

The glass transition temperature of random copolymers: 1. Experimental data and the Gordon–Taylor equation*

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Glass transition temperatures T_g for a wide variety of (A-random-B) copolymers have been determined by means of d.s.c., with A, B = methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, 2-ethyl hexylacrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, iso-butyl methacrylate, t-butyl methacrylate, acrylonitrile, styrene and vinyl chloride, respectively. The composition of the AB copolymers was varied from 0 to 100% (w/w) in steps of 20%, thus yielding a data set of more than 400 T_g values. All types of T_g versus composition dependence were recovered, resulting in linear, convex, concave and sigmoidal shapes. In most cases, a satisfying description of the data was achieved via a one-parameter fit according to the Gordon–Taylor equation. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The glass transition temperature T_g is an important property of polymeric systems which determines their range of applicability. Below T_g the material is brittle, whereas it is ductile, leathery or liquid above T_g . The specific properties depend on the molar mass of the polymer chains and on whether the polymeric system is semi-crystalline, amorphous or cross-linked. In the following, we deal with amorphous systems consisting of linear chains which are not cross-linked.

A convenient method to adjust T_g according to a given application is to copolymerize monomers A and B in a certain ratio A/B. The monomers are chosen in such a way that the T_g values of the respective homopolymers, T_{gA} and T_{gB} , lie above and below the glass transition temperature which has to be checked. In general, T_{gAB} of the random copolymer lies between T_{gA} and T_{gB} . The actual T_{gAB} value depends, however, on the ratio A/B. A typical example of the application of random copolymers is water-based latex dispersions for wall painting. In this case, T_g must be low enough to allow for the formation of a continuous film of the latex particles after the evaporation of the water. On the other hand, T_g must be high enough that the resulting films are not sticky.

In this paper, we present data of glass transition temperatures of a wide variety of AB random copolymers synthesized from methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (nBA), iso-butyl acrylate (iBA), t-butyl acrylate (tBA), 2-ethyl hexylacrylate

(EHA), methyl methacrylate (MMA), ethyl methacrylate (EMA), n-butyl methacrylate (nBMA), iso-butyl methacrylate (iBMA), t-butyl methacrylate (tBMA), acrylonitrile (AN), styrene (S) and vinyl chloride (VC), respectively. The composition of the AB copolymers was varied from 0 to 100% (w/w) in steps of 20%.

The motivation for the present study was to understand in which ways the specific shape of the T_{gAB} curves depends on the chemical nature of the constituents A and B of the copolymers. This approach is not new: it is of course known that many years ago Illers presented systematic studies on AB random copolymers too^{1,2}. Our approach differs in that we take a closer look at the group of acrylates.

Fits according to the phenomenological Gordon–Taylor equation have been performed as a first-order approach to the data set. A more intense discussion of models for the description of glass transition temperatures of AB random copolymers will be given in the second part of our study³.

EXPERIMENTAL

The random copolymers were polymerized in emulsion under starved conditions. That is, the monomers A and B were fed to the vessel in the appropriate ratio so slowly that the polymerization reaction proceeded by the quasi-instantaneous consumption of the available monomers—irrespective of the polymerization parameters r . This procedure guarantees the randomness of the sequence distribution along the chain. The combinations of monomers used are listed in Table 1.

* Dedicated to Professor G. V. Schulz on occasion of his 90th birthday

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Table 1 Combinations of the monomers used for the synthesis of AB copolymers

	MA	EA	BA	iBA	tBA	EHA	MMA	EMA	BMA	iBMA	tBMA	S	AN	VC
MA		×	×	×	×	×	×	×	×	×	×	×	×	×
EA			×	×	×	×	×	×	×	×	×	×	×	×
BA				×	×	×	×	×	×	×	×	×	×	×
iBA					×	×	×	×	×	×	×	×	×	
tBA						×	×	×	×	×	×	×	×	
EHA							×	×	×	×	×	×	×	×
MMA								×	×	×	×	×	×	×
EMA									×	×	×	×	×	×
BMA										×	×	×	×	×
iBMA											×	×	×	
tBMA												×	×	
S													×	

