Thermochimica Acta, 72 (1984) 17–29
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

SEQUENCE DISTRIBUTION - GLASS TRANSITION CORRELATION IN DONOR - ACCEPTOR COPOLYMER SYSTEMS.

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Herrn Prof.Dr.H.Gerrens zu seinem 60.Geburtstag herzlich gewidmet

ABSTRACT

Copolymers of butylmethacrylate and of methylmethacrylate with donor N-(2-hydroxyethyl)carbazolyl methacrylate and acceptor methacryloyl-ß-hydroxyethyl-3,5-dinitrobenzoate respectively, exhibit specific glass transition behaviour. The copolymers with donor HECM show positive deviations from additivity rules for the glass transition behaviour and require diad sequence Tg-contribution, whilst the copolymers with acceptor DNBM show negative deviations and triad sequence Tg-contribution in explaining experimental Tg-data. Activation energies of viscous flow in the molten state behaves similar.

INTRODUCTION

Polymer glass transitions are one of the most studied phenomenons in polymers in that the glass transition is accompanied by dramatic changes particularly of mechanical properties. Due to the fact that the transition from viscoelastic state to the rigid glassy solid is characterized by a viscosity level of 10^{14}Pa, glass transition may be considered also an universal "isoviscous" state of the polymers.

Taking into account the general importance of glass transition in polymers there are known attempts to correlate Tg-data with various properties like expansion coefficients(1) and different structural factors, mainly those related to the backbone chain stiffness as cohesive energy densities or solubility parameters(2).

Although the flow of polymers in the molten state is directly dependent on the glass transition, no attempts are known to correlate Tg-data with activation energies of the viscous flow. Such correlation, as evidenced in Fig.1, resembles to other known Tg - polymer property rules.

0040-6031/84/$03.00

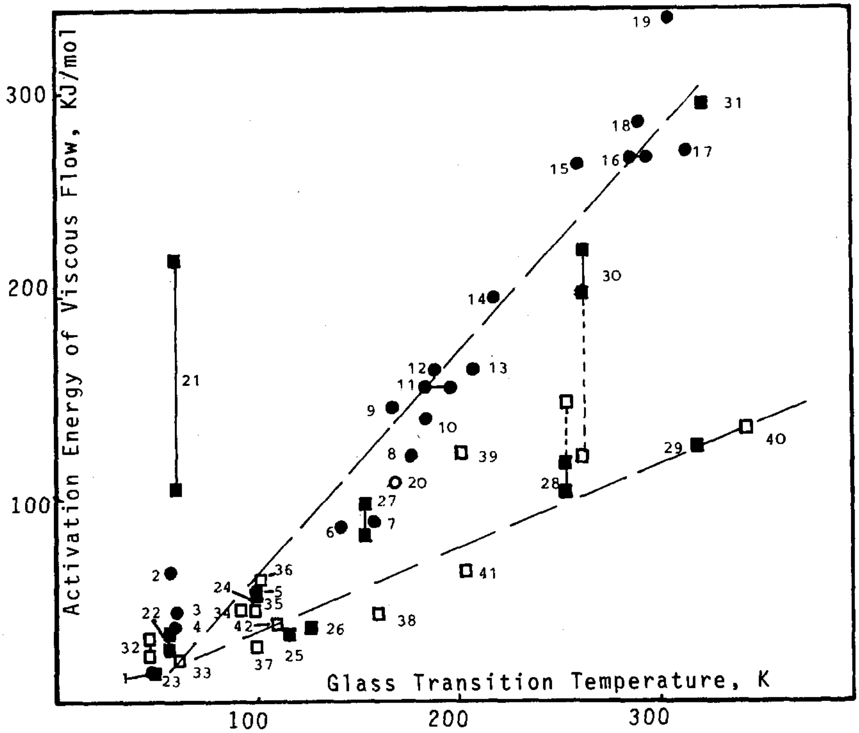


Fig.1 Activation energy of flow - glass transition correlation

●, own data; ■ ,E_a data from ref.3 and □ , from ref.4.
o, E_a calculated from data published by FERRY (6)

