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GLASS - TRANSITION IN DONOR AND ACCEPTOR ACRYLIC COPOLYMERS

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ABSTRACT

T_g vs. composition studies on acrylic(methacrylic) copolymers of donor 2-(9-carbazolyl)ethyl acrylate(methacrylate) and of acceptor 2(3,5-dinitrobenzoyloxy)ethyl acrylate(methacrylate) have evidenced specific T_g vs. composition dependences. The acrylic(methacrylic) copolymers of the donor show always positive deviations from additivity of the T_g suggesting reduced mobility do to donor acceptor-like interactions. The T_g behaviour of the acceptor copolymers is much more complex showing an inversion from reduced to increased mobility of the copolymeric chain as the acceptor content is increased.

INTRODUCTION

Although the thermodynamic phase transition character is yet in discussion, the glass transition is one of the most investigated phenomena in polymers as it is accompanied by typical changes in volume, enthalpy, and especially in mechanical properties. Taking into account the assumed freezing in of possible conformational changes at T_g and the same viscosity level of all polymers in the glassy solid state, the glass transition is considered to be an universal "iso free volume" and "isoviscous" state, respectively.

Due to the importance of T_g, attempts are known to correlate T_g data with various properties and structural factors, mainly those related with chain mobility (ref.1 and 2). For copolymers, beside additivity rules, various sequence distribution glass transition correlations are known. The application of the latter has suggested essential differences in the T_g behaviour of donor-methacrylate and acceptor-methacrylate copolymer systems (ref.3) and in the present paper the study is extended to donor and acceptor - acrylate copolymer systems.

SEQUENCE DISTRIBUTION - GLASS TRANSITION CORRELATIONS

As it has been shown in the foregoing paper (ref.3), both the additivity rules of FOX (ref.4) and of DIMARZIO and GIBBS (ref.5) can be extended to account for nonlinearity in glass transition-composition dependences of random copolymers, due to the differences in interaction of the two monomeric units.

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We prefer, in the following, the diad and triad sequence approximations of the DiMarzio and Gibbs rule, because Tg_{AB} of the alternating copolymer, if not experimentally accesible, can be evaluated from experimental T_g data of the copolymer, and because the validity ranges of the diad and triad sequence approximations are strictly delimited.

Starting with the DiMarzio and Gibbs additivity rule for the copolymer T_g

$$T_g = n'_A Tg_A + n'_B Tg_B \tag{1}$$

Barton's diad approximation (ref.6) considers specific interactions and thus accounts for differences in Tg contributions of the hetero AB diads as compared to those of the homo AA and BB diads. The T_g values of the latter diads are those of the respective homopolymers, whereas the T_g of the AB diads is assumed to be given by the T_g of the corresponding alternating copolymer. The T_g of the random copolymer will then be given by the equation:

$$T_g = n'_{AA} Tg_{AA} + n'_{BB} Tg_{BB} + (n'_{AB}+n'_{BA}) Tg_{AB} \tag{2}$$

Here n'_{ij} are the weighted mole fractions of the rotatable bonds, RB, in the respective diad sequences

$$n'_{ij} = (n_{ij} RB_{ij}) / \sum n_{ij} RB_{ij} \tag{3}$$

with n_{ij} the mole fractions of the corresponding diads.

The mole fractions of the diads are related with the mole fractions n_i of the comonomer units in the random copolymer via the respective kinetic probabilities, P_{ij}, of addition in radical copolymerization of the two monomers to the growing radical.

$$\begin{aligned} n_{ij} = n_i P_{ij} \quad &\text{and} \quad n_{ii} = n_i P_{ii} \\ \text{and} \qquad & \\ P_{ij} = 1 / (1+r_i X) \quad &\text{and} \quad P_{ii} = 1 - P_{ij} \end{aligned} \tag{4}$$

$X = M_1/M_2$ is the ratio of the monomer feed and r_i are the copolymerization reactivity ratios.

Equation (2) shows the Tg_{AB} value to be graphically obtainable from experimental T_g data of the copolymers in the $Tg-(n'_{AA}Tg_{AA}+n'_{BB}Tg_{BB})$ versus $(n'_{AB}+n'_{BA})$ representation. Linearity of the experimental data with zero intercept and Tg_{AB}-slope will confirm the validity of the diad sequence approximation for the T_g contribution of random copolymers.