The latex dispersions which were obtained after completion of the polymerization were thoroughly dried. From the resulting polymer films, samples of about 20 mg were punched out for the heat flow d.s.c. measurements, which were performed on a Mettler TA 4000. The purging gas was nitrogen. The samples were first cooled to temperatures about 50°C below the respective glass transition temperature, then heated at a rate of 20 K min⁻¹ up to $T_g + 50$ K and quench cooled to temperatures below T_g . The procedure was cycled until a fixed T_g value had been reached. T_g was taken as the midpoint temperature, i.e. the temperature where half of the increment in specific heat—which is proportional to the heat flow measured—had occurred. No corrections with respect to the finite sample mass and the finite heating rate were made.

The procedure just described could not be applied for copolymers containing tBA or tBMA because of degradation effects above 120°C. That is why the glass temperature of the pure tBMA polymer was estimated by extrapolation to a content of 100% of the glass temperatures of the available copolymers containing tBMA. The glass temperature of the homopolymer of nBMA cannot be determined reproducibly because of the small changes in specific heat capacity at the glass transition. Once more, the glass temperature of nBMA

was determined by extrapolation. In addition, it must be noted that it is difficult to obtain a reliable value for the glass temperature of systems containing a large fraction of AN because of the unexpected broadness of the transition region. All temperatures were recorded in degrees Celsius.

When comparing glass temperatures determined in different laboratories, care must be taken that the samples are measured under the same conditions. The glass transition temperature which is determined in a d.s.c. experiment depends on the drying procedure, the rate at which the sample is cooled prior to the actual measuring run, the heating rate, the sample mass, and the way T_g is extracted from the thermogram (onset temperature, point of inflection or midpoint temperature). It has been shown that in the case of polystyrene, which exhibits a well-defined and narrow glass transition, differences of up to 8 K among values from different sources can be found and explained⁴. This point must be kept in mind when comparing our data with data presented in the literature, e.g. Ref. 5.

RESULTS

The T_g values which have been measured are compiled in Tables 2 to 13, and depicted as functions of the respective

Table 2 Glass transition temperatures and Gordon–Taylor coefficient C of copolymers of MA

MA (%)	T_g (°C)													
	EA	BA	iBA	tBA	EHA	MMA	EMA	BMA	iBMA	tBMA	S	AN	VC	
0	-8	-43	-17	55	-58	105	67	32	64	102	107	105	77	
10						102						102		
20	-3	-27	-10	42	-43	91	52	24	46	87	91	99	62	
30						76						91		
40	5	-13	-1	34	-22	65	36	20	32	66	71	81	52	
50						53						73		
60	11	-2	7	29	-9	46	29	15	28	45	53	65	41	
70						38						56		
80	16	10	16	26	6	34	23	17	24	30	36	43	32	
90						30		19				30		
100	22	22	22	22	22	22	22	22	22	22	22	22	22	
C	1.05	1.15	1.06	0.38	1.08	0.65	0.28	-	0.28	0.7	0.9	1.5	0.8	

Table 3 Glass transition temperatures and Gordon–Taylor coefficient C of copolymers of EA

EA (%)	T_g (°C)											
	BA	iBA	tBA	EHA	MMA	EMA	BMA	iBMA	tBMA	S	AN	VC
0	-43	-17	55	-58	105	67	32	64	102	107	105	77
20	-32	-13	35	-50	81	45	10	38	82	84	91	60
40	-25	-12	21	-39	50	21	-1	21	51	61	74	39
60	-19	-10	8	-29	24	7	-7	6	26	37	48	21
80	-14	-10	0	-18	5	-3	-8	-1	6	12	23	6
100	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8
C	1.4	0.8	0.52	0.95	0.67	0.4	0.13	0.42	0.72	0.97	1.6	0.8

Table 4 Glass transition temperatures and Gordon–Taylor coefficient C of copolymers of BA