1,Poly(dimethylsiloxane);2,Co(.10DNBButyl-.90DMS);3,Polybutadiene; 4,Polybutadiene 15000,5,Poly(isobutylene);6,head-to-head Polypropylene;7,head-to-tail PP;8,blend PBMA/HECacetate;9,blend block(HECM-BMA-HECM)/DNBacetate;10,blend Co(.10DNBButyl-.90DMS)/Co(.10HECM-.90BMA);11,Poly(BMA) and copolymers with 1-1o% DNBM resp. HECM; 12,blend block(HECM-BMA-HECM)/Poly(DNBM);13,blend(.10HECM-.90MMA)/(.10DNBM-.90BMA);14blend(.10DNBM-.90MMA)/HECacetate;15,Poly(DNBM); 16,Poly(MMA) and copolymers with 1-10% DNBM resp. HECM; 17,Poly(HECM);18,Co(.25HECM-.75DNBM);19,Co(.50HECM-.50DNBM);20, Poly(n-octylmethacrylate);21,Poly(tetrafluorethylene);22,Polyethyleneglycole;23,Poly(DMS);24,PIB;25,Poly(decamethyleneadipate); 26,Poly(diethyleneadipate);27,iso-PP with 9%a;28,PVC;29,Polycarbonate of bisphenole A;30,PS;31,Celluloseacetobutirate;32,linear PE; 33,cis PB;34,Polyoxymethylene;35 and 36,PIB;37,Polyethyleneglycoleether;38,PP;39,Poly(4methyl-1-pentene);40,Poly(alpha-methylstyrene) 41,Poly(vinylacetate);42 SB rubber.

In Fig.1 are included besides own results different literature data for which concomitant were accesible both activation energies of viscous flow(3,4) and Tg values(5).

As we are interessted in the influence of CT-interactions on viscoelastic properties of polymer systems containing donor and acceptor groups respectively, a series of random copolymers were synthesized and in this paper an attempt is made to correlate the obtained results with Tg measurements and sequence distribution data of D/A groups containing copolymers. Activation energies of the viscous flow in the molten state were computed using isochrone viscoelastic curves according to the method described elsewhere(7).

SEQUENCE DISTRIBUTION - GLASS TRANSITION PREDICTIONS

To predict glass transition temperatures of random copolymers two main approaches are recommended in literature. These are the additivity rules of FOX(8)

$$\frac{1}{Tg} = \frac{w_A}{Tg_A} + \frac{w_B}{Tg_B} \qquad (1)$$

and of DIMARZIO and GIBBS(9)

$$Tg = n'_A Tg_A + n'_B Tg_B \qquad (2)$$

where Tg represents the glass transition temperature of the copolymer. Tg_A and Tg_B are the glass transitions of the homopolymers of the monomers M_A and M_B respectively, w_i the weight fractions and n'_i the weighted mole fractions of rotatable bonds of the respective monomeric units in the copolymer,

$$n'_i = \frac{n_i \beta_i}{\Sigma n_i \beta_i} \qquad (3)$$

with β_i the number of rotatable bonds in the monomeric unit, i, and n_i the mole fraction of the component i,

$$n_i = \frac{i}{\Sigma i} \qquad (3a)$$

i is the content of the component i in the copolymer, which may be determined experimentally or calculated according to the conventional radical copolymerization theory based on stationary state approximation, using the monomer reactivity ratios, r_i, and the ratio of the monomer feed, X.

For binary copolymers

$$\frac{a}{b} = \frac{r_A X + 1}{r_B/X + 1} \qquad \text{where} \quad X = \frac{A}{B}$$

A and B being the concentrations of the monomers and

$$n_A = \frac{r_A X + 1}{r_A X + r_B/X + 2} \qquad (4)$$

Linear approximations, however, generally are not satisfactory for most copolymers and nonlinear dependences are often observed, showing both positive and negative deviations from additivity and frequently even maxima or minima in the Tg-composition curves of the copolymres$^{(10,11)}$.

These deviations are explained by the fact that additivity rules neglect interactions in copolymers, which imply that properties of an AB or a BA sequence may be quite different from those of an AA or a BB sequence. Therefore it will be necessary to account for the sequence distribution in order to achieve more accurate prediction of copolymer Tg.

Consequently both additivity rules were extended to account for sequence distribution.

