

Glass temperatures of random copolymers of electron-donor and electron-acceptor monomers

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Abstract

The composition dependence of the glass temperatures of copolymers containing monomeric units with electron-donor and/or electron-acceptor groups shows serious deviations from additivity. For electron-donor/electron-acceptor copolymers these deviations are more or less symmetric and, depending on the length of the spacer between the interacting groups and the methacrylic polymeric backbone, they vary from positive for the short ethyl spacer to negative for longer spacers.

Glass temperatures of copolymers of methyl and *n*-butyl acrylates (methacrylates) with the respective electron-donor or electron-acceptor monomers always show asymmetric deviations from additivity. These deviations are mostly positive and situated on the donor-poor side for the donor copolymers and negative and situated on the acceptor-rich side for the acceptor copolymers. The deviations are more pronounced for the methacrylates and decrease from the methyl to the *n*-butyl ester.

INTRODUCTION

Two different ways to relate the glass temperature of random copolymers with their composition are recommended in the literature. One of these approaches proceeds from the expression deduced by Di Marzio and Gibbs [1] with the assumption of additivity of the flexible bond contributions of the monomeric units to T_g . The second attempt is based on the Fox version of the equation of Gordon and Taylor [2]. This expression has been deduced with the assumption of volume additivity. The Fox equation [3]

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MODELLING of the GLASS TEMPERATURE of RANDOM COPOLYMERS

Di Marzio - Gibbs (1959) [1]

$$T_g = n'_A T_{gA} + n'_B T_{gB} \quad (1)$$

n'_i fraction of flexible bonds

$$n'_i = n_i g_i / \sum n_i g_i$$

n_i mole fraction of monomeric units in copolymer

g_i number of flexible bonds contributing to conformational changes

Gordon - Taylor (1952) [2]

$$T_g = [w_A T_{gA} + K w_B T_{gB}] / [w_A + K w_B]$$

w_i weight fraction; for volume additivity

$$K = \rho_A \Delta \alpha_B / \rho_B \Delta \alpha_A \approx T_{gA} / T_{gB}$$

Fox (1956) [3]

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad (2)$$

Diad Sequence Contribution to T_g

Barton (1970) [6]

$$T_g = n'_{AA} T_{gA} + n'_{BB} T_{gB} + (n'_{AB} + n'_{BA}) T_{gAB} \quad (1a)$$

T_{gAB} glass Temperature of strictly alternating copolymer

n'_{ij} mole fraction of flexible bonds in diads

Johnston (1976) [7]

$$\frac{1}{T_g} = \frac{w_A p_{AA}}{T_{gA}} + \frac{w_B p_{BB}}{T_{gB}} + \frac{w_A p_{AB} + w_B p_{BA}}{T_{gAB}} \quad (2a)$$

p_{ij} probability of addition of monomer i to growing radical j

Triad Sequence Contribution to T_g

Ham (1975) [8]

$$T_g = n'_{AAA} T_{gA} + n'_{AAB} T_{gAAB} + n'_{ABA} T_{gABA} + n'_{BAB} T_{gBAB} + n'_{ABB} T_{gABB} + n'_{BBB} T_{gB} \quad (1b)$$

T_{gAAB} , T_{gABA} , T_{gBAB} and T_{gABB} fitting parameter

n'_{ijj} mole fraction of flexible bonds in triads

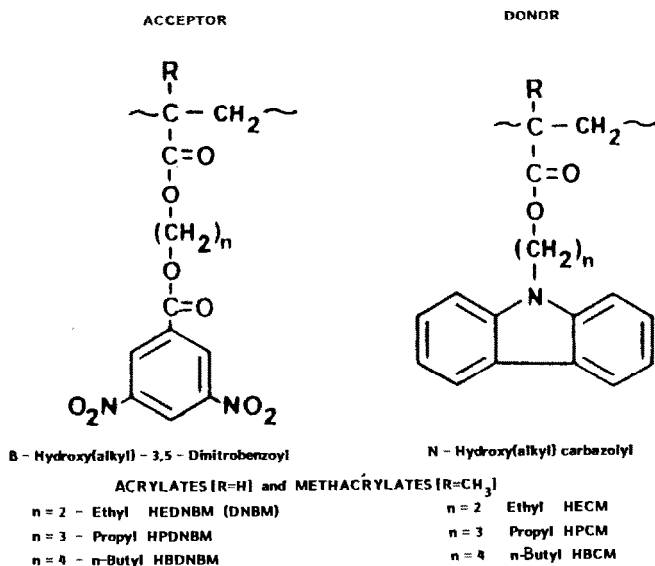
Scheme 1.

results if the approximate value for $K = T_{gA} / T_{gB}$ is used in the Gordon-Taylor expression instead of the exact ratio obtained for volume additivity $K = \rho_A \Delta \alpha_B / \rho_B \Delta \alpha_A$ (ρ_i are the densities and $\Delta \alpha_i$ the increments at T_g of the expansion coefficients). The approximate value of K supposes the validity of the Simha-Boyer rule [4], $\Delta \alpha T_g = 0.133$ neglecting the concomitant influence of the very similar densities of polymers.