BA (%)	T_g (°C)											
	iBA	tBA	EHA	MMA	EMA	BMA	iBMA	tBMA	S	AN	VC	
0	-17	55	-58	105	67	32	64	102	107	105	77	
20	-20	26	-55	76	41	9	37	77	74	80	52	
40	-24	5	-52	41	12	-13	7	40	41	64	30	
60	-30	-13	-49	8	-11	-24	-12	6	13	38	2	
80	-35	-27	-46	-18	-26	-34	-28	-17	-16	4	-15	
100	-43	-43	-43	-43	-43	-43	-43	-43	-43	-43	-43	
C	1.78	0.63	1	0.82	0.65	0.53	0.62	0.86	0.86	1.75	1	

Table 5 Glass transition temperatures and Gordon–Taylor coefficient C of copolymers of iBA

iBA (%)	T_g (°C)									
	tBA	EHA	MMA	EMA	BMA	iBMA	tBMA	S	AN	
0	55	-58	105	67	32	64	102	107	105	
20	36	-50	80	49	16	38	80	82	87	
40	24	-43	54	27	2	19	66	55	76	
60	6	-33	26	8	-9	6	41	29	54	
80	-8	-24	3	-5	-12	-7	22	6	21	
100	-17	-17	-17	-17	-17	-17	-17	-17	-17	
C	0.72	1	0.87	0.75	0.41	0.54	1.52	0.95	2	

Table 6 Glass transition temperatures and Gordon–Taylor coefficient C of copolymers of tBA

tBA (%)	T_g (°C)							
	EHA	MMA	EMA	BMA	iBMA	tBMA	S	AN
0	-58	105	67	32	64	102	107	105
20	-43	95	63	23	58	105	98	101
40	-22	81	54	25	46	88	87	96
60	-2	69	49	34	41	71	77	83
80	22	61	47	39	45	63	65	69
100	55	55	55	55	55	55	55	55
C	0.63	0.64	-	-	-	1.04	1.03	2.27

monomer composition in *Figures 1–12*. The data are ordered according to the scheme of *Table 1*. Included in the tables are characteristic constants C , which were obtained by fitting the Gordon–Taylor equation⁶ to the data sets. The Gordon–Taylor equation is given by

$$T_g = (T_{gA}w_A + KT_{gB}w_B)/(w_A + Kw_B) \quad (1)$$

where w_A and w_B are the weight fractions and T_{gA} and

T_{gB} the glass transition temperatures of the respective homopolymers. T_{gA} and T_{gB} are assigned such that $T_{gA} < T_{gB}$. In the original version of volume additivity the parameter $K = (\rho_1/\rho_2)(\Delta\alpha_2/\Delta\alpha_1)$ has a well-defined significance (ρ_i is the density and $\Delta\alpha_i = \alpha_{\text{melt}} - \alpha_{\text{glass}}$ is the increment at T_g of the expansion coefficient of the respective component i). But generally K is considered a real fitting parameter C . Depending on the actual value

Table 7 Glass transition temperatures and Gordon–Taylor coefficient *C* of copolymers of EHA

EHA (%)	T_g (°C)							
	MMA	EMA	BMA	iBMA	tBMA	S	AN	VC
0	105	67	32	64	102	107	105	77
20	66	42	3	32	60	62	102	44
40	30	10	-16	3	29	24	66	22
60	-12	-15	-34	-21	-12	-7	42	-12
80	-30	-39	-49	-42	-35	-34	-15	-28
100	-58	-58	-58	-58	-58	-58	-58	-58
<i>C</i>	0.78	0.8	0.55	0.67	0.73	0.68	2	0.86

Table 8 Glass transition temperatures and Gordon–Taylor coefficient *C* of copolymers of MMA

MMA (%)	T_g (°C)						
	EMA	BMA	iBMA	tBMA	S	AN	VC
0	67	32	64	102	107	105	77
20	83	48	69	105	103	104	70
40	91	63	80	102	103	101	67
60	97	83	95	102	106	97	76
80	102	94	99	102	109	101	94
100	105	105	105	105	105	105	105
<i>C</i>	2.8	1.36	1.35	-	-	-	-

Table 9 Glass transition temperatures and Gordon–Taylor coefficient *C* of copolymers of EMA