Taking into account the number of rotatable bonds is not well defined in monomers with bulky side groups and with possible resonance of π-electrons, best linearity and closest to zero intercept of equation (2) can be used as criterion for rotatable bond determination.

For illustration the respective experimental and calculated data are presented in Table 1 for the Poly(donor-co-acceptor) system 2-(3,5-dinitrobenzoyloxy)ethyl methacrylate - DNBM/ 2-(9-carbazolyl)ethyl methacrylate HECM; the latter for different values of possible rotatable bonds in the DNBM containing diad sequences. Best agreement between experimental and calculated copolymer T_g data is obtained for the closest to zero intercept of equ.(2). The perfect linearity of the data presented in accordance with equ.(2) is evidenced in Fig.1b.

Table 1. Diad Sequence Approximation of the (DNBM-HECM) copolymer System

HECM mole %	T_g, exp., K		T_g, calc., K		
		RB(HE/HE)	14	14	16
		RB(DN/DN)	18	18	24
		RB(HE/DN)	16	20	20
		intercept	.1	0	.1
		Tg(AB)	413.5	410.1	411.4
0	353.1				
12.7	371.5		368.6	370.3	369.3
25.0	382.8		381.4	382.8	382.0
37.5	391.9		391.4	391.9	391.7
50.0	397.2		398.9	398.6	398.9
62.5	405.2		404.2	403.4	403.9
75.0	406.6		407.5	406.6	407.0
87.3	407.3		408.9	408.3	408.5
100	408.6				

For the same copolymer system, triad sequence approximation results in no additional improvement in the calculated T_g vs. composition dependence as shown in Fig.1a.

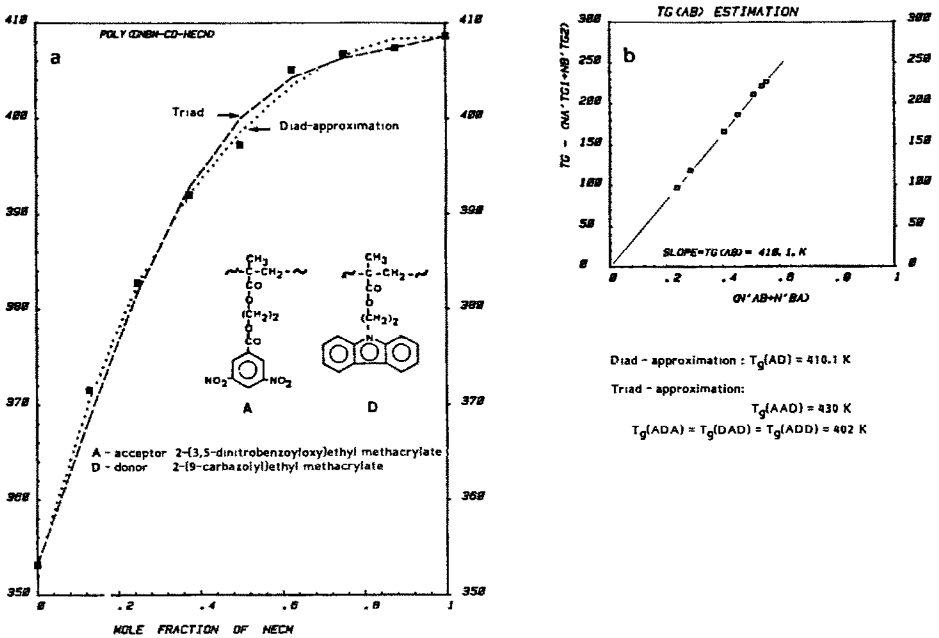

Fig.1 T_g vs. Composition Dependence of the DNBM-HECM Copolymer System
a.Diad and Triad Sequence Approximation, b.Tg_{AB} evaluation

Good linearity of experimental data presented in accordance with equ.(2) and as close as possible to zero situated intercept is always characterized by no substantial improvement if the diad sequence approximation is substituted by the triad sequence approximation in the calculation of the T_g vs. composition dependence for random copolymers. This is confirmed by all the studied acrylic(methacrylic)/donor copolymer systems and may therefore be used as validity criterion for the diad approximation.

Nonlinearity of equ.(2) accounts for further extension of the additivity rule to improve the T_g vs. composition relationship of copolymers; but, because of the impossibility of measuring or evaluating of the T_g contribution of higher sequences, the corresponding relations become essentially parametrized equations, requiring computing procedures for closest fit of experimental T_g data.