It has been shown recently that the two equations based, respectively, on volume additivity and flexible bond additivity are in fact equivalent due to the correlation between T_g and the mass of the monomeric unit weighted by the number of flexible bonds [5].

Taking into account that most of the experimental T_g versus composition data of random copolymers do not obey these simple additivity rules the equations were extended assuming sequence distribution effects. The resulting expressions are shown in Scheme 1.

Generally the contributions to T_g of the homodiads as well as of the homotriads are equated to the respective glass temperatures of the homopolymers. Correspondingly T_{gAB} is assumed to represent the glass temperature of the strictly alternating copolymer. If this value is not accessible experimentally it can be computed from the T_g data of the copolymer and the corresponding homopolymers and the probabilities of formation of the different possible bonds in diads p_{ij} and their mole fractions obtained from the copolymerization ratios. In the equations for triad sequence contributions to T_g , the respective T_g values of the heterotriads are real fitting parameters.



Scheme 2.

$T_{g_{AB}}$ can be calculated in the Barton diad model from the experimental $T_{g_{AB}}$ data by linearization of eqn. (1a), whereas the Johnston approach (eqn. (2a)) requires a multiple regression analysis program. This may be the reason why the Barton approach tends to be preferred in the literature.

In previous studies concerning the T_g versus composition dependence of donor or acceptor groups containing copolymers of acrylates [9] and of methacrylates [10], respectively, it has been observed that nonlinearity and/or an excessive scatter of the experimental T_g data represented according to the linearized Barton equation (see eqn. (1'a)) indicate the inapplicability of the diad supposition. The triad approximation has been used in such cases.

$$T_{g_{AB}} = \left[T_g - (n'_{AA}T_{g_A} + n'_{BB}T_{g_B}) \right] / (n'_{AB} + n'_{BA}) \quad (1'a)$$

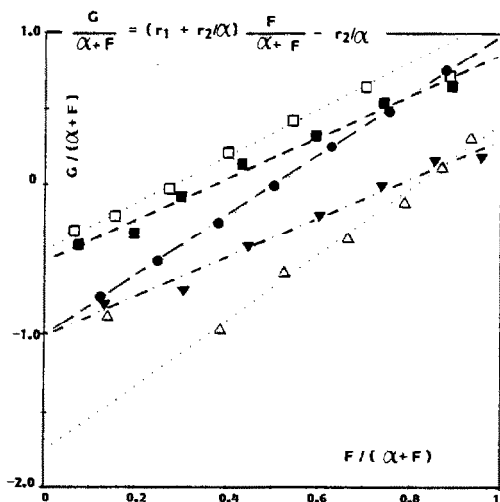
Study of the T_g versus composition behaviour of random copolymers of the electron donor *N*-(2-hydroxyethyl)carbazolymethacrylate (HECM) with the electron acceptor β -hydroxyethyl-3,5-dinitrobenzoyl methacrylate (HEDNBM (DNBM)) (for structures see Scheme 2) has shown serious positive deviation of T_g values from the supposed additivity [11]. These copolymers were synthesized by Percec and co-workers [11] and used for rheological measurements. The corresponding T_g values were determined using a Perkin-Elmer DSC-2 at heating rates between 2.5 and 20 K min⁻¹. The T_g values used in this study were obtained by extrapolating the initial T_g values to zero heating rate.

Positive deviations of T_g have also been observed in blends of PHECM with poly(hydroxyalkyl)DNBM in spite of the supposed plastifier effect of the increased length of the alkyl spacer in the polyacceptors [12].

EXPERIMENTAL

The synthesis of the donor/acceptor copolymers with intramolecular charge transfer interactions has been carried out by radical copolymerization according to the method described by Simionescu et al. [13]. Details concerning the synthesis of the copolymers of HEDNBM with *N*-(2-hydroxyalkyl)carbazolyl methacrylate are presented elsewhere [14]. The alkyl spacer in the carbazolyl donor was increased from ethyl (HECM) to propyl (HPCM) and *n*-butyl (HBCM). Similarly the alkyl spacer was increased in the copolymers of HECM with β -hydroxyalkyl-3,5-dinitrobenzoyl methacrylate in the order from ethyl (HEDNBM), propyl (HPDNBM) to *n*-butyl (HBDNBM). Due to the inhibitory action of the dinitrobenzoyl group difficulties were encountered in the synthesis of the respective homopolymers and copolymers containing a surplus of acceptor with the longer propyl and mainly *n*-butyl alkyl spacers.

The respective copolymerization reactivity ratios have been evaluated according to the Kelen–Tüdös method [15] (see Fig. 1). The values obtained (included in Table 1) were used for calculation of diad and triad



$$G = \frac{([M_1]/[M_2])(d[M_1]/d[M_2] - 1)}{d[M_1]/d[M_2]}$$

$$F = \frac{([M_1]/[M_2])^2}{d[M_1]/d[M_2]}$$

M_i concentration of monomers

dM_i concentration of copolymer components

α arbitrary constant ($\alpha > 0$)

Fig. 1. Evaluation of the reactivity ratios for donor/acceptor copolymers by the Kelen–Tüdös method: ●, P(HEDNBM-co-HECM); □, P(HPDNBM-co-HECM); △, P(HEDNBM-co-HPCM); ■, P(HBDNBM-co-HECM); ▼, P(HEDNBM-co-HBCM).

