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GLASS TRANSITION BEHAVIOUR OF ACRYLIC DONOR OR ACCEPTOR COPOLYMERS - HOMOPOLYMERS AND THEIR POLYMER BLENDS WITH EDA COMPLEXATION

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SUMMARY

Glass transition temperature (T_g) vs. composition studies on acrylic copolymers of electron donor N-(2-hydroxyethyl)carbazolyl-acrylate and of electron acceptor β-hydroxyethyl-3,5-dinitrobenzoyl acrylate show specific nonlinear composition dependences comparable with those of the methacrylate copolymers. Blends of methylacrylic donor and n-butylacrylic acceptor copolymers or vice versa are compatible, if the incooperated donor or acceptor groups exceed about 35 mole percent. The application of the virial equation - an extended Gordon-Taylor equation - for the T_g of compatible polymer blends, composed of homopolymer acrylic or methacrylic donor and homopolymer acrylic or methacrylic acceptor implies both strong energetic interactions of the heterocontacts and associated free-volume effects due to conformational rearrangements in the neighbourhood of the binary heterocontacts.

INTRODUCTION

The interpolymeric electron donor-acceptor (EDA) complexes of poly(N-(2-hydroxyethyl)carbazolyl methacrylate) (PHECM) and poly(β-hydroxyethyl-3,5-dinitrobenzoyl methacrylate) (PDNBM) show a single glass transition temperature (T_g) over the entire blend composition range and unique dynamic mechanical properties (refs. 1-3). This has been the starting point for several investigations concerning the use of interchain EDA interactions to induce polymer-polymer miscibility in poly(methylmethacrylate) - poly(n-butylmethacrylate) blends (refs. 4,5). The most important drawbacks of the methacrylate homo- and copolymers with carbazolyl- or 3,5-dinitrobenzoyl-groups incooperated are the high glass transition temperatures (419.2 K/367.2 K) and their brittleness. The decrease of both glass transition temperature and brittleness of the homo- and copolymers can be realized either by the increase of the distance of the pendant donor or acceptor groups or by the increase of the flexibility of the polymer backbone like in the case of the acrylate copolymers (ref. 6).

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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 the methacrylate donor and methacrylate acceptor copolymer systems (ref. 7) and in the present paper the study is extended to the corresponding acrylate donor and acrylate acceptor copolymer systems.

The second aim of this paper is to investigate the miscibility of the poly-(methylacrylate) - poly(n-butylacrylate) blends with increased interacting donor-acceptor groups using the criterion of a single T_g.

Experimental studies on T_g vs. composition dependence of binary compatible polymer blends are the subject of several empirical equations, containing fitting parameters. Recently, a new concept was developed (refs. 8,9) starting with the idea that besides conformational energy barriers, contacts due to interaction are responsible for both conformational and 'free' volume distribution. This new concept was applied to both the homopolymer methacrylate donor-acceptor blends (refs. 8-10) and to the acrylate blend.

RANDOM COPOLYMERS: SEQUENCE DISTRIBUTION - T_g CORRELATIONS

The additivity rules of Fox and of Gibbs - Di Marzio can be extended to account for nonlinearity in T_g vs. composition dependences of random copolymers. Starting with the Gibbs - Di Marzio additivity rule, Barton's diad approximation (ref. 11) accounts for specific interactions reflected in different T_g contributions of the hetero AB and of the homo AA and BB diads:

$$T_g = N'_{AA} T_{gAA} + N'_{BB} T_{gBB} + (N'_{AB} + N'_{BA}) T_{gAB} \quad (1)$$

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

Ham (ref. 12) expanded Barton's equation accounting for triad contributions and assuming $T_{gABA} = T_{gBAB}$ and the equivalence of the reversed triad sequences, i.e. $N_{AAB} = N_{BAA}$ and $N_{BBA} = N_{ABB}$. The former assumption of Ham, i.e. $T_{gABA} = T_{gBAB}$, may be reconsidered at least for copolymers of monomers with very different specific interactions and bulkiness of the side groups. So the triad approximation can be formulated as follows:

$$T_g = N'_{AAA}\, T_{gAAA} + N'_{BBB}\, T_{gBBB} + N^{\blacktriangle}_{AAB}\, T_{gAAB} + N^{\blacktriangle}_{BBA}\, T_{gBBA} + \\ + N'_{ABA}\, T_{gABA} + N'_{BAB}\, T_{gBAB} \qquad (2)$$

The mole fractions of the diads and triads are related to the mole fractions of the comonomers in the copolymer via the copolymerization probabilities of the well known kinetic relations. Because of the impossibility of measuring or evaluating the T_g contributions of the triad sequences, in contrast of the T_{gAB} of the diad sequence, the eqn. (2) becomes in fact a four parameter fit equation.