EMA (%)	T_g (°C)					
	BMA	iBMA	tBMA	S	AN	VC
0	32	64	102	107	105	77
20	42	64	99	96	95	61
40	48	65	91	87	78	52
60	51	65	86	80	74	57
80	61	64	81	76	70	64
100	67	67	67	67	67	67
<i>C</i>	1	-	1.66	0.75	0.35	-

Table 10 Glass transition temperatures and Gordon–Taylor coefficient *C* of copolymers of BMA

BMA (%)	T_g (°C)				
	iBMA	tBMA	S	AN	VC
0	64	102	107	105	77
20	60	94	84	91	54
40	55	78	64	75	41
60	50	65	47	62	31
80	44	54	40	41	24
100	32	32	32	32	32
<i>C</i>	1.9	1.26	0.5	0.94	-

of *C* the T_g versus composition curves deviate from linearity defined by $C = 1$. The Gordon–Taylor equation is, however, not applicable for systems where one of the copolymer possesses a glass transition temperature which is outside the temperature range enclosed by T_{gA} and T_{gB} .

For fitting the data it is convenient to linearize equation (1) as follows:

$$T_g - T_{gA} = C(T_{gB} - T_g)w_B/w_A \quad (2)$$

A plot of $T_g - T_{gA}$ versus $(T_{gB} - T_g)w_B/w_A$ yields *C* via linear regression. The solid lines in the figures were

Table 11 Glass transition temperatures and Gordon–Taylor coefficient *C* of copolymers of iBMA

iBMA (%)	T_g (°C)		
	tBMA	S	AN
0	102	107	105
20	99	95	102
40	96	81	96
60	83	72	80
80	79	66	76
100	64	64	64
<i>C</i>	1.7	0.44	1.3

Table 12 Glass transition temperatures of copolymers of tBMA

tBMA (%)	T_g (°C)	
	S	AN
0	107	105
20	100	103
40	103	96
60	105	98
80	106	100
100	102	102
<i>C</i>	-	-

Table 13 Glass transition temperatures of S/AN copolymers

S (%)	T_g , AN (°C)
0	105
20	105
40	117
60	112
80	107
100	107
<i>C</i>	-

obtained by inserting the resulting values of *C* into equation (1) and plotting the corresponding glass temperatures.

DISCUSSION

In order to save space, each series of copolymers is only presented and discussed once, according to the scheme of Table 1. That means that in the case of the tBMA copolymers, for example, we present the data of the tBMA copolymers with S, and AN, respectively, in a table and a figure, whereas the rest of the tBMA copolymers are found in the tables and figures of the respective aforementioned copolymers.