TABLE 1
Copolymerization ratios and T_g increments of diads and triads for donor/acceptor copolymers

Copolymer	r_A	r_B	T_{gA}	T_{gB}	T_{gAB}	T_{gABA}	T_{gBAB}	T_{gABB}
<i>Poly(acceptor-co-donor)</i>								
P(HEDNBM-co-HECM)	1	1	353.1	410.6	423	410	410	405) ^a
P(HEDNBM-co-HPCM)	1.31	0.27	353.1	350.6	389.5	395	360	360
P(HEDNBM-co-HBCM)	0.99	0.30	353.1	362.3	348	270	290	405) ^a
P(HPDNBM-co-HECM)	0.38	0.99	336.7	410.6	385 (?)	T_g data almost additive		
P(HBDNBM-co-HECM)	0.52	0.86	330.2	410.6	328 ^c	310	410	410
<i>Poly(acrylate / methacrylate-co-donor)</i>								
P(MMA-co-HECM)	0.87	0.33	386.7	410.6	412	415	405	405) ^a
P(MA-co-HECA)	1.51	0.49	282.4	371.3	392	370	370	350
P(BMA-co-HECM)	0.91	0.21	285.8	410.6	401.5 ^b			
P(BA-co-HECA)	0.34	0.26	218.4	371.3	325	265	370	370
<i>Poly(acrylate / methacrylate-co-acceptor)</i>								
P(MMA-co-HEDNBM)	1.01	0.60	386.7	353.1	340	420	260	260
P(MA-co-HEDNBA)	0.72	2.33	282.4	325.8	295	306	282	282
P(BMA-co-HEDNBM)	0.71	0.54	285.8	353.1	303	322	293	293
P(BA-co-HEDNBA)	0.7	2.0	218.4	325.8	303	315	270	270

^a Diad assumption is quite acceptable, no essential improvement by triad assumption.

^b Diad assumption is valid.

^c T_g value published by Parada and Percec [12].

sequence distributions in the copolymers. In the monomer pairs HECM/HPDNBM and HPCM/HEDNBM (dotted lines) in each case one experimental point was omitted in calculating the respective reactivity ratios.

The glass temperatures of the copolymers were determined on a Perkin-Elmer DSC 4 in nitrogen at the heating rate of 10 K min^{-1} . For the T_g evaluation the second heating scans were always used as they proved to be reproducible. The glass temperatures shown in Table 1 are the temperatures at which the change in heat capacity reached half its maximum value.

The T_g versus composition fit of the experimental T_g data was carried out by applying the diad and triad sequence approaches of Barton [6] and Ham [8], respectively (equations are shown in frames in Scheme 1).

RESULTS AND DISCUSSION

The DSC thermograms in the glass transition range of the copolymers (HEDNBM-co-H(alkyl)CM) are shown in Fig. 2(top). It is remarkable that the copolymers P(HEDNBM-co-HECM) and P(HEDNBM-co-HPCM) exhibit relatively increased T_g values, whereas the copolymers P(HEDNBM-co-HBCM) show a relative decrease of their T_g values. The enlargement of the T_g range in the copolymers is shown in Fig. 2(bottom).

The different dependences of the T_g versus composition data of the copolymers are quite evident in Fig. 3. In Fig. 3(a) are presented the attempts of fitting the experimental T_g data of the copolymers according to the models of diad sequence contributions (dotted lines) and of triad sequence contributions (broken lines). For poly(HEDNBM-co-HECM) both the T_g data of the copolymers synthesized by Percec and co-workers [11] (full circles) and of the copolymers synthesized by Simionescu et al. [14] (open circles) are shown. The agreement of the data is quite satisfactory taking into account the different modes used for T_g evaluation.

The $T_{g_{AB}}$ values of the corresponding heterodiads were calculated using the linearized equation of Barton (1'a) (see Fig. 4). The number of flexible bonds has been admitted to be additive in both the respective diads and triads.

In attempting to apply the triad sequence model (eqn. 1b) the corresponding contributions to T_g of the triad sequences have been chosen by trying to use at least the same values for couples of triads.

Because of this modified fitting procedure the values shown in Table 1 for the acrylic and methacrylic copolymers both of the diad $T_{g_{AB}}$ and of the triad contributions to T_g are slightly different from the previously published data. It is evident that a real improvement of the fit of the experimental T_g data achieved by using the triad assumption is observed only for the (HEDNBM-co-HPCM) system although the diad sequence supposition is still acceptable.