Assuming equivalence of reversed triad sequences, i.e. $n_{AAB}=n_{BAA}$ and $n_{ABB}=n_{BBA}$ and $Tg_{ABA}=Tg_{BAB}$, HAM (ref.7) expanded Barton's equation to the form:

$$T_g = n'_{AAA}Tg_{AAA}+n'_{BBB}Tg_{BBB}+n'_{AAB}Tg_{AAB}+n'_{BBA}Tg_{BBA}+(n'_{ABA}+n'_{BAB})Tg_{ABA} \quad (5)$$

The latter supposition of Ham, i.e. $Tg_{ABA}=Tg_{BAB}$, may be reconsidered at least for copolymers of monomers with very different specific interaction and bulkiness of the side groups. The triad approximation can then be rewritten as follows:

$$T_g=n'_{AAA}Tg_{AAA}+n'_{BBB}Tg_{BBB}+n'_{AAB}Tg_{AAB}+n'_{BBA}Tg_{BBA}+n'_{ABA}Tg_{ABA}+n'_{BAB}Tg_{BAB} \quad (6)$$

The mole fractions of the triads are related to the mole fractions of the comonomers in the copolymer via the copolymerization probabilities of the well known kinetic relations.

EXPERIMENTAL

The copolymerization of Methyl- (MMA) and of Butylmethacrylate (BMA) with the electron-donor HECM and the electron-acceptor DNBM, respectively, as well as,the reactivity ratios and the molecular weights of the copolymers (all higher than Mn=40,000) are presented elsewhere (ref.8). The copolymers of Butylacrylate (BA) with the donor 2-(9-Carbazolyl)ethyl acrylate (HECA) (Mn in the range 20,000 to 30,000) and of the Methylacrylate (MA) with the acceptor 2-(3,5-Dinitrobenzoyloxy)ethyl acrylate (DNBA) were synthesized by radical copolymerization with AIBN at 60°C. Due to the reduced reactivity of DNBA the molecular weights of the respective copolymers were only of about Mn=6,000. Nevertheless, possible molecular weight influences on T_g were neglected because of the reduced polydispersity of the copolymers. Details of the synthesis of the acrylic monomers, the copolymerization, and the characterization of the copolymers will be published in detail later.

T_g data of all studied copolymers were measured on PERKIN-ELMER DSC 2 and DSC 7 instruments, at different heating rates and are extrapolated to zero heating rate.

RESULTS AND DISCUSSION

For all studied acrylic(methacrylic) copolymers of the electron donor HECA and HECM, respectively, T_g vs. composition dependences obey exclusively the diad sequence approximation as shown in Fig.2. Triad sequence approximation never results in visible improvement of the calculated T_g behaviour of the random copolymers. The cornered shape of the calculated T_g vs. composition dependence curves is a result of the stepwise calculating procedure of the used computer programme.

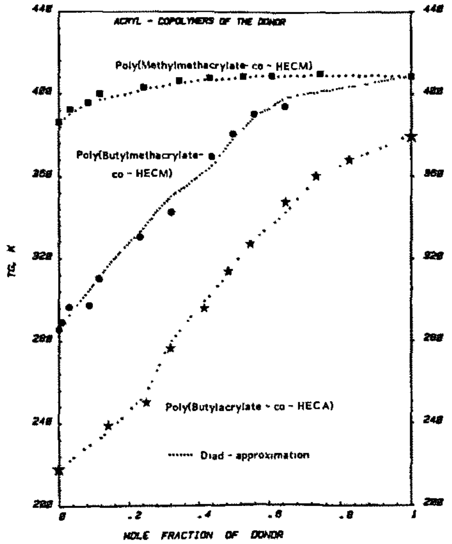

Fig.2 T_g vs. Composition of Acrylate (Methacrylate) Copolymers of the Donor in Diad Sequence Approximation.

The similarity with the T_g vs. composition dependence of the purely donor-acceptor copolymer system in Fig.1 is evident with positive deviation from additivity being characteristic of all these copolymer systems. A decrease in fractional free volume and/or reduced mobility are responsible for this increase in the copolymer T_g. Similar interactions may be concluded and acrylate(methacrylate) groups seem to act as acceptor for the electron-donor HECA and HECM groups, respectively.

The Tg_{AB} data of the alternating copolymers caculated from the slopes of the straight lines in accordance with equ.(2) are presented in Table 2.