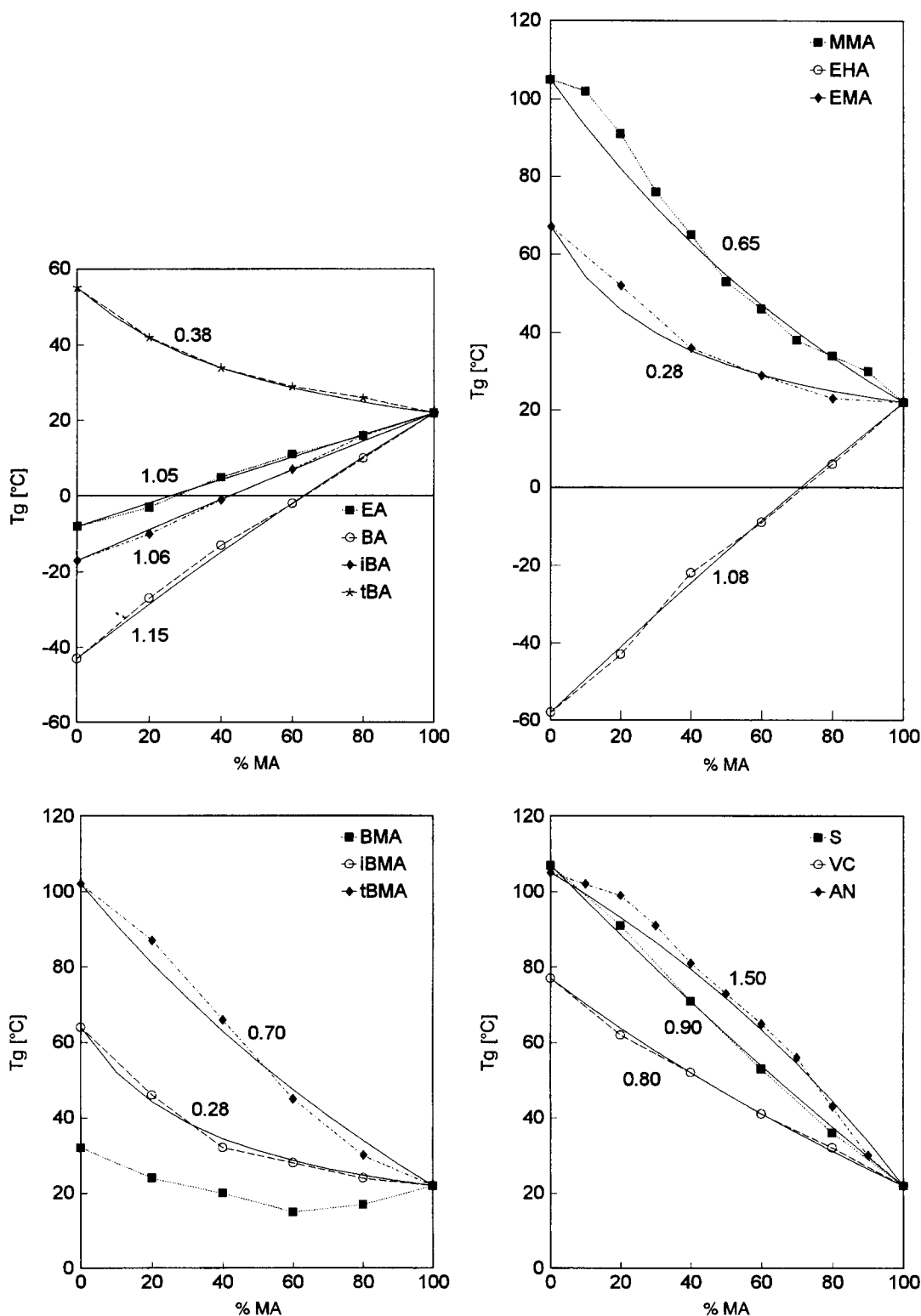


Figure 1 Glass transition temperatures of copolymers of MA. Solid lines denote data from the Gordon–Taylor equation. Numbers on the curves indicate the respective values of the C parameter

Copolymers of MA (Table 2 and Figure 1)

In most cases the agreement between the experimental data and the description via the Gordon–Taylor equation is satisfactory, i.e. the differences between the respective values are within experimental error (<2 K). Only in the case of the MA/BMA copolymers does the Gordon–Taylor equation not apply, since the T_g

curve exhibits a minimum with values below the glass temperatures of the respective homopolymers. In three cases (MA/MMA, MA/EMA and MA/AN) one observes positive deviations of the measured data from the Gordon–Taylor curve at MA contents up to about 40%. The MA/tBMA copolymer exhibits a slightly sigmoidal shape.