COMPATIBLE POLYMER BLENDS: COMPOSITION DEPENDENCE - T_g CORRELATIONS

The composition dependence of the T_g of many binary compatible polymer blends can be described by the empirical Gordon-Taylor equation (ref. 13), originally developed to predict the T_g of binary random copolymers

$$T_g = (w_1\, T_{g1} + K\, w_2\, T_{g2}) \,/\, (w_1 + K\, w_2) \qquad (3)$$

where w_i is the weight fraction and T_{gi} is the T_g of the blend component i and K is supposed to be an arbitrary fitting parameter. For volume additivity and using weight fractions instead of volume fractions, the constant K can be defined as

$$K = \rho_1\, \Delta\alpha_2 \,/\, \rho_2\, \Delta\alpha_1 \,. \qquad (4)$$

ρ_i being the respective densities and $\Delta\alpha_i = (\alpha_L - \alpha_{G1})$ the difference of the expansion coefficient increments at T_g. Assuming the validity of the Simha-Boyer rule (ref. 14) $\Delta\alpha\, T_g = 0.133$ ('universal' constant) the K parameter can be finally expressed as:

$$K = K'\, (T_{g1}/T_{g2}) \qquad \text{with} \qquad K' = \rho_1 \,/\, \rho_2 \approx 1. \qquad (4a)$$

Several modifications of eqn. (3) have been published to describe the T_g behaviour of more complex systems involving strong intermolecular interactions like electron donor-acceptor interactions or hydrogen bonds. A very common approach is the Kwei equation (ref. 15)

$$T_g = (w_1\, T_{g1} + K\, w_2\, T_{g2}) \,/\, (w_1 + K\, w_2) + q\, w_1\, w_2 \qquad (5)$$

According to Kwei q depends on the strength of the interaction.

Thermodynamic support for the quadratic concentration term was given by Kanig (ref. 16). The new concept developed by Brekner et al. (ref. 8,9), based on Flory-Huggins lattice theory results in a virial equation (third power equation) with respect to the corrected weight fraction of the stiffer polymer component 2:

$$(T_g - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)w_{2c} - (K_1 + K_2)w_{2c}^2 + K_2 w_{2c}^3 \qquad (6)$$

where $w_{2c} = K w_2/(w_1 + K w_2)$ - with w_i the weight fractions of the components, i, and K the Gordon-Taylor "additivity" parameter.

K_1 is essentially related to the differences between the shares of the interaction energies, E_{ij}, of the hetero- and homocontacts to be overcome at T_g for allowing the characteristic conformational mobilities in the polymer melt. In addition are included the energetic perturbations in the molecular surroundings due to contact formation:

$$\begin{aligned} K_1 = {} & (2E_{12}-E_{11}-E_{22}) + (2e_{12-1}-e_{11-1}-e_{22-1}) + (e_{11-2}-e_{11-1}) + \\ & + (e_{22-1}-e_{22-2}) \;/\; (T_{g2}-T_{g1}) \end{aligned} \qquad (7)$$

The term e_{ij-k} describes the energetic perturbations in the molecular surrounding k (k=i or k=j) of the binary contact ij.

K_2 includes only the differences between the energetic perturbations in the molecular surroundings of the binary contacts:

$$K_2 = (2e_{12-1}-e_{11-1}-e_{22-1}) - (2e_{12-2}-e_{11-2}-e_{22-2}) \;/\; (T_{g2}-T_{g1}) \qquad (8)$$

The parameters K_1 and K_2 are still molecular weight dependent and related to orientation effects of the hetero interaction in the blend. Identical effects of the neighbourhood perturbations ($K_1 \neq 0$ and $K_2 = 0$) provide the Kwei equation (5) and if both $K_1 = 0$ and $K_2 = 0$ the Gordon-Taylor equation (3) for volume additivity is assured.