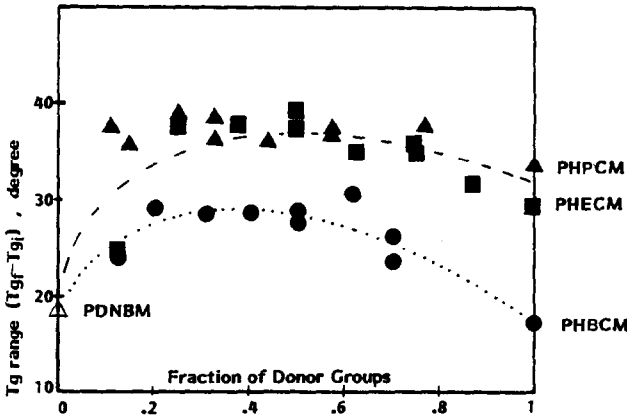
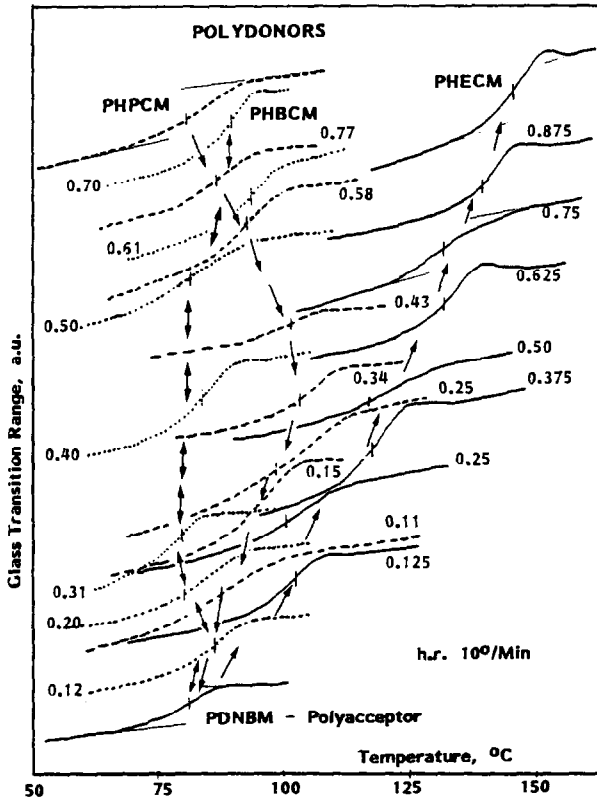


Fig. 2. DSC thermograms in the glass transition range of poly(HEDNBM-co-N-hydroxy(alkyl)carbazolyl)methacrylates. Top, glass transition range; bottom, enlargement of the glass transition range in copolymers: ■, P(HEDNBM-co-HECM); ▲, P(HEDNBM-co-HPCM); ●, P(HEDNBM-co-HBCM).

To give a real image of the deviations from additivity of the glass temperatures of the donor/acceptor copolymers, the relative deviations from additivity weighted by the difference between the two T_g values of the respective homopolymers are presented in Fig. 3(b).