The Fox relationship was applied in diad sequence approximation by JOHNSTON$^{(10)}$

$$\frac{1}{Tg} = \frac{w_{AA}}{Tg_{AA}} + \frac{w_{BB}}{Tg_{BB}} + \frac{w_{AB}}{Tg_{AB}} \qquad (5)$$

where $w_{AA}=w_A P_{AA}$, $w_{BB}=w_B P_{BB}$ and $w_{AB}=w_A P_{AB}+w_B P_{BA}$.

P_{ii} and P_{ij} are the probabilities of addition in radicalic copolymerization of the respective monomer to the growing radical with final i monomeric unit.

$$P_{ij} = 1/(1+r_i X_i) \quad \text{and} \quad P_{ii} = 1 - P_{ij} \qquad (6)$$

Tg_{AA} and Tg_{BB} are the glass transitions of the homopolymers, $Tg_{AB}=Tg_{BA}$ of the alternating copolymer and w_{ii} resp. w_{ij} the corresponding weight fractions of the diads in the copolymer. If the glass transition of the alternating copolymer is not accesible, computerized multiple regression analysis is recommended to solve for Tg_{AB}.

BARTON's$^{(11)}$ extension of the DiMarzio-Gibbs' additivity rule in the diad approximation (eqn.7) may be preffered, because a method is offered of evaluating Tg_{AB}-value from experimental Tg data.

$$Tg = n'_{AA}Tg_{AA} + n'_{BB}Tg_{BB} + (n'_{AB}+n'_{BA})Tg_{AB} \qquad (7)$$

The mole fractions of the diad sequences are calculated according to

$$n_{AA} = n_A P_{AA} \quad \text{and} \quad n_{BB} = n_B P_{BB} \qquad (8)$$

respective

$$n_{AB} + n_{BA} = 1 - (n_{AA} + n_{BB}) \qquad (9)$$

whilst the weighted mole fractions of the rotatable bonds in the respective monomeric pairs of diad sequences are obtained using equation (3).

If the Tg values of the homopolymers are known, Tg_{AB} of the alternating copolymer can be evaluated graphically from experimental Tg data of the copolymers using relation (7) in the form:

$$Tg - (n'_{AA}Tg_{AA}+n'_{BB}Tg_{BB}) = (n'_{AB}+n'_{BA})Tg_{AB} \qquad (10)$$

If the diad approximation is valid, the points should fall on a straight line with zero intercept and slope = Tg_{AB}.

The diad assumption is not valid in all copolymer systems and some copolymer exhibit strong triad effects. The invalidity of the diad approximation is evidenced either by the nonlinearity of eqn.(10), or by the fact that experimental Tg values of the homopolymers have to be modified for satisfactory representation of Tg-composition data of copolymers$^{(12,13)}$.

The only problem in application of Tg-composition relations for copolymers in higher sequence distribution assumption is the impossibility of measuring or evaluation of Tg contribution of such sequences$^{(14)}$. Consequently the relationships become essential parameterized equations, asking for analysis procedures for closest fit of the experimental Tg data.

Nevertheless an extension of the Barton approach for triad contribution to glass transition temperature of random copolymers has improved in some cases the Tg-composition relationship.

Taking into account the equivalence of reversed sequences, i.e. $n_{AAB}=n_{BAA}$ etc.,Barton's equation was expanded by HAM$^{(12)}$ to the form:

$$Tg = n'_{AAA}Tg_{AAA}+n'_{BBB}Tg_{BBB}+n'_{AAB}Tg_{AAB}+n'_{ABB}Tg_{ABB}+ \\ +(n'_{ABA}+n'_{BAB})Tg_{ABA} \qquad (11)$$

assuming $Tg_{ABA}=Tg_{BAB}$.

This last assumption, however, may be discutable at least taking into account specific interactions of donor and acceptor groups respectively in random copolymers containing these groups.

Consequently in our case the triad approximation was used in the form:

$$Tg = n'_{AAA}Tg_{AAA}+n'_{BBB}Tg_{BBB}+n'_{AAB}Tg_{AAB}+n'_{ABB}Tg_{ABB}+ \\ +n'_{ABA}Tg_{ABA}+n'_{BAB}Tg_{BAB} \qquad (12)$$

The mole fractions of the triads were calculated using the expressions:

$$n_{AAA}=n_A P_{AA}^2 \;,\; n_{AAB}=n_A P_{AA} P_{AB} \text{ and } n_{ABA}=n_A P_{AB} P_{BA}$$
$$n_{BBB}=n_B P_{BB}^2 \;,\; n_{BBA}=n_B P_{BB} P_{BA} \text{ and } n_{BAB}=n_B P_{BA} P_{AB} \qquad (13)$$

EXPERIMENTAL

The characteristics of the studied homopolymers are shown in Table I.