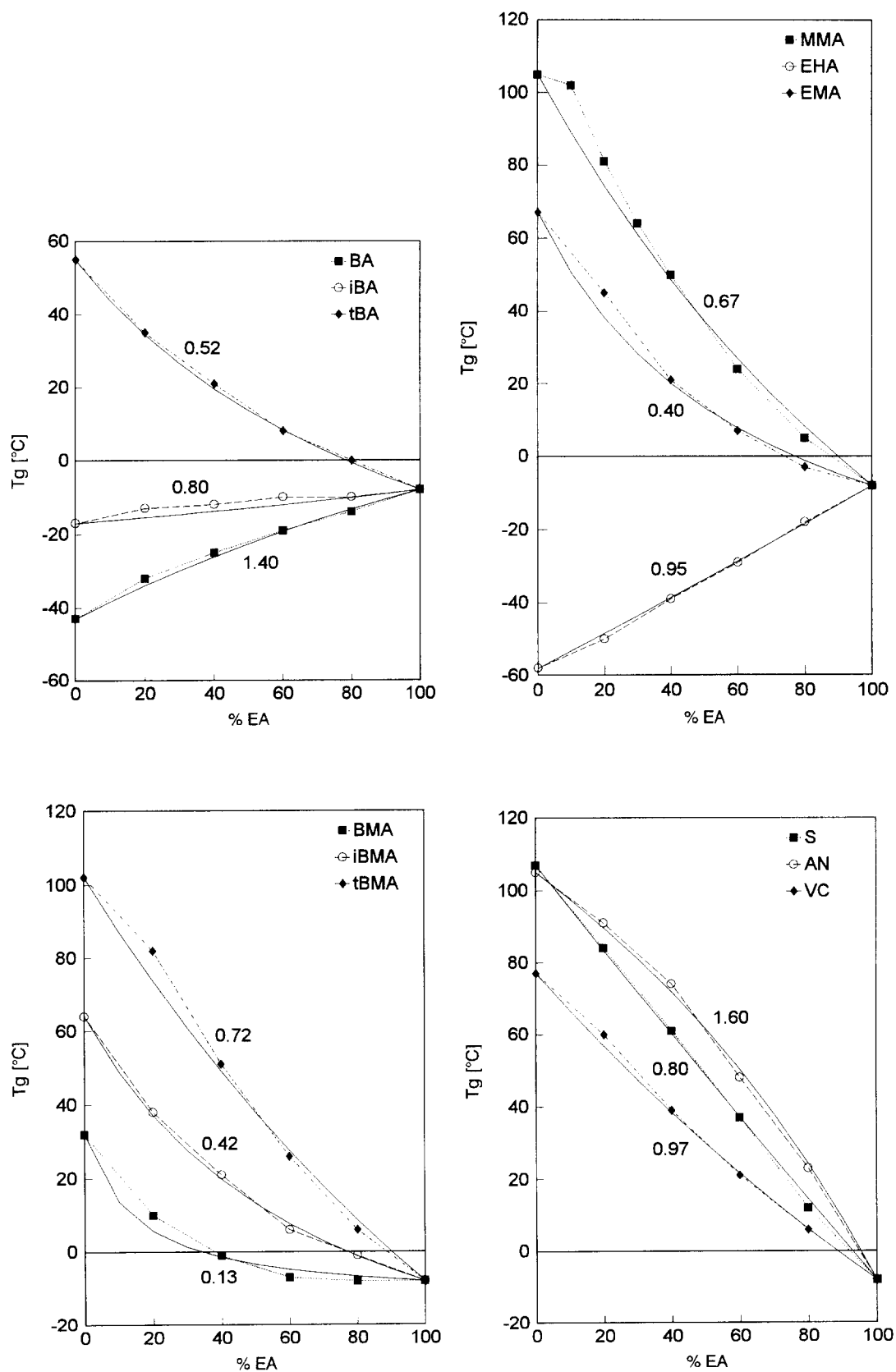


Figure 2 Glass transition temperatures of copolymers of EA. Solid lines denote data from the Gordon–Taylor equation

Copolymers of EA (Table 3 and Figure 2)

As with the MA copolymers, a positive deviation of the T_g values from Gordon–Taylor behaviour can be observed at EA values up to about 40% in the cases of the MMA and EMA copolymers. Unlike the respective

MA copolymers the EA/S copolymers behave regularly. The EA/tBMA curve exhibits a sigmoidal shape as well. A clear deviation of the data from the Gordon–Taylor equation is seen for the EA/tBMA copolymers.