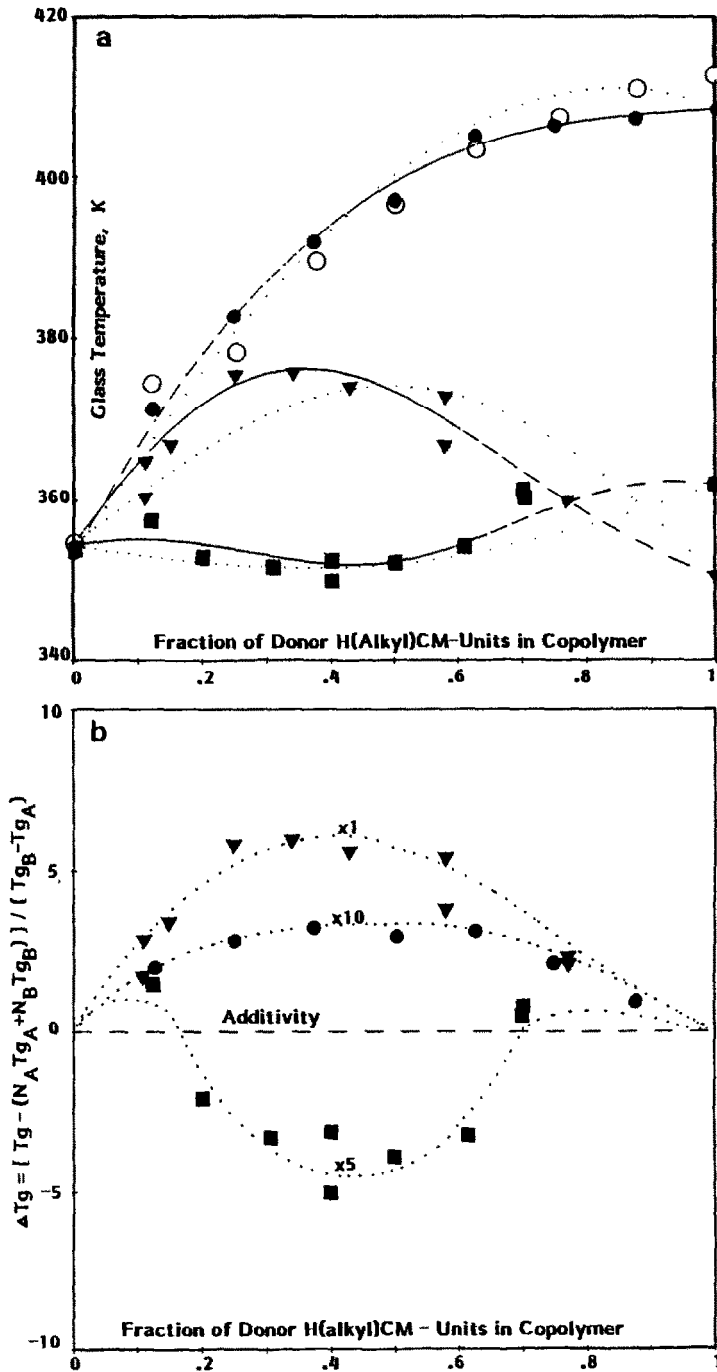


Fig. 3. Glass temperature vs. composition of poly(HEDNBM-co-*N*-hydroxy(alkyl)carbazoly) methacrylates. (a) Diad and triad sequence contribution models. (b) Deviation from additivity of the glass temperature. ●, P(HEDNBM-co-HECM) copolymer of Percec and co-workers [11]. ○, P(HEDNBM-co-HECM) copolymer of Simionescu et al. [14]; ▼, P(HEDNBM-co-HPCM); ■, P(HEDNBM-co-HBCM).

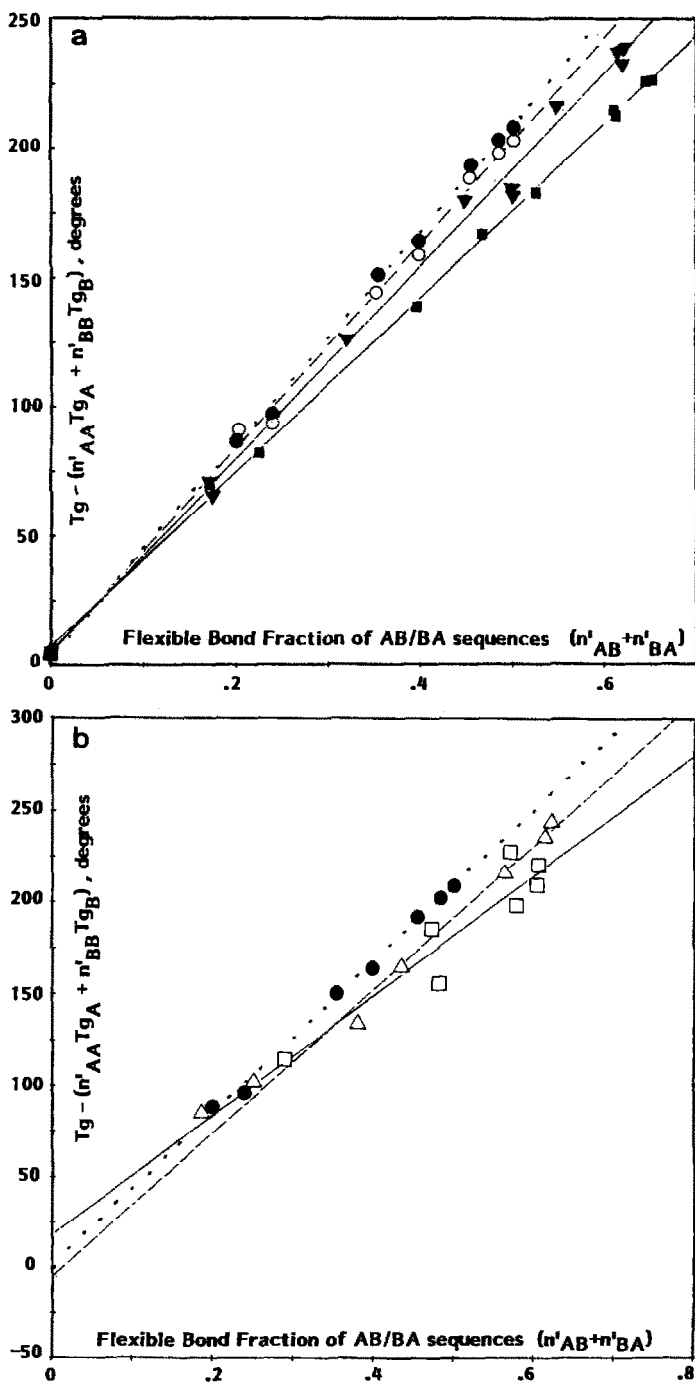


Fig. 4. Evaluation of the T_{gAB} contribution to the copolymer glass temperature. (a) poly(HEDNBM-co-*N*-hydroxy(alkyl)carbazoyl)methacrylates (key to signs used is given in Fig. 3). (b) Poly(β -hydroxy(alkyl)dinitrobenzoyl-co-HECM)methacrylates. ●, P(HEDNBM-co-HECM); Δ , P(HPDNBM-co-HECM); \square , P(HBDNBM-co-HECM).