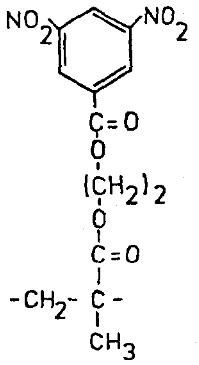
TABLE I.

Characteristics of the homopolymers

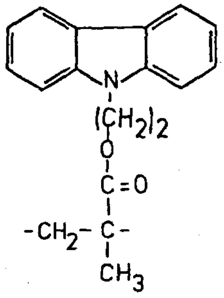
Polymer	$\bar{M}_w$ [a)]	Tg,K [b)]
Poly(Butylmethacrylate)	55000	285.8
Poly(Methylmethacrylate)	45500	386.8
Poly(DNBM)	12000	353.1 [c)]
Poly(HECM)	57000	408.6 [d)]

a) by gel-chromatography in $CHCl_3$ using PS standards
b) by DSC, extrapolated to zero heating rate
c) Poly(Methacryloyl-ß-hydroxyethyl-3,5-dinitrobenzoate)
d) Poly(N-(2hydroxyethyl)carbazolyl methacrylate)

ACCEPTOR, DNBM



DONOR, HECM



Copolymers of BMA and MMA respectively with acceptor DNBM or donor HECM were synthezised by radical copolymerization with AIBN in dioxane at 60°C.

The monomer reactivity ratios were calculated according to the KELEN-TODÖS method. The molecular weights of the copolymers were in the range of 60000 to 40000 for the copolymers with DNBM and of 55000 to 90000 for the copolymers with HECM. Details will be published.

Glass transition temperatures were measured by differential scanning calorimetry with a PERKIN-ELMER DSC2 and are extrapolated to zero heating rate.

Viscoelastic measurements in the melt were executed on an INSTRON model 3250 Rotary Rheometer using the excentric rotating disk method. Activation energies of viscous flow in the molten state were computed using both isotherm and isochrone curves of viscoelastic properties by the method described elsewhere(7,14).

RESULTS AND DISCUSSION

The attempt to correlate glass transition temperatures with composition data of the studied copolymers (determined by UV-VIS spectrometry) in the assumption of diad sequence contribution is illustrated in Fig. 2 and 3.

The glass transition temperatures of the respective alternating copolymers Tg_{AB}, were evaluated graphically according to eqn.(10), the obtained values being used in both approachs of Johnston (eqn.5) and of Barton (eqn.7).

It is evident that Tg of copolymers with the donor HECM of both BMA and MMA obey the diad sequence assumption quite acceptable. As it has been shown(15) some improvement can be achieved in the triad sequence approximation, but the faultless linearity of eqn.(10) was considered to justify the supposition of the validity of the assumption of the diad sequence contribution to Tg of the random copolymers with the donor HECM. It may be, however, important to emphasize that at least for the poly(MMA-co-HECM) system the Johnston approach is more satisfactory and that both systems show positive deviation from simple additivity rule, suggesting a stiffener effect of the interactions in these systems.

On the contrary any diad sequence assumption failed for the copolymers of BMA and MMA respectively with the acceptor monomer DNBM. The invalidity of the diad sequence approachs is also suggested by the excessive scatter of the data used for Tg_{AB} estimation according to eqn.(10), as shown in Fig.4 for the poly(BMA-co-DNBM) and in Fig.5 for the poly(MMA-co-DNBM) system.

The deviations from simple additivity rule are complex in both systems, positive in copolymers with low acceptor DNBM content and pronounced negative in copolymers with higher acceptor DNBM content.

This behaviour is also evidenced by the glass transition temperature contribution of the triad sequences, computed for best fit of experimental data as shown in Table II. It may be therefore concluded that interactions in these system exhibits sooner softener effect if the DNBM content is relative high.

