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The Effect of Composition on Cooperative Relaxation Properties of Random Copolymers

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Summary

The theory of ADAM and GIBBS (1965) has been extended to include a description of the composition dependences of relaxation times and of the glass transition temperature of a random copolymer using the known thermodynamic and viscoelastic parameters of homopolymers. Comparison with a number of copolymer systems shows that theoretical equations adequately correspond to experimental data if the sequence distribution effect is not operative.

Introduction

In the main viscoelastic region the configurational motions of polymers possess a cooperative character, which is reflected in relaxation times. Their temperature dependence was adequately described in terms of the thermodynamic theory by ADAM and GIBBS (1965) (AG theory). The dependence of the relaxation times of random copolymers on composition has been described by the free-volume equation of FUJITA and KISHIMOTO (1961), assuming the additivity of free volumes of constituent homopolymers (ILAVSKÝ and HASA 1968). ILLERS (1966) has summarized the reported theoretical relations describing a change of the glass transition temperature of random copolymers with composition. Relations which reflect the sequence distribution effect of constituting monomers have been reported by JOHNSTON (1976).

This paper extends the AG theory for description of the composition dependence of relaxation times and of the glass transition temperature. The equations are compared with experiments reported in the literature. The modified theory presented here does not take into account the sequence distribution effect, and is therefore suited only for such copolymer systems in which this effect is not operative.

Theory

The probability of a cooperative configurational rearrangement of the polymer $W(T)$ is given by the

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relation (ADAM and GIBBS 1965)

$$W(T) = A \exp[-m/TS_{conf}(T)] \sim 1/\tau(T) \qquad (1)$$

where A is constant in a good approximation, T is absolute temperature, S_{conf} is the configurational entropy, m is a quantity introduced into the AG theory and characteristic of a given compound and τ is a relaxation time. Assuming that the difference between the isobaric heat capacities of glass and of the equilibrium melt ΔC_p is temperature-independent, ADAM and GIBBS (1965) expressed the configurational entropy of the polymer through

$$S_{conf}(T) = \int_{T_2}^{T} (\Delta C_p/T)dT = \Delta C_p \ln(T/T_2) \qquad (2)$$

At T_2, the configurational entropy reaches zero and all the cooperative relaxation processes cease to exist. We will assume that Eqs (1) and (2) hold also for random copolymers. BARTON (1970) suggested an equation for the dependence of T_{2C} of the copolymer on composition,

$$T_{2C} = y_A T_{2A} + y_B T_{2B} \qquad (3)$$

in which, as below, the indices A and B denote homopolymers (or monomers) and C denotes the copolymer. The y's are fractional parts of the number of all rotatable groups pertaining to the individual components. For the isobaric heat capacity it is possible to use the relation

$$\Delta C_{pC} = x_A \Delta C_{pA} + x_B \Delta C_{pB} \qquad (4)$$

in which x_A, x_B are the molar fractions of comonomers. For m_C of the copolymer it is assumed in this paper that it also varies linearly with the molar composition:

$$m_C = x_A m_A + x_B m_B \qquad (5)$$

After substitution of Eqs (2)-(5) into Eq.(1), the probability of a cooperative configurational rearrangement W_C of the random copolymer is expressed through

$$W_C(K_1,T) = A \exp[-(K_1 m_A + m_B)/(K_1 \Delta C_{pA} + \Delta C_{pB}) \ln(K_2 T)]$$
$$K_1 = x_A/x_B , \qquad K_2 = (K_1 n_A + n_B)/(K_1 n_A T_{2A} + n_B T_{2B}) \qquad (6)$$

where n is the number of rotatable groups per one mer. $a_C = W_C(K_1,T)/W_C(K_1',T)$ is the ratio of relaxation times at compositions K_1' and K_1, thus indicating the horizontal shift factor of viscoelastic curves in the time - composition superposition of the random copolymer.