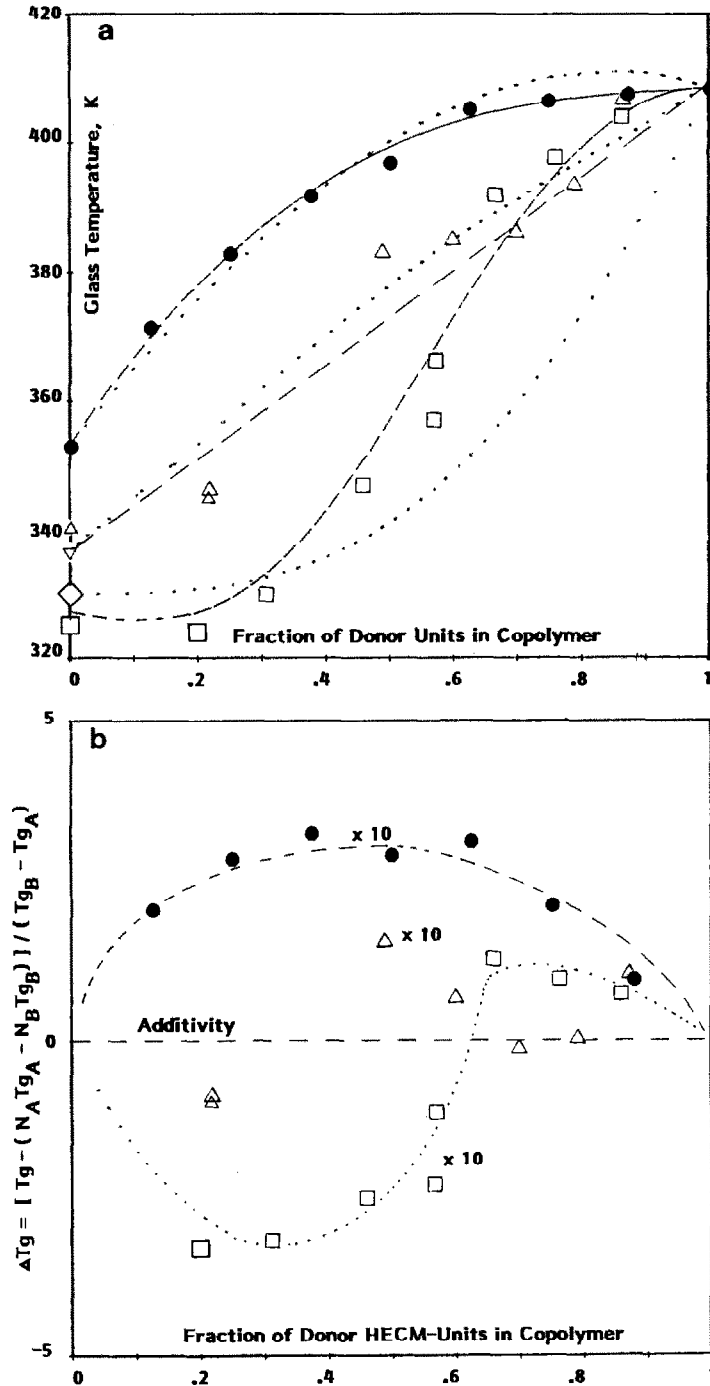


Fig. 5. Glass temperature vs. composition of poly(β -hydroxy(alkyl)dinitrobenzoyl-co-HECM)methacrylates. (a) Diad and triad sequence contribution models. (b) Deviation from additivity of the glass temperature (key to signs used is given in Fig. 4(b)).

It is remarkable that in this representation the copolymers of the system with the propyl spacer (HEDNBM-co-HPCM) show the largest (positive) deviations from additivity. Starting with the longer *n*-butyl spacer, the plastifier influence of the longer side group acts causing even negative deviations from additivity. At the same time is evident the relative symmetry of the T_g versus composition behaviour for all studied donor/acceptor systems containing the different alkyl spacers between the carbazol donor group and the polymer backbone.

The glass temperature versus composition dependence of the donor/acceptor copolymers with the increasing alkyl spacer length between the dinitrobenzoyl acceptor group and the methacrylic backbone is much more sophisticated as is shown by the respective curves in Fig. 5. Unfortunately there are real uncertainties concerning the variation of the T_g of the copolymers in the range of high acceptor content. Because of the difficulties encountered in the synthesis of the respective copolymers only minimal amounts were available for measurements, rendering more difficult the exact evaluation of the glass temperature. For the respective acceptor homopolymers the data of Parada and Percec [12] are also included.

It seems that the T_g versus composition dependence is nearly additive for the copolymers with the propyl spacer in the acceptor unit, whereas the copolymers with the *n*-butyl spacer show s-shaped curves (see Fig. 5(b)). For both systems the scatter of the data is very large if they are used to evaluate the $T_{g_{AB}}$ contribution of the respective alternating copolymers (Fig. 4(b)).

Applying the sequence contribution models for the T_g versus composition behaviour (Fig. 5(a)) the fit of the experimental T_g data of the copolymers with the propyl spacer in the acceptor unit is superior when using the diad sequence model (dotted line) than for the additivity rule (broken line). For the copolymers with the *n*-butyl spacer in the acceptor unit only the triad sequence contribution model allowed the fit of the experimental T_g data.

The influence of the dilution by substitution of the respective interacting groups in polyacrylates and polymethacrylates by methyl or by *n*-butyl ester groups has been intensively investigated in connection with the study of the influence of the charge transfer interaction on the mechanical dynamic properties of donor/acceptor polymer blends [16].