EXPERIMENTAL

Copolymers of methyl- (MA) or of n-butylacrylate (BA), respectively with the electron donor N-(2-hydroxyethyl)carbazolyl acrylate (HECA) (Mw 21.000 to 91.000) or with the electron acceptor β-hydroxyethyl-3,5-dinitrobenzoyl acrylate (DNBA) (MA-copolymers: Mn about 6.000, BA-copolymers - synthesized indirectly: Mw 36.000 to 130.000 (for sequence distribution calculation: $r_1 = 0.7$ and $r_2 = 2.0$)) were obtained by radical copolymerization. Due to the reduced reactivity of DNBA the molecular weights of the MA-co-DNBA copolymers were only of about Mn 6.000. Nevertheless possible molecular weight influences on T_g can be neglected as demonstrated by comparable T_g data of the MA-co-DNBA copolymers (acceptor content below 10 mole%) synthesized indirectly by group transfer copolymerization (GTP) with molecular weights of Mw 35.600 to 78.300. A BA-co-DNBA copolymer (Mw 53.300) was synthesized in a similar way while MA-co-HECA and BA-co-HECA copolymers (Mn about 4.900 to 10.400) could be obtained by direct GTP copolymerization. Details on the synthesis, the copolymerization (included reactivity ratios) and the characterization of both the copolymers and homopolymers are presented elsewhere (refs. 17-19).

All blends were obtained by freeze-drying from dioxane solution followed by vaccum drying to constant weight.

Glass transition temperatures were measured by DSC at different heating rates, using a Perkin-Elmer DSC 7. The T_g temperatures defined by the inflexion point of the DSC-curves were extrapolated for zero heating rate.

RESULTS AND DISCUSSION

For the studied acrylic copolymers of the electron donor HECA, T_g vs. composition dependences obey the diad sequence approximation as shown in Fig. 1 (table 1).

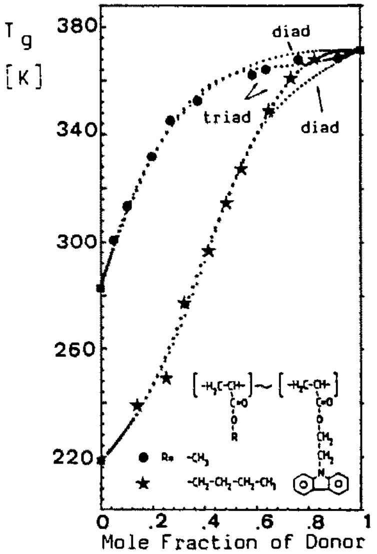

Fig.1 T_g vs. composition of acrylate copolymers of the donor in diad and triad approximation

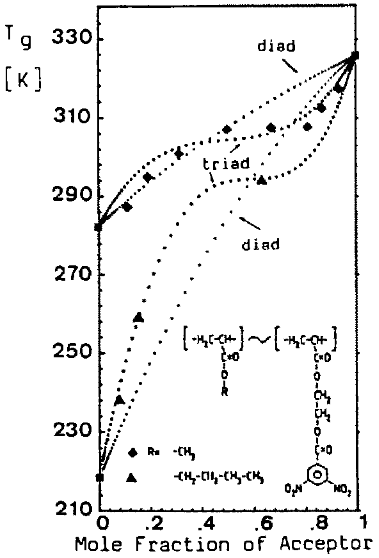

Fig.2 T_g vs. composition of acrylate copolymers of the acceptor in diad and triad approximation

Positive deviations from additivity are characteristic of the donor copolymer systems. A decrease in fractional free-volume and/or reduced mobility is responsible for this increase in the copolymer T_g. Similar interactions may be concluded for both systems and the acrylate groups seem to act as an acceptor for the electron donor HECA group.

The improvement of the calculated T_g behaviour by applying the triad sequence approximation at high contents of HECA groups can be explained by structural influences of the methyl- or n-butyl groups on the interactions between the acrylate and the electron donor groups. The ability to provide enough free-volume for optimal interaction is better with the n-butylacrylate than with the methylacrylate monomer units.