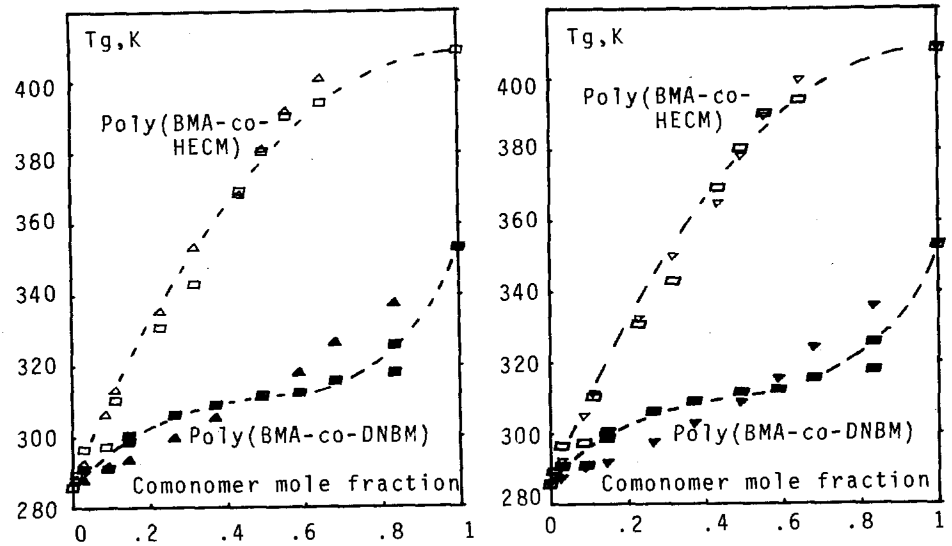


Fig.2 Dependence of Tg on composition for copolymers of butylmethacrylate in the diad assumption Left:eqn.(5), right:eqn.(7). ■ , □ experimental data ▲ , △ data by eqn.(5), ▼ , ▽ data by eqn.(7)

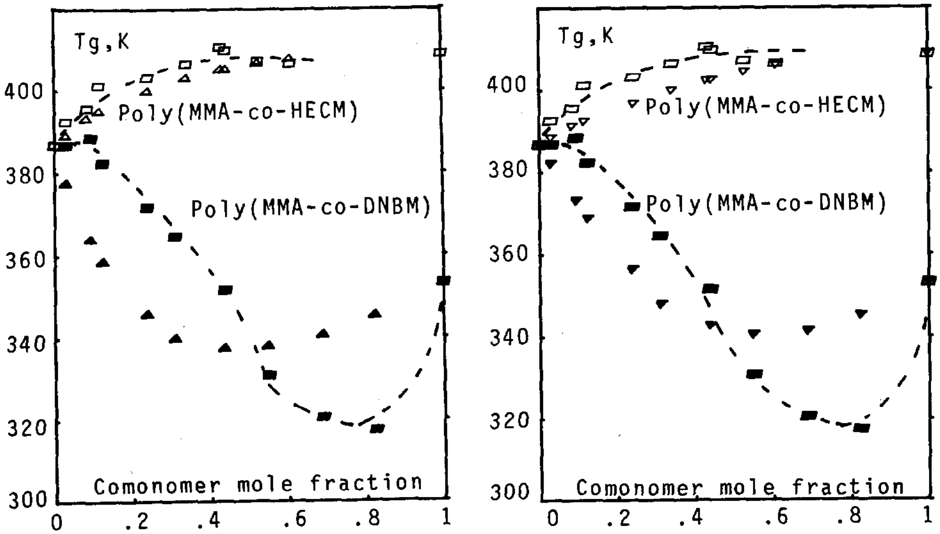


Fig.3 Dependence of Tg on composition for copolymers of methylmethacrylate in the diad assumption (Symbols as in Fig.2)