In parallel has been analyzed the glass temperature of the corresponding copolymers [9,10]. In Fig. 6 are shown comparative T_g versus composition curves for the corresponding copolymers of methyl and *n*-butyl acrylates and methacrylates containing either the donor *N*-hydroxyethylcarbazolyl (Fig. 6(a)) or the acceptor β -hydroxy-di-nitrobenzoyl group (Fig. 6(b)).

The donor copolymers obey the diad sequence contribution model more or less accurately. The deviations from this assumption are, however, much more accentuated for the donor acrylate copolymers and the respective

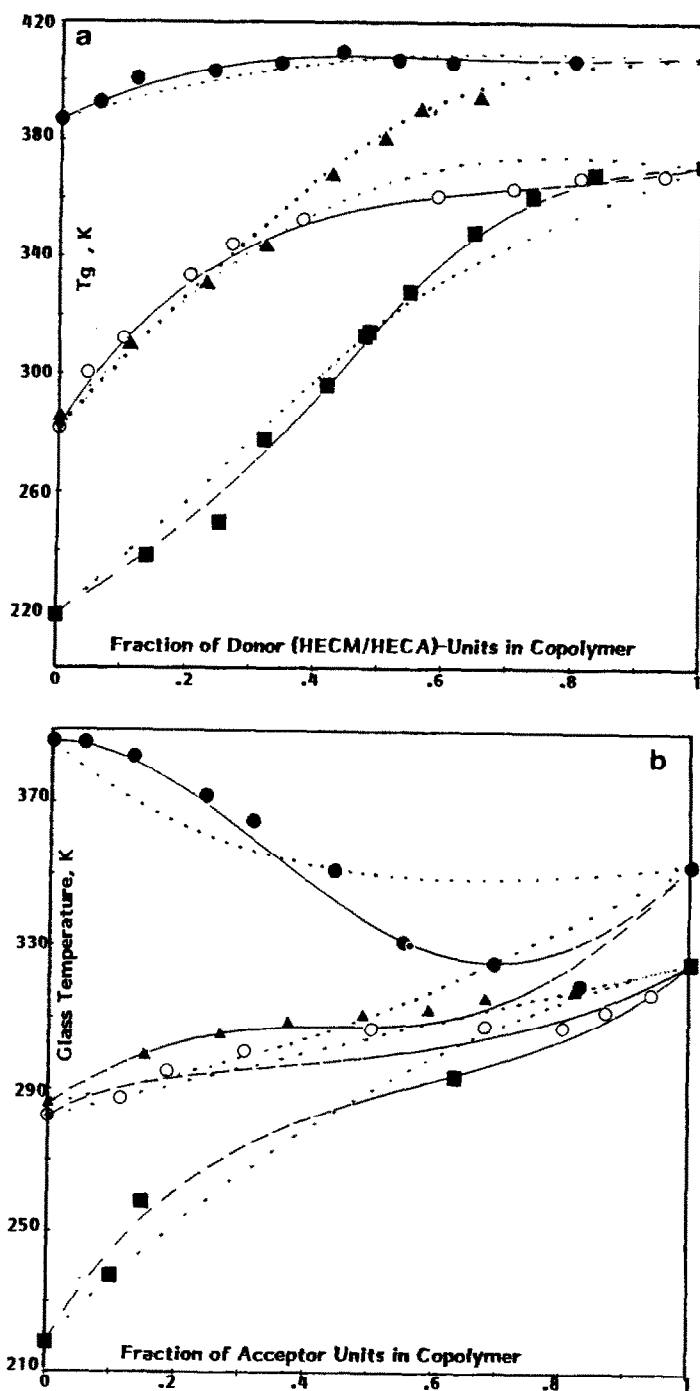


Fig. 6. Glass temperature vs. composition of copolymers containing donor or acceptor groups. (a) Poly(HECA/HECM/-co-Methyl/*n*-Butyl)acrylates and methacrylates. ●, P(MMA-co-HECM); ○, P(MA-co-HECA); ▲, P(BMA-co-HECM); ■, P(BA-co-HECA). (b) Poly(HEDNBA/HEDNBM-co-methyl/*n*-butyl)acrylates and methacrylates. ●, P(MMA-co-HENDBM); ○, P(MA-co-HEDNBA); ▲, P(BMA-co-HEDNBM); ■, P(BA-co-HEDNBA).