Table 1. T_g Increments and rotatable bonds (RB) of Diads and Triads

Diad-Sequence Approximation for Acrylcopolymers

System	T_g(AA)/RB K	T_g(AB)/RB K	T_g(BB)/RB K	intercept
MA-co-HECA (A/B)	282.4/ 6	374.1/12	371.3/14	0.5
BA-co-HECA (A/B)	218.4/14	346.5/ 6	371.3/ 6	0
MA-co-DNBA (A/B)	282.4/10	305.5/13	325.8/16	- 3.3
BA-co-DNBA (A/B)	218.4/16	298.6/16	325.8/16	4.4

Triad-Sequence Approximation for Acrylcopolymers

System	T_g Increments of the Triads, K					
	AAA/RB	AAB/RB	ABA/RB	BAB/RB	BBA/RB	BBB/RB
MA-co-HECA (A/B)	282.4/ 9	390.0/13	375.0/16	362.5/16	340.0/18	371.3/21
BA-co-HECA (A/B)	218.4/24	235.0/23	300.0/23	365.0/22	385.0/22	371.3/21
MA-co-DNBA (A/B)	282.4/15	320.0/16	350.0/17	310.0/20	210.0/22	325.8/24
BA-co-DNBA (A/B)	218.4/24	385.0/24	380.0/24	220.0/24	200.0/24	325.8/24

A - Acrylate sequence, B - Donor- or Acceptor sequence

The complex T_g vs. composition dependences of the acrylic copolymers of the electron acceptor DNBA, are shown in Fig. 2. Any attempt of diad approximation fails and only the triad approximation allows the reproduction of the experimental T_g data. It is obvious that the introduction of small amounts of acceptor monomer in the acrylic copolymers results always in an increase in the polymer stiffness. On the contrary, inclusion of small amounts of acrylic comonomer in the acceptor copolymer shows an accentuated softening effect, reflected in both the shapes of the T_g vs. composition curves and the T_g triad parameters (table 1). This suggests an inversion of the donor-acceptor interaction in the above copolymer systems. For small amounts of the acceptor comonomer, the acrylic groups seem to act donor-like, resulting in a decreased polymer mobility. Copolymers of reversed composition, i.e. with higher acceptor monomer content, seem to be accompanied by an acceptor activity of the acrylic group with repulsion and the corresponding increase in fractional free-volume and chain mobility.

The T_g vs. composition dependences of the acrylate copolymers are comparable with those of the corresponding methacrylate copolymers and demonstrate the similarity of the interactions in the acrylate and methacrylate copolymers (ref. 6).

Taking into account that the criterion for compatibility of polymer blends is the occurrence of a single T_g, it is possible to discriminate incompatible cross mixtures of methyl- and n-butyl-acrylate copolymers below 10 mole % (D:A 1:1 mole:mole) and compatible mixtures above 35 mole % interacting groups (Fig. 3,4).

