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The Effect of Sequence Distribution on Glass Transition of Donor-Acceptor Copolymer Systems

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SUMMARY

T_g studies on copolymers of methyl methacrylate and of butyl methacrylate with N-(2-hydroxyethyl) carbazolyl methacrylate as electro-donor and respective with methacryloyl-ß-hydroxyethyl-3,5-dinitrobenzoate as electro-acceptor comonomer have shown that the glass transition behaviour can only be explained by the effect of triad sequences. Introduction of the electro-donor (or electro-acceptor) group into a methacrylate triad allways increases the T_g contribution of the homopolymer triad, whilst the introduction of a methacrylate group into the electro-donor (acceptor) triad decreases the respective T_g contribution.

INTRODUCTION

To explain sequence distribution effects on glass transition of random copolymers two main approaches may be discussed. By extension of the Fox equation, JOHNSTON (1969) has taken into account the dyad sequence distribution in the copolymer deriving the equation

$$\frac{1}{T_g} = \frac{w_A \cdot P_{AA}}{T_{AA}} + \frac{w_a \cdot P_{AB} + w_B \cdot P_{BA}}{T_{AB}} + \frac{w_B \cdot P_{BB}}{T_{BB}} \quad . (1)$$

T_g is the glass transition temperature of the copolymer containing weight fractions w_A and w_b of the two monomer units. A and B. P_{ij} are the formation probabilities of different linkages (HARWOOD, 1968) which should contribute to the copolymer glass transition with a respective parameter T_{ij}. (It is also supposed that $T_{AB}=T_{BA}$). T_{AA} and T_{BB} are generally accepted to be the glass transition temperatures of the corresponding homopolymers.

The second approach is suggested by BARTON (1970) and is based on the Gibbs-Di Marzio theory of the glass transition

$$T_g = N'_{AA} \cdot T_{AA} + N'_{BB} \cdot T_{bb} + (N'_{AB} + N'_{BA}) \cdot T_{AB} \quad . \quad (2)$$

Here N'_{ij} are the weighted mole fractions of rotatable bonds pertaining to the respective dyads.

Contrary to Johnston's approach, where T_{AB} is calculated by a computerized multiple regression analysis programe, Barton suggests a mode of calculation from T_g-data of the copolymers by the linearization of equation (2) in a $T' = T_g - N'_{AA} \cdot T_{AA} - N'_{BB} \cdot T_{BB}$ versus $(N'_{AB} + N'_{BA})$ plot.

Critical aspects of both dyad approaches are presented by HAVLICEK et al.(1981),which finally use Barton's approximation corrected for equilibrium transition temperature T_2. The authors further mention that triad or higher approximations contain unfortunately some experimentally inaccessible parameters.

Nevertheless, an extension of the Barton approach for triad contribution to glass transition temperature of random copolymers has improved in some cases the T_g-sequence distribution correlation. The T_{ijk}-values of the triads were choosen for closest fit of the experimental T_g data (HAM, 1975).

In the present paper an attempt is made to correlate T_g data of copolymers of both methylmethacrylate (MMA) and butylmethacrylate (BMA) with N-(2-hydroxyethyl)carbazolyl methacrylate (HECM) as electro-donor monomer and methacryloyl-ß-hydroxyethyl-3,5-dinitrobenzoate (DNBM) as electro-acceptor monomer. Supplemetary are shown the results of a T_g-sequence distribution study of (DNBM-co-HECM) copolymers described by SIMIONESCU et al (1980).

EXPERIMENTAL AND DISCUSSIONS

The copolymerization behaviour and the reactivity ratios of the studied systems BMA-co-DNBM, BMA-co-HECM, MMA-co-DNBM and MMA-co-HECM will be published elsewhere.

Glass transition temperatures were measured by differential scanning calorimetry with a PERKIN-ELMER DSC-2 and are extrapolated to zero heating rate.

Fig. 1 shows the data obtained by application of the Barton approach to the poly(DNBM-co-HECM) system. Dyad sequence distribution (Fig.1b) was computed taking into account the reactivity ratio and composition data published by Simionescu et al.