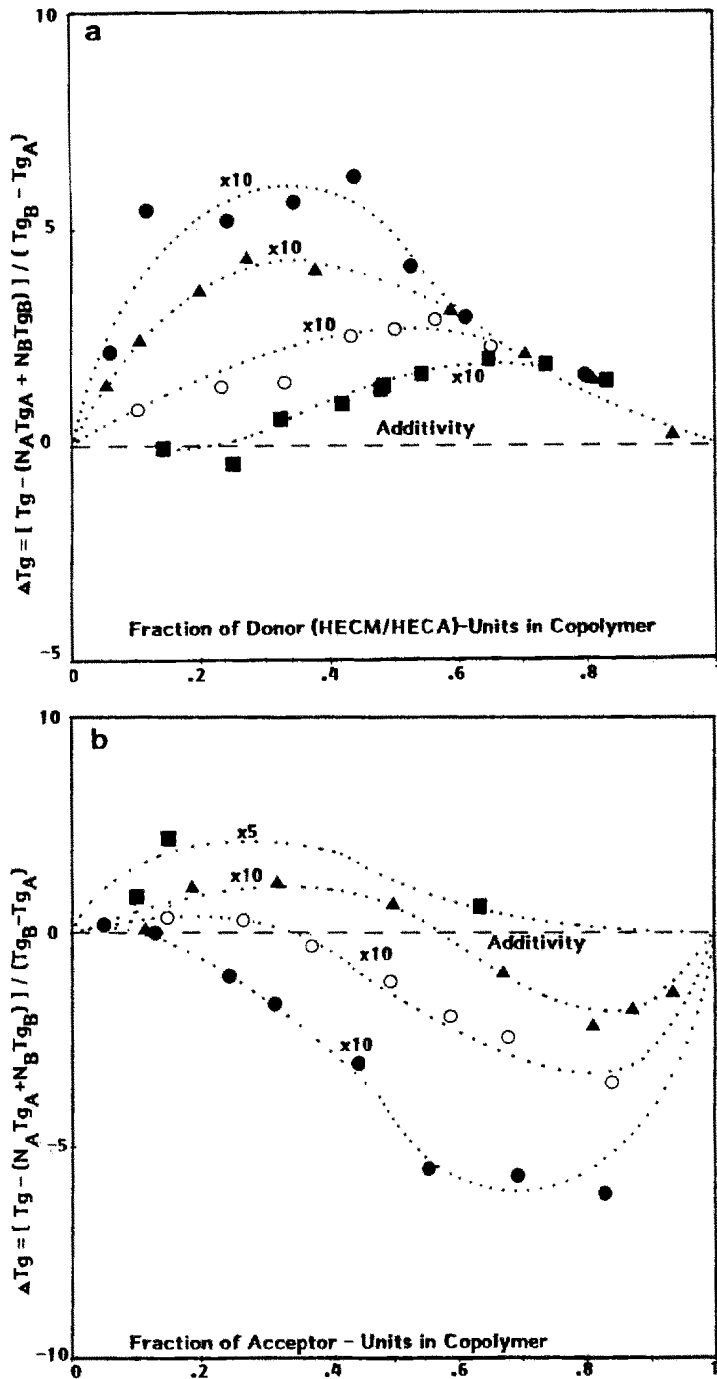


Fig. 7. Deviation from additivity of the glass temperature of copolymers containing donor or acceptor groups. (a) Poly(HECA/HECM-co-methyl/*n*-butyl)acrylates and methacrylates (key to signs used is given in Fig. 6(a)). (b) Poly(HEDNBA/HEDNBM-co-methyl/*n*-butyl)acrylates and methacrylates (key to signs used is given in Fig. 6(b)).

slightly s-shaped curves are better adapted by the triad sequence contribution model (Fig. 6(a)). The acceptor copolymers show, on the contrary, exclusive s-shaped curves (see Fig. 6(b)).

The difference between the T_g behaviour of the donor and acceptor acrylic and methacrylic copolymers is obvious by examining the corresponding relative deviations from additivity (Fig. 7).

The donor copolymers show only positive deviations from additivity of the glass temperature. These deviations decrease in the order methyl methacrylate > *n*-butyl methacrylate > methyl acrylate > *n*-butyl acrylate donor copolymers. The maximum of T_g deviation shifts at the same time from the acceptor-rich to the donor-rich copolymers (Fig. 7(a)).

The glass temperature behaviour of the acceptor copolymers is quite the opposite. The methacrylates mainly show large negative deviations from additivity (methyl > *n*-butyl) whereas the acrylates show increasing positive deviations. The negative deviations are situated in the donor-rich part whereas the positive deviations are exhibited in the acceptor-rich part.

This behaviour suggests different interactions between donor and ester groups on the one site and between acceptor and ester groups on the other site. The interactions are more pronounced for the methacrylates than for the acrylates. The donor–ester interaction is accompanied by a decrease in free volume (increase of T_g), whereas the acceptor–ester interaction is inconsistent, depending on the ratio of acceptor to ester groups in the copolymer.

A possible explanation of the different T_g behaviour of the donor–(meth)acrylate and the acceptor–(meth)acrylate copolymers, may be associated with a slight acceptor action of the (meth)acrylic groups in both cases. The donor–(meth)acrylate interaction would then result in an attraction, i.e. in a reduction of the free volume (increase of T_g), whereas the acceptor–(meth)acrylate interaction will be accompanied sooner by a repulsion, i.e. by an increase of the free volume (decrease of the T_g below the additivity value).

CONCLUSION

The glass temperature behaviour of donor and/or acceptor groups containing copolymers suggests not only the different influence of the length of the alkyl spacer between the interacting group and polymer backbone but also a distinct influence of the donor and acceptor groups themselves. These differences are accentuated in copolymers containing methyl or *n*-butyl ester groups. The copolymers containing donor groups obey the diad sequence contribution assumption more or less accurately, whereas the acceptor groups containing copolymers always show s-shaped curves requiring the application of the triad sequence contribution model.

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