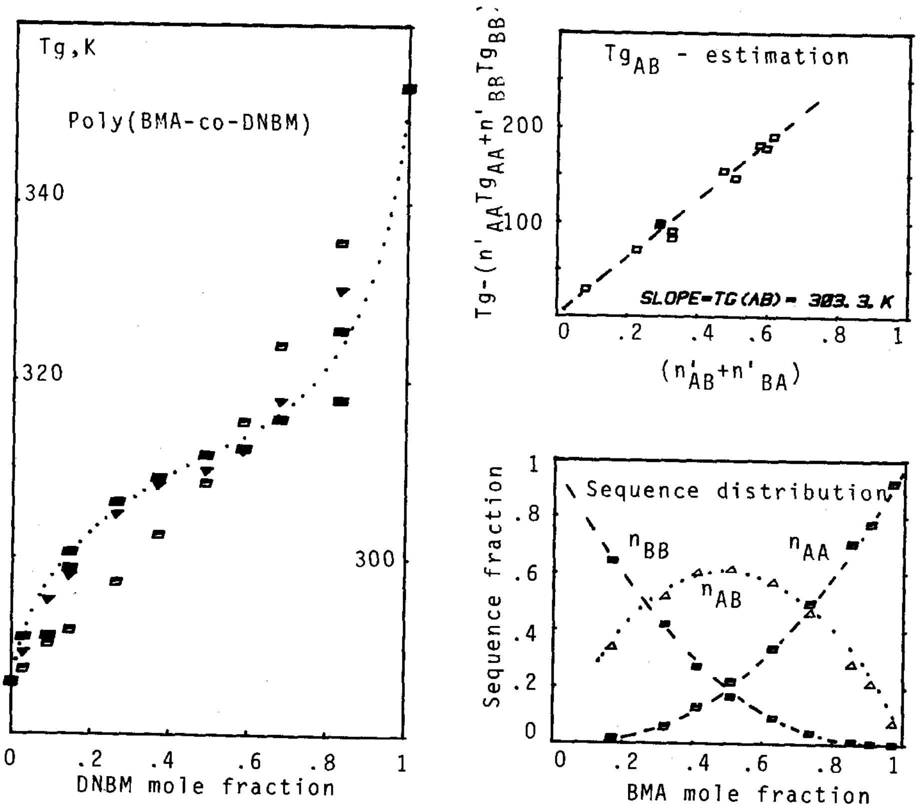


Fig.4 Dependence of Tg on composition of the Poly(BMA-co-DNBM) in diad and triad sequence contribution assumption
Right:Computed diad sequences for Tg_{AB} estimation according to eqn.(10).
■ experimental data, ▪ diad approximation, eqn.(7)
▼ triad approximation, eqn.(12)

TABLE II Glass Transition Contribution of Diad and Triad Sequences in Random Copolymers

Copolymer System	Tg contribution, in K				
	Tg_{AB}	AAB	ABA	BAB	ABB
Poly(DNBM-co-HECM)	417.1				
Poly(BMA-co-DNBM)		340	311	308	270
Poly(BMA-co-HECM)	401.4				
Poly(MMA-co-DNBM)		410	370	280	250
Poly(MMA-co-HECM)	406.6				

In Table II are included TG_{AB} values of the copolymer systems obeying the diad sequence contribution assumption, inclusive of the Poly(DNBM-co-HECM) system published yet$^{(15)}$.