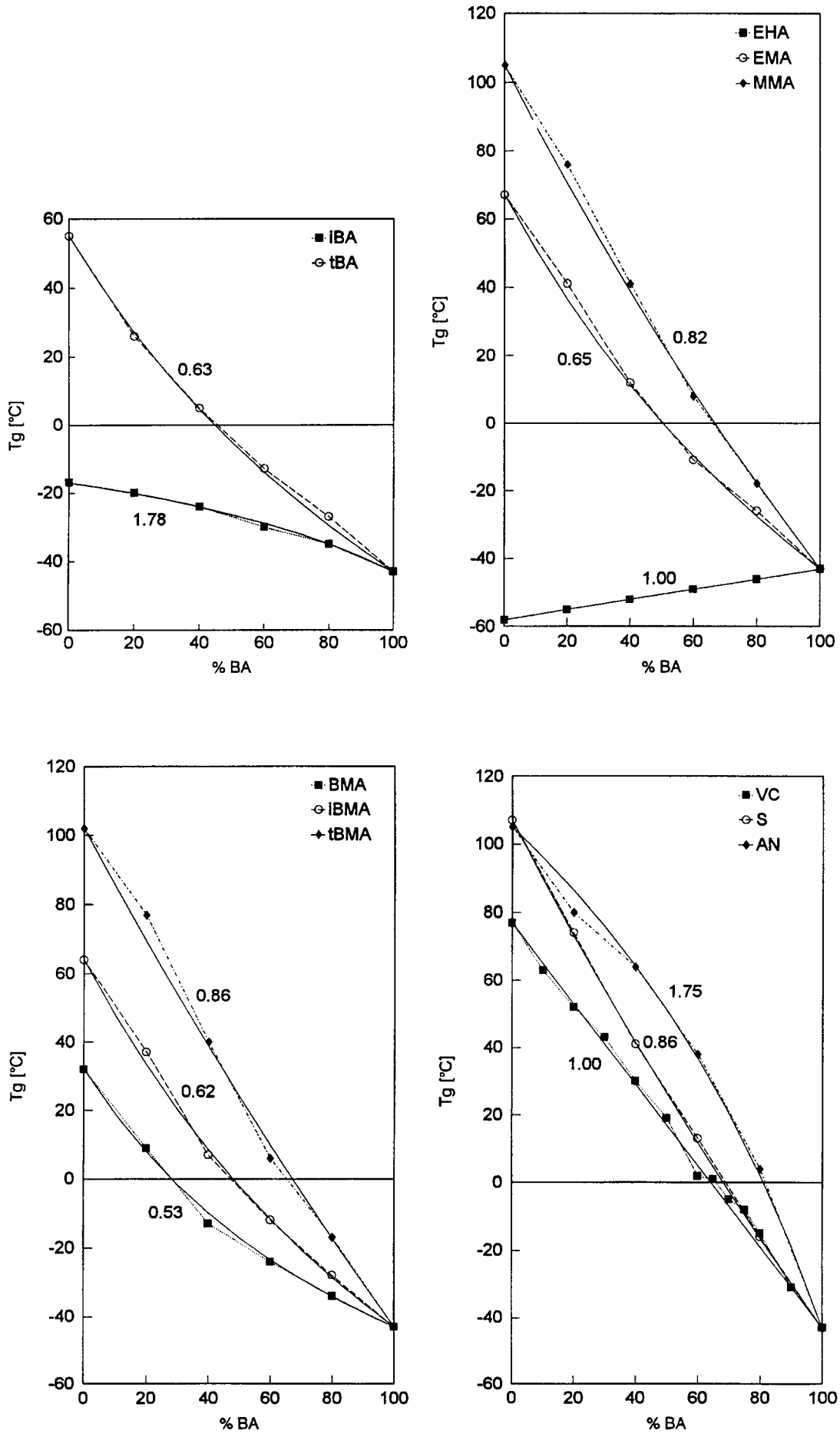


Figure 3 Glass transition temperatures of copolymers of BA. Solid lines denote data from the Gordon–Taylor equation