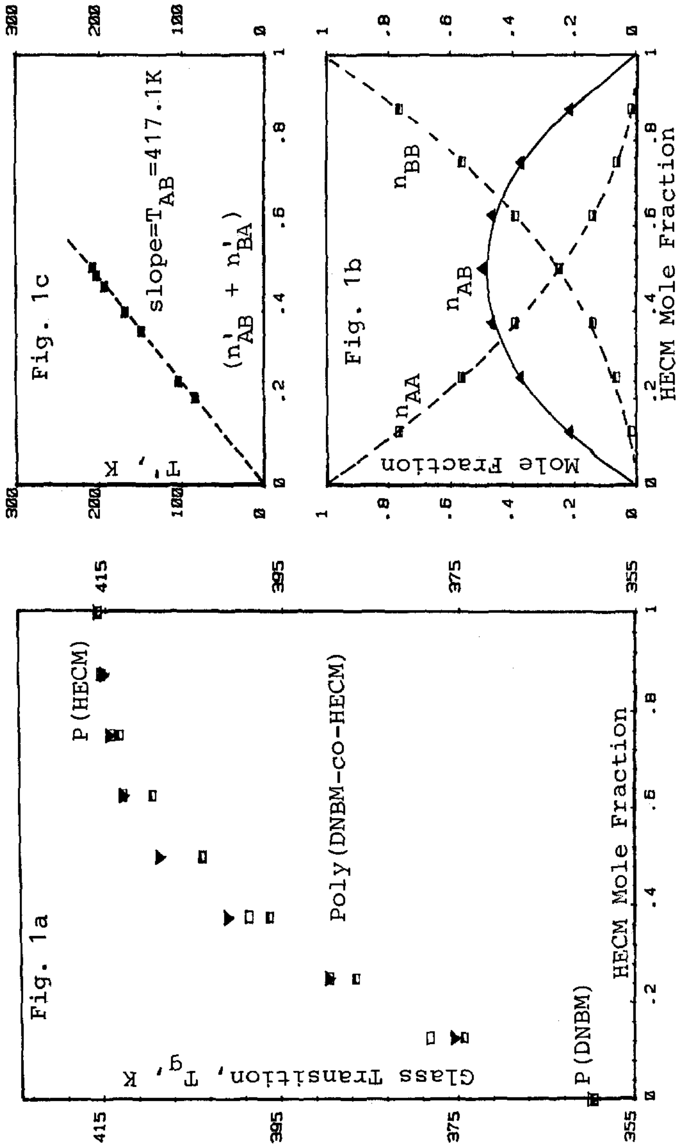

Fig. 1. T_g- sequence distribution study of (DNBM-co-HECM) copolymers. □ - experimental T_g-data ; ■ - calculated data in the dyad approximation ; ▶ - calculated data in the triad approximation

Using the linearized form of Barton's equation (2), T_{AB} (417.1 K) of the AB-sequences was obtained from the slope of the curve (Fig.1c). Then the T_g values of the copolymers were calculated with equation (2) and compared with the experimental data (Fig. 1a). The correlation is satisfactory and only insignificant improved by application of the triad approximation of Ham.

However, the application of the dyad approximation to correlate T_g data of the copolymers of MMA and BMA with respective DNBM and HECM failed in both Burton's and Johnston's versions. Fig.2 shows for exemplification the results for the poly(BMA-co-DNBM) system. This failure of the dyad approach may be due to the fact, that in opposition to the first system the latters are not azeotropic in their copolymerization behaviour.

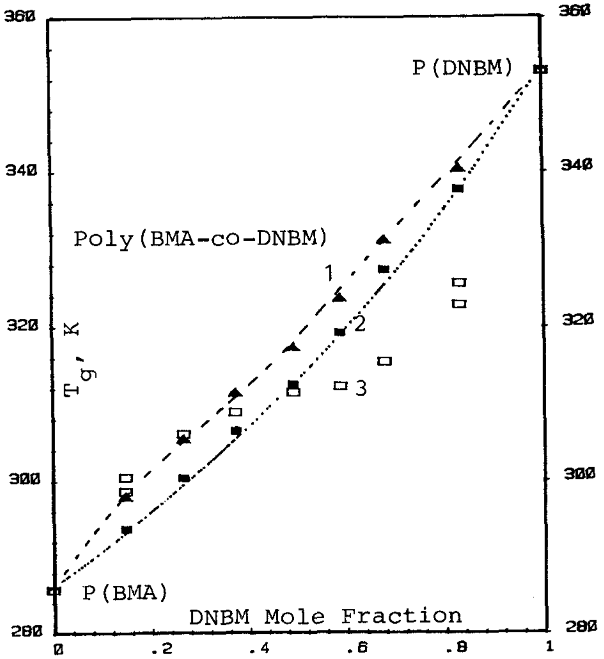

Fig.2 T_g- sequence distribution study of (BMA-co-DNBM) copolymers.

□ - *experimental data;* ■ - *Barton's approach*

▲ - *Johnston's approach*

Consequently, Ham's triad approximation derived from the Barton approach was used to correlate T_g-composition data of the copolymers with the triad sequence distribution in the poly(BMA-co-DNBM) and poly(BMA-co-HECM) - Fig.3 - and in the poly(MMA-co-DNBM) and poly(MMA-co-HECM) systems - Fig.4.

In order to choose the T_{ijk}-parameters of the triad contribution to the glass transition of the copolymers, the T_{AB} values of the dyads were calculated according to Barton's method using the reactivity ratios to be published. Subsequently the T_{ijk} data of the triads which give the best fit of the experimental T_g-composition data of the copolymers were obtained by multiple iteration procedure.