The expression for the dependence of glass transition temperature T_{gC} of the copolymer on composition may be based on one of the following two assumptions (HAVLÍČEK et al. 1978):(i) The configurational entropy at the glass transition temperature varies linearly with the molar composition of the copolymer. Substitution of Eqs (3) and (4) into Eq. (2) gives in this case

$$\ln(K_2T_{gC}) = [K_3\ln(T_{gA}/T_{2A}) + \ln(T_{gB}/T_{2B})]/(K_3 + 1)$$
$$K_3 = x_A\Delta C_{pA}/x_B\Delta C_{pB} \qquad (7)$$

(ii) The probability of a cooperative configurational rearrangement at T_g (measured in the same way) is the same for all the glassforming compounds. Then, Eq. (6) gives an alternative relation for the glass transition temperature of the random copolymer:

$$T_{gC}(K_3+1)\ln(K_2T_{gC}) = K_3T_{gA}\ln(T_{gA}/T_{2A})+T_{gB}\ln(T_{gB}/T_{2B}) \qquad (8)$$

Results and Discussion

Experiments was compared with theory using five systems of copolymers studied earlier: 2-hydroxyethyl methacrylate and 2-(hydroxyethoxy)ethyl methacrylate (HEMA-HEOEMA) (ILAVSKÝ and HASA 1968), HEMA and n-butyl methacrylate (HEMA-BMA) (ILAVSKÝ and KOLAŘÍK 1969), methyl methacrylate and BMA (MMA-BMA)(WADA et al. 1964), MMA and methyl acrylate (MMA+MA)(FUJINO et al. 1961), and styrene and 2-methoxyethyl methacrylate (S-MEMA) (ILAVSKÝ et al. 1979). Experimentally determined data on homopolymeric components of these systems are given in Table I, along with the thermodynamic parameters of the AG theory calculated by using approximate relations (HAVLÍČEK et al. 1978 b):

$$m = 2\Delta C_p c_1^g T_g \ \ln(T_g/T_2) \qquad (9)$$

and

$$T_2 = [T_g(1 + \varepsilon) - c_2^g]/2 \qquad (10)$$

where

$$\varepsilon = \exp[c_2^g/(c_2^g - T_g)] \qquad (11)$$

c_1^g and c_2^g are constants of the WILLIAMS-LANDEL-FERRY equation (1955) (FERRY 1970) related to T_g.

System S-MEMA, for which viscoelastic and thermodynamic data on several copolymers are available, makes possible confrontation of assumptions represented by Eqs (3)-(5) with experiment (Fig.1). Departures of ΔC_p data from the theoretical dependence are smaller than uncertainty involved in the determination of this quantity; hence, it may be said that experiment is not at variance with Eq. (4). Scatter of the values of m is probably due to the determination of c_1^g and c_2^g, which may be subjected to error. Agreement between T_2 values determined using Eq. (10) with Eq. (3) is comparatively good.

TABLE I

Viscoelastic and thermodynamic parameters of pure polymeric components of copolymer systems

Polymer	T_g [K]	c_1^g	c_2^g [K]	ΔC_p [J/molK]	m [kJ/mol]	T_2 [K]	n
PHEMA	370a)	14.0	47.0	36.4d)	57.8	322	6
PHEOEMA	284a)	13.7	42.4	62.8d)	90.4	240	9
PHEMA	358a)	17.7	70.0	36.4d)	106	284	6
PBMA	292a)	17.7	70.0	29.7d)	90.8	218	7
PMMA	374a)	17.1	52.6	34.2e)	69.1	320	4
PBMA	282a)	14.6	61.6	29.7d)	64.5	217	7
PMMA	390b)	14.4	62.6	34.2e)	70.3	325	4
PMA	285b)	14.8	60.6	22.6f)	48.6	221	4
PS	368c)	11.1	42.0	34.3e)	34.2	325	3
PMEMA	285c)	16.9	34.8	36.8d)	47.8	249	6

a) T_g determined dilatometrically

b) T_g determined from the maximum of activation energy

c) T_g determined as temperature at which the Young modulus E(600s) reached $10^{1.5}$ MPa

d) BIROŠ

e) WUNDERLICH (1962)

f) WRASIDLO (1974)