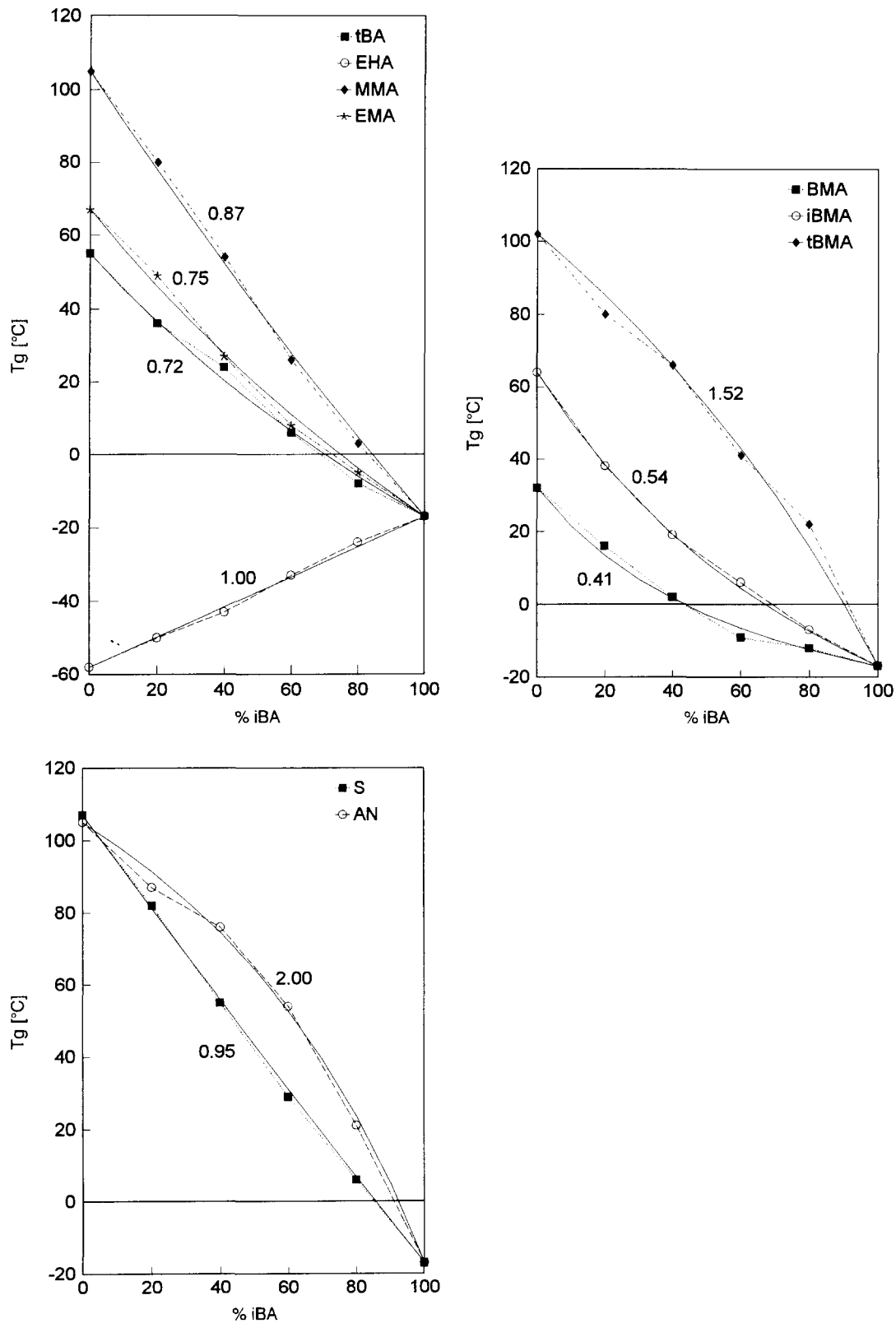


Figure 4 Glass transition temperatures of copolymers of iBA. Solid lines denote data from the Gordon–Taylor equation

Copolymers of BA (Table 4 and Figure 3)

Again a similar behaviour of the MMA and EMA copolymers and a sigmoidal composition dependence of the BA/tBMA system are found. The discrepancy between the experimental values and the Gordon–Taylor prediction in the case of the 20BA/80AN copolymer might be due to difficulties with the

determination of glass temperatures in systems with a large AN content.

Copolymers of iBA (Table 5 and Figure 4)

For iBA/tBMA copolymers one finds an inverse sigmoidal behaviour as compared to the tBMA copolymers discussed above. For the 20iBA/80AN copolymer