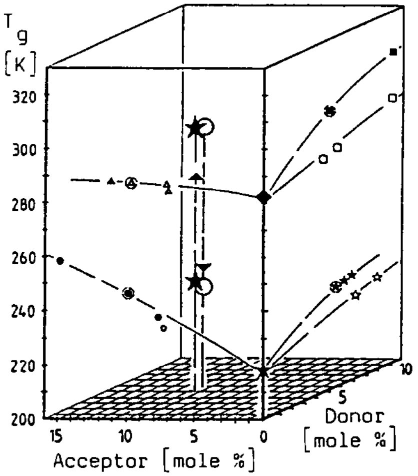

Fig.3 Compatible-incompatible blends of donor and acceptor acrylate copolymers

▲ MAHE5.0/MADN9.9 ★ MAHE5.0/BADN9.9
▼ BAHE5.7/BADN9.9 ○ BAHE5.7/MADN9.9

Copolymere:	rad.	GTP
MAHE	■	□
MADN	▲	△
BAHE	★	☆
BADN	●	○

Components of the blends ○

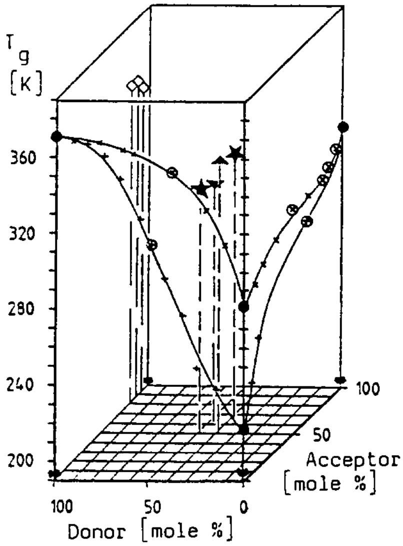

Fig.4 Compatible blends of donor and acceptor acrylate copolymers

▲ MAHE37.6/MADN50.0 ✱ MAHE37.6/BADN63.0
▼ BAHE48.2/BADN63.0 ★ BAHE48.2/MADN50.0
◇ PHECA/MADN86.9 1:1
PHECA/MADN93.8 1:2 PHECA/MADN80.5 2:1

Copolymere:		
	MAHE/MADN	×
	BAHE/BADN	+

Components of the blends ○

The compatible polymer blends show T_g data above or near the T_g of the stiffer component implying strong charge transfer interactions accompanied by the reduction of the free-volume or reduced mobility of the polymer chains. The blend of the homopolymer donor PHECA and methylacrylate copolymer with high acceptor content shows in principle the same behaviour. Mixtures of 1:2 or 2:1 D:A are examined to evaluate the influence of existing termolecular complexes in the solid state as demonstrated in solution with acetate models (ref. 20). The T_g of the D:A mixture 2:1 is closer to the T_g of the stiffer component compared with the T_g of the 1:2 mixture showing that weight and not molar stoichiometry determines the chain mobility.

The T_g vs. composition dependence of the acrylate/methacrylate blends of homopolymer donor PHECA/PHECM and homopolymer acceptor PDNBA/PDNBM, shown in Fig.5 exhibits positive deviations from additivity.

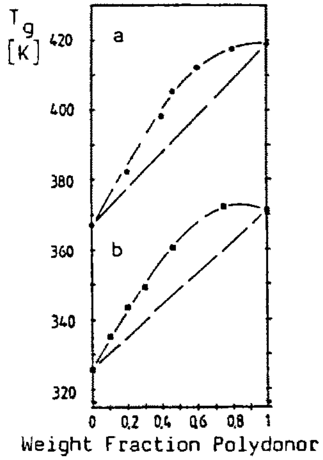

Fig.5 T_g vs. composition curves of
a - PHECM/PDNBM blends
b - PHECA/PDNBA blends

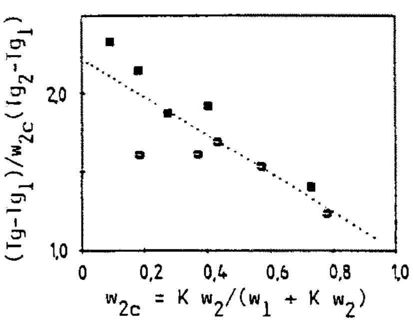

Fig.6 T_g-composition data for blends of
▫ PHECM 31000/PDNBM 24200
■ PHECA 23000/PDNBA 3700
according equation (6)- K' = 1.0. (Numerals behind polymer abbreviations denote the number-average molecular weights) 2: polydonor

The analysis in accordance to eqn. (6) (Fig. 6) assuming equal densities of the blend components, K' = 1 (or 0.8/1.2) provides for the acrylate blend $K_1 = 1.30$ (i.e. 1.88/0.87) and $K_2 = -0.29$ (i.e. 0.42/-0.77) suggesting that strong energetic interactions exist between the blend components. In addition there are conformational rearrangements in the neighbourhood of binary heterocontacts since orientation effects induce energetic disturbance in the molecular surroundings of the binary contacts ($K_2 \neq 0$). The negative K_2-value implies a stronger energetic disturbance due to the stiffer donor component.

Assuming similar energetic perturbations of the neighbourhood the corresponding K_1-value of the methacrylate blend (Fig. 7) suggests smaller energetic contact interactions. The stronger negative K_2-value of the methacrylate blend results from larger energetic chain orientation effects and conformational rearrangements in the main chain.