Table 2. T_g Increments of Diads and Triads

Diad-Sequence Approximation for Acrylcopolymers of the Donor

System	Tg Polyacryl K	Tg AB-Diad K	Tg Polydonor K
Methylmethacrylate / HECM	386.8	410.6	408.6
Butylmethacrylate / HECM	285.8	399.7	408.6
Butylacrylate / HEC A	218.4	327.3	379.6

Triad-Sequence Approximation for Acrylcopolymers of the Acceptor

System	T_g Increments of the Triad, K					
	AAA	AAB	ABA	BAB	ABB	BBB
Methylmethacrylate/DNBM	386.8	410	370	280	250	353.1
Butylmethacrylate / DNBM	285.8	342	310	310	265	353.1
Methylacrylate / DNBA	268.2	390	330	280	230	325.1

A - Acrylatesequence, B - Acceptorsequence

The T_g vs. composition dependence of the acrylic(methacrylic) copolymers of the electron-acceptor DNBA and DNBM, respectively, is much more complex. The nonlinearity of the data presented in accordance with equ.(2) is remarkable and any attempt at diad approximation fails as evidenced in Fig.3 for the methylmethacrylate/DNBM copolymer system.

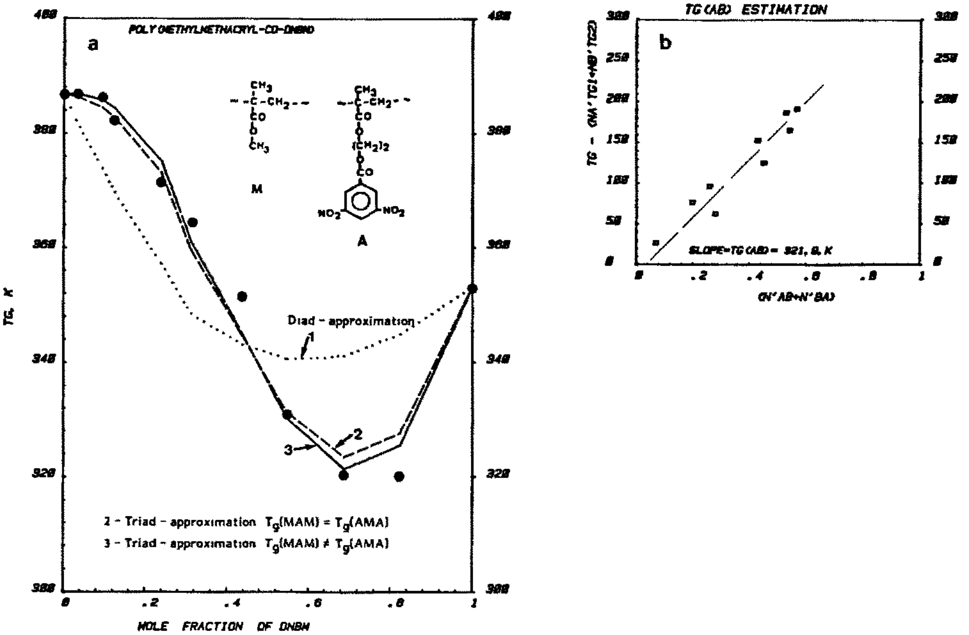

Fig. 3 T_g vs. Composition of the Methylmethacrylate - Acceptor DNBM Copolymers in Diad and Triad Sequence Approximation

Only the triad approximation allows the reproduction of the experimental T_g dependence for these acrylic(methacrylic) electron acceptor copolymers. The difference in bulkiness of the side groups seems to be responsible for the better representation of the data by equ.(5) or equ.(6), respectively. For all the copolymer systems of the methylester of the acrylates(methacrylates), which are much smaller than the bulky acceptor DNBM or DNBA groups, triad approximation with $Tg_{MAM} \neq Tg_{AMA}$ gives a better fit of the experimental T_g data. On the contrary, for the BMA/DNBM copolymer system, in which the side groups are of similar size, triad approximation with $Tg_{ABA} \neq Tg_{BAB}$ shows no better concordance than the approximation with $Tg_{ABA} = Tg_{BAB}$ (Fig.4).

All T_g vs. composition curves of the studied acrylic(methacrylic) copolymers of the acceptor DNBA and DNBM are shown in Fig.5 and the corresponding triad sequence T_g parameters are included in Table 2.