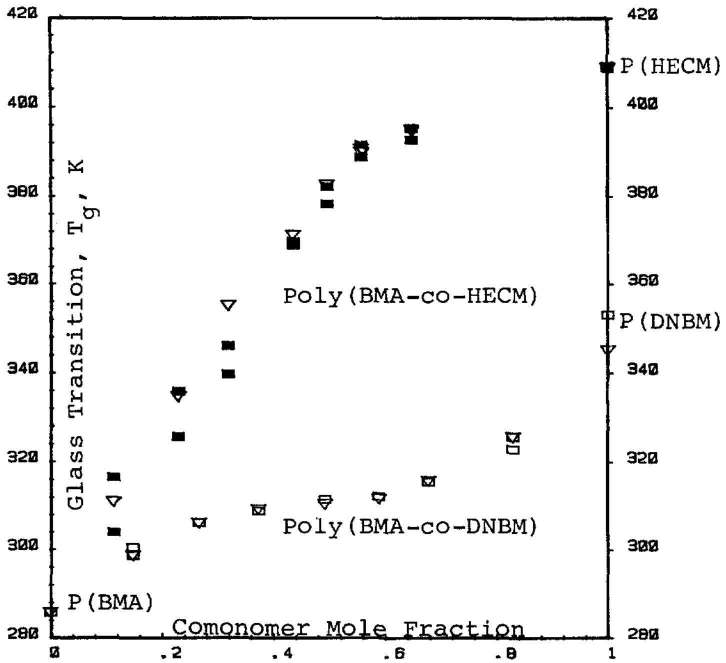

Fig.3 T_g composition correlation of BMA copolymers

□ - *experimental data of the copolymers with DNBM*

■ - *experimental data of the copolymers with HECM*

▼ - *calculated data in the triad distribution approximation*

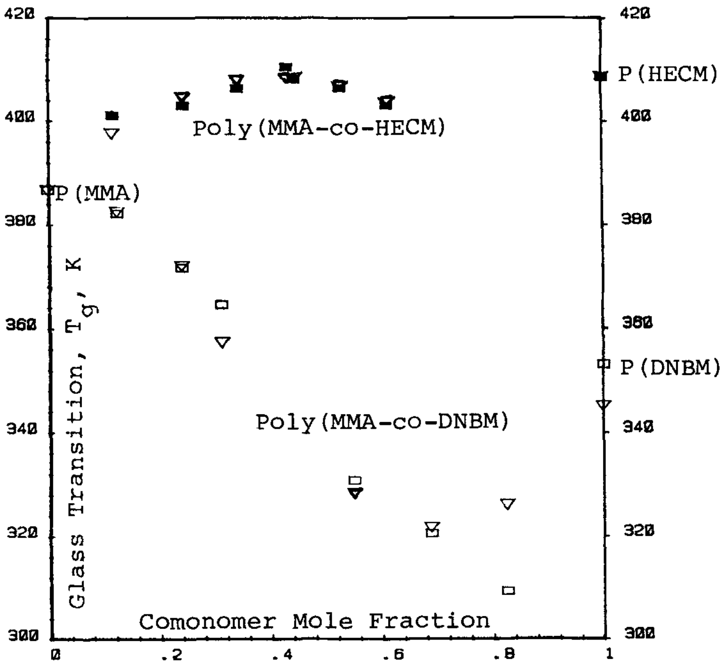

Fig.4 T_g composition correlation of MMA copolymers (same signification of signs as in Fig.3)

The used T_{ijk} parameters together with the computed T_{AB} values are listed in table I.

Table I. The glass transition parameters of the triads

System	T_{AB}	Glass Transition Parameters [K]					
		T_{AAA}	T_{AAB}	T_{ABA}	T_{BAB}	T_{BBA}	T_{BBB}
(BMA-co-DNBM)	310.1	285.8	345.0	311.2	310.0	270.0	345.0^x
(BMA-co-HECM)	407.6	285.8	375.0	403.0	403.0	365.0	408.6
(MMA-co-DNBM)	376.3	386.8	412.0	358.0	322.0	220.0	345.0^x
(MMA-co-HECM)	410.9	386.8	430.0	418.0	408.0	365.0	408.6

^{x}The experimental T_g value of Poly(DNBM) was 353.1 K; T_{AAA} and T_{BBB} are the respective T_g's of the homopolymers.

Some interesting regularities may be noted without further comment:

-The introduction of an electro-donor or an electro-acceptor group into a methacrylate triad (T_{AAA}) always increases the T_g related to the homopolymers, whilst the introduction of a methacrylate group in the donor or respective the acceptor triad (T_{BBB}) decreases the T_g related to the homopolymer. The increasing effect is more accentuated for the donor group, whilst the decreasing effect for the acceptor group.

-Starting from the computed T_{AB} values, the disproportionation between the T_{ABA} and T_{BAB} contributions to the best fit is more accentuated in the methylmethacrylate systems, where the differences in the sizes of the side groups are greater.

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