Both, stronger intermolecular interactions and a more reduced influence of the stiffer donor component on the binary heterocontacts are explainable by the more flexible polymer backbone of the acrylates and the smaller molecular weights. The high flexibility of the acrylate main chain and less polymeric restrictions allow the optimal steric conformation of the EDA complexes and chain orientations due to the heterocontacts have a reduced life time and are not so dominant.

This interpretation of the K_1- and K_2-parameters is supported by polymer blends of the methacrylate polydonor PHECM with various polyacceptors poly(ω(hydroxyethyl)-3,5-dinitrobenzoyl methacrylate) (PDNBM-n) and by the polydonors poly(N-alkylcarbazol-3-yl-methylmethacrylate) (PHMCM-n) with the polyacceptor poly(β-hydroxyethyl-3,5-dinitrobenzoyl methacrylate) (PDNBM-2) (Fig. 8).

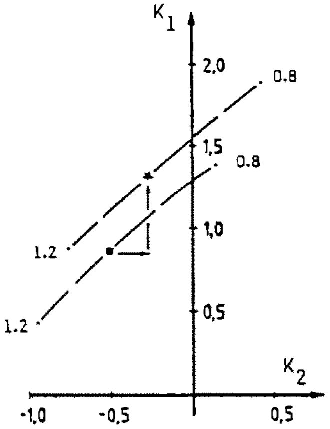

Fig. 7 K_1 vs. K_2 plot of the fitting parameters ✱ PHECA/PDNBA blend
■ PHECM/PDNBM blend
Numbers in the plot denote to other than K' = 1 (0.8, 1.2).

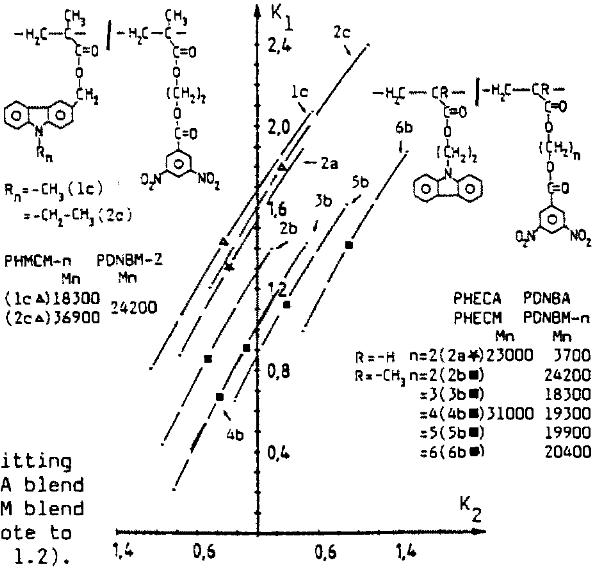

Fig. 8 K_1 vs. K_2 plot of the fitting parameters polydonor/polyacceptor: ✱ acrylate
■ ▲ methacrylates
Range of variations: K'values - see Fig. 7

Increasing the spacer length of the acceptor side chain in the mixtures PHECM/PDNBM-n provides higher K_1- and K_2-values. This behaviour is easily understood by the side chain decoupling between the acceptor interacting side group and the polymer main chain which improves optimal EDA complex conformation. Comparing the acrylate donor-acceptor blend with the series of methacrylate donor-acceptor blends the energetic interactions are comparable with those of the blend PHECM/PDNBM-6 exhibiting the strongest energetic interactions. Not comparable are however, the chain orientation effects expressed in the K_2-value. Due to the decoupling effect in the PHECM/PDNBM-6 system there are less conformational rearrangements in the main chain and the energetic perturbations of the stiffer component on the binary heterocontacts are negligible.

An exceptional position according to the K_1- and K_2-values show the PHMCM-n/PDNBM-2 blends. The strongest energetic interactions and only small chain orientations can be derived from the corresponding K_1- and K_2-values. The PHMCM-2/PDNBM-2 blend is an additional exception. It is the only blend showing both a single T_g and a decomplexation endotherm at 185°C on DSC thermograms (ref.21). Phase separation of this blend is kinetically controlled while all other systems presented are thermodynamically controlled, showing the decomplexation above the decomposition temperature.

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