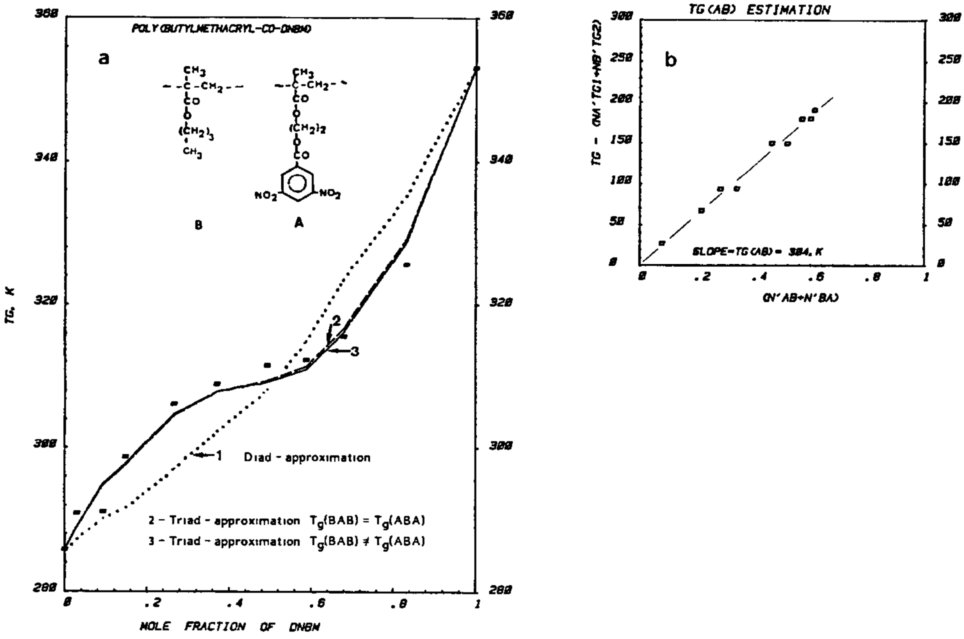

Fig.4 T_g vs. Composition of the Butylmethacrylate - Acceptor DNBM Copolymers in Diad and Triad Sequence Approximation

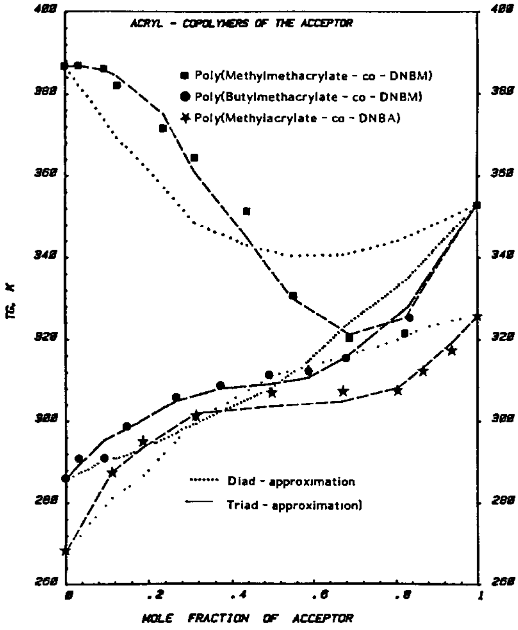

Fig.5 T_g vs. Composition of Acrylate (Methacrylate) Copolymers of the Acceptor in Diad and Triad Sequence Approximation

It is evident that the introduction of small amounts of acceptor monomer in the acrylic(methacrylic) copolymers results always in an increase in the polymer stiffness, confirmed by both the shapes of the T_g vs. composition curves in the 0 to 0.4 acceptor mole fraction range and the substantially increased Tg_{AAB} parameters. On the contrary, inclusion of small amounts of acrylic(methacrylic) comonomer in the acceptor copolymer shows an accentuated softening effect. This suggests an inversion of the donor-acceptor interaction in the above copolymeric systems. For small amounts of acceptor comonomer, the acrylic(methacrylic) groups seem to act donor like, resulting in a decreasing polymer mobility. Copolymers of reversed composition, i.e. with higher acceptor monomer content, seem to be accompanied by an acceptor activity of the acrylic(methacrylic) group with repulsion and a corresponding increase in fractional free volume and chain mobility; the observed decrease in the copolymer T_g being the consequence.

Additional studies will be needed to clarify the formulated assumtions concerning the T_g vs. composition dependences of copolymers on the nature and size of the interacting monomeric units.

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