitative description of the dependences of T_g of
random copolymers on their overall chemical composition
as equations of Johnston and Barton, analyzed in detail
earlier (PODEŠVA and PROCHÁZKA 1979, PODEŠVA and BIROŠ
1980). The contribution made by Eq.(7) consists pre-
dominantly in a physically better justified approach
to the glass transition phenomenon.
We also found the differences between the results
yielded by Eqs(7) and (9) to be smaller than the ex-
perimental error of the determination of T_g (5 K at
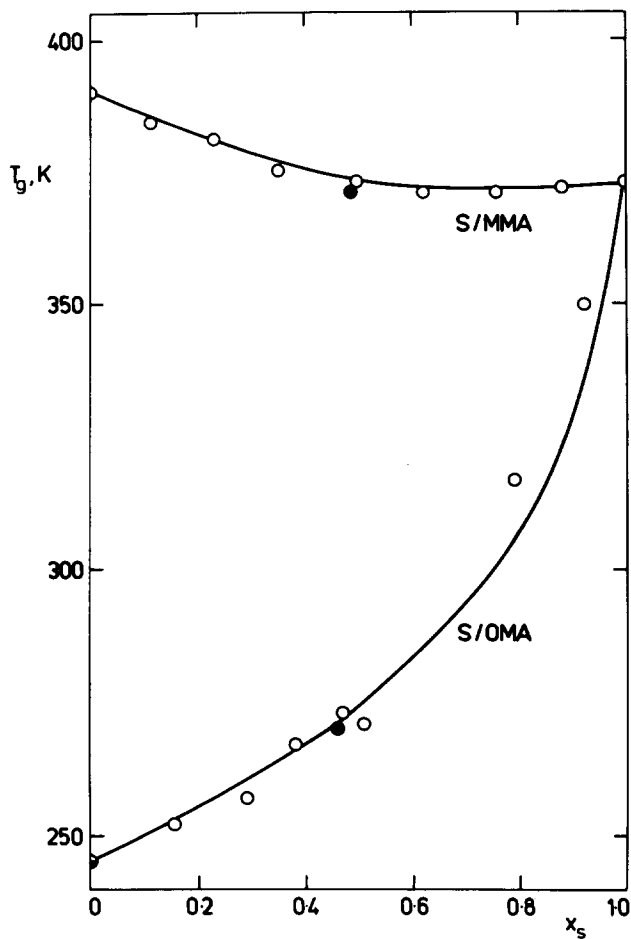most, in the part of the compositional scale where T_g

Figure 2. Dependence of the glass transition tempera-
ture, T_g, of random styrene/methyl methacry-
late (S/MMA) and styrene/n-octyl methacrylate
copolymer on the mole fraction of styrene,
x_s.
Solid lines correspond to Eq.(7); ○ - homo-
polymers and random copolymers; ● - alter-
nating copolymers; ◐ - extrapolated value
(PODEŠVA and BIROŠ 1980)

changes steeply, otherwise $1-2$ K). This fit suggests that, respecting the model of Adam and Gibbs, the conservation of the value of relaxation time at T_g is adequately described by the additivity of the configurational entropy of random copolymers on the dyad approximation.

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