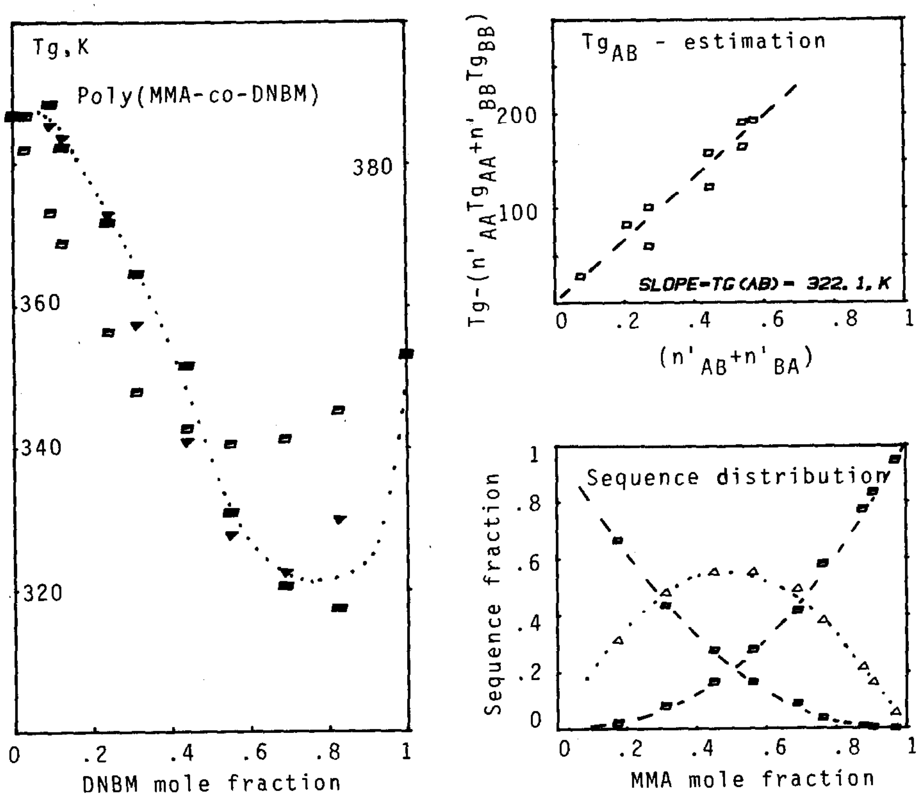


Fig.5 Dependence of Tg on composition of the Poly(MMA-co-DNBM) in diad and triad sequence contribution assumption (Explanation as in Fig.4)

Taking into account the four parameter character of eqn.(12), the values of the glass transition contribution of triad have only a relative significance. But indiferent of the values chosen for best fit of experimental Tg data allways Tg(ABA)≠Tg(BAB) and Tg(AAB)>>Tg(BBA) for the studied copolymer systems with acceptor DNBM.

The differences in interaction effects in the studied copolymer systems seem to be supported also by some at first unexpected viscoelastic measurement data.

So it was observed in the blend with low molecular donor component - N-(2hydroxyethyl)carbazolylacetate - of the acceptor copolymer Co(.90BMA-.10DNBM) with a ratio of 1:1 of the D/A groups, that the rubber plateau is substantial extended to higher temperatures, i.e. lower frequencies, suggesting some kind of thermoreversible network formation by CT-interaction of the D/A groups in the system

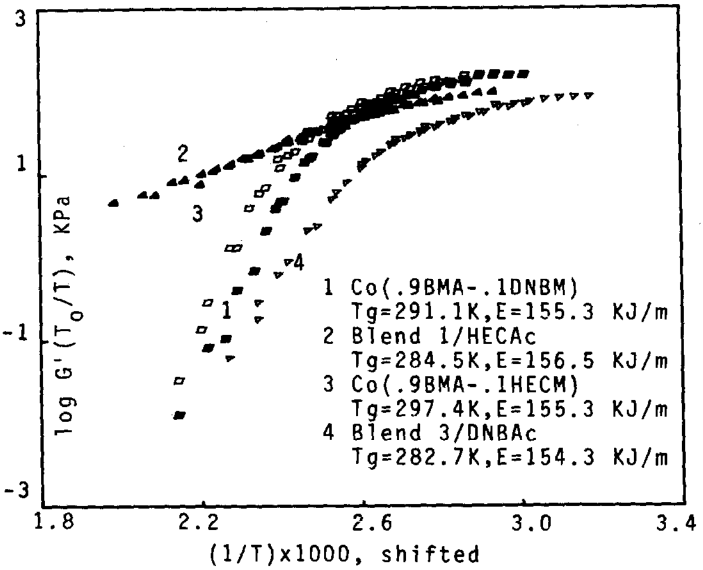


Fig.6 Isochrone composite curves of the storage moduli in polymer systems with CT interaction.

The blend of donor Copoly(.90BAM-10HECM) with the low molecular DNBAcetate - acetyloyl-ß-hydroxyethyl-3,5-dinitrobenzoate - with the same ratio of D/A groups, on the contrary, exhibited pronounced plasticizing effect only, when compared with the copolymer as evidenced in Fig.6 by the isochrone composite curves of the storage moduli, G', for instance. The effect is dramatic, although the differences in Tg and E_a values are less significant.

Finnaly it may be emphasized that data of activation energy of viscous flow in the molten state show the same trend depending on the composition of copolymers (Fig.7), confirming the validity of the introductory suggested general rule of correlation between Tg and E_a data of polymer systems, which plead for similar molecular origin of both the phenomena.