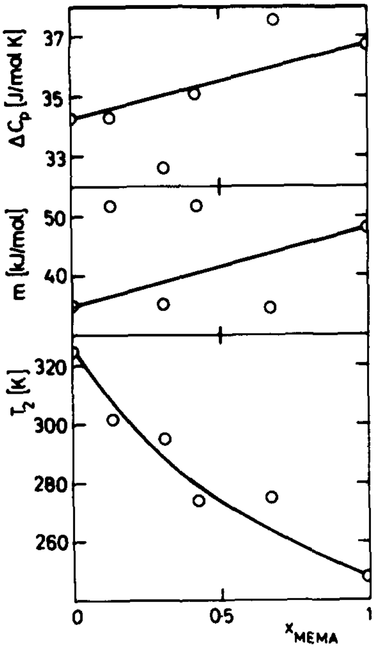

Fig.1 Composition dependence of heat capacity ΔC_p and thermodynamic parameters m and T_2 of AG theory for system S-MEMA. Points ΔC_p obtained by measuring individual copolymers S-MEMA (BIROŠ). Points m and T_2 calculated using constants c_1, c_2(ILAVSKÝ et al.) by means of Eqs (9)-(11). Curves calculated from Eqs (3)-(5) and data given in Table I.

Experimentally obtained compositional dependences of shift factors for all the five copolymer systems along with theoretical dependences of α_C are given in Fig.2. The fit observed there indicates that the extended AG theory adequately reflects the cooperative character of molecular motions of random copolymers in the viscoelastic region.

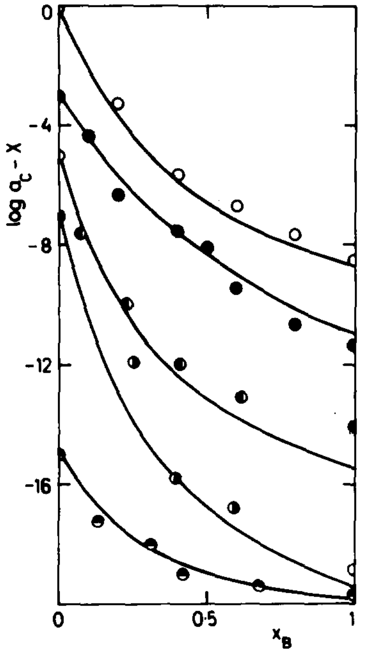

Fig.2

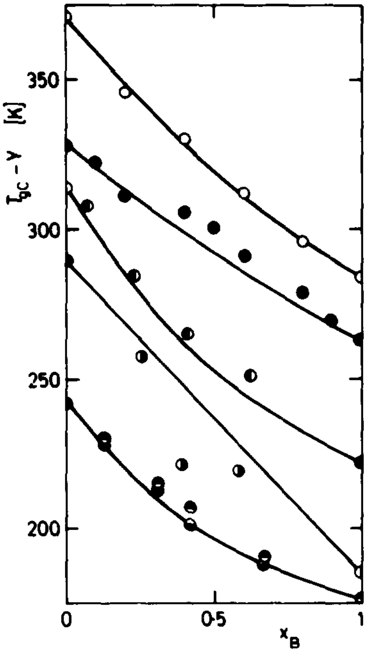

Fig.3

Fig.2 Compositional dependences of shift factors of random copolymers

○ HEMA-HEOEMA, X=0, T=373 K; ● HEMA-BMA, X=3, T=358 K, ◐ MMA-BMA, X=5, T=373 K; ◑ MMA-MA, X=7, T=374 K; ◓ S-MEMA, X=15, T=373 K; —— theoretical curves given by Eq. (6)

Fig.3 Compositional dependences of glass transition temperature of random copolymers

○ HEMA-HEOEMA, Y=0 K; ● HEMA-BMA, Y=30 K; ◐ MMA-BMA, Y=60 K; ◑ MMA-MA, Y=100 K; ◒ (◓ DSC data) S-MEMA, Y=120 K; —— theoretical curves given by Eq. (7)

Also, the fit between experiment and theory for the dependence of T_g on copolymer composition is satisfactory in the first approximation (Fig.3). The dependences according to Eqs (7) and (8) differ from each other by 1.2 K at most; for this reason, only curves according to Eq. (7) are given in Fig.3. It should be stressed that the relations derived here do not take into account the sequence distribution effect, and therefore are not suited for such systems in which this effect is operative. For instance, BEEVERS (1962) prepared copolymers methyl methacrylate - styrene, the T_g´s of which exhibit a pronounced minimum depending on composition and assigned to the sequence distribution effect (BARTON 1970, JOHNSTON 1976). The equations given above predict however an approximately linear T_g-composition dependence for this system.

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