Concerning the interactions, which are quite different, supplementary studies are imposed before any discussion is possible.

ACKNOWLEDGEMENTS

The syntheses of the copolymers were executed by Mr.H.Northfleet Neto. Financial support by Deutsche Forschungsgemeinschaft and by AIF is gratefully acknowledged.

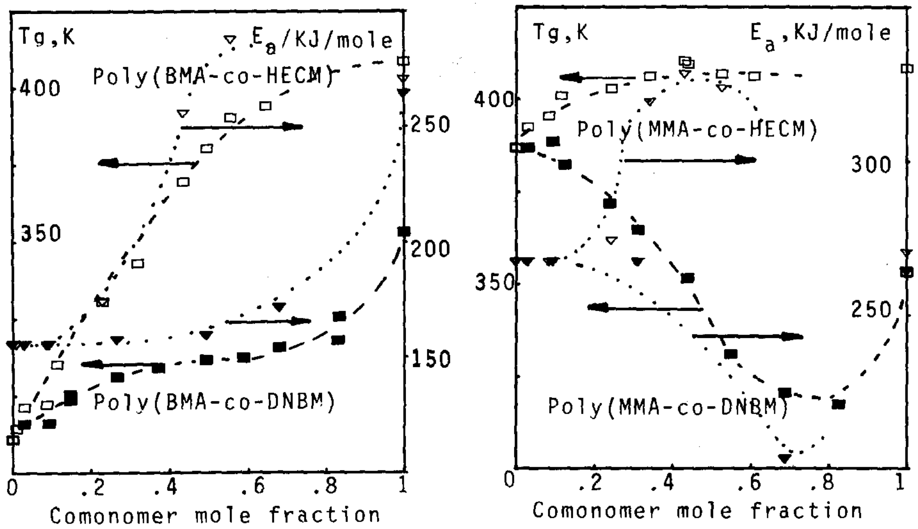


Fig.7 Glass transition temperature and activation energy of viscous flow of donor and acceptor groups containing copolymers.
Left:Copolymers of BMA with DNBM and HECM respectively
Right:Copolymers of MMA

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ABBREVIATIONS

M_A - monomer A, molecular weight of monomer A
A - molar concentration of monomer A in the polymerization feed
X - ratio of monmer feed in radicalic binary copolymerization
a - content of monomer A in binary copolymer
n_A, n_{AA}, n_{AAA} - mole fraction of component A, of diad sequences, of triad sequences in binary copolymer
w_A, w_{AA}, w_{AAA} - weight fraction of component A, of diad sequences, of triad sequences in binary copolymer
$\beta_A, \beta_{AA}, \beta_{AAA}$ - rotatable bonds in monomeric unit A, in diads AA, in triads AAA
n'_A, n'_{AA}, n'_{AAA} - weighted mole fraction of rotatable bonds in A, in AA or in AAA
r_A - reactivity ratio of monomer A in binary copolymerization
p_{AB}- probability of addition in radicalic copolymerization of monomer B to the growing radical with final monomeric unit A
Tg - glass transition temperature of polymer (copolymer)
Tg_A- glass transition temperature of homopolymer A
Tg_{AA}, Tg_{AAA} - contribution to glass transition temperature of diad sequences AA or triad sequences AAA
G' - storage modulus
Pa - Pascal
T_o - reference temperature of viscoelastic composite curves, general T_o=Tg+90 K
T - temperature of measurement of viscoelastic properties
E - apparent activation energy of viscous flow of polymer melt
Poly(A-co-B) - copolymers of monomer A with monomer B, general
Co(.90A-.10B)- copolymer of monomer A with monomer B, containing 0.90 mole fraction of monomer A
block(HECM-BMA-HECM) - triblock with BMA central block
a - in connection with polymer name stands for atactic
DNBButyl - methyl, n-butyl-3,5-dinitrobenzoate siloxanoyl
DNBacetate - β-hydroxyethyl-3,5-dinitrobenzoylacetate
HECacetate - N-(2hydroxyethyl)carbazolylacetate
blend - if not otherwise stated the components are mixed to assure 1:1 Donor/Acceptor ratio in the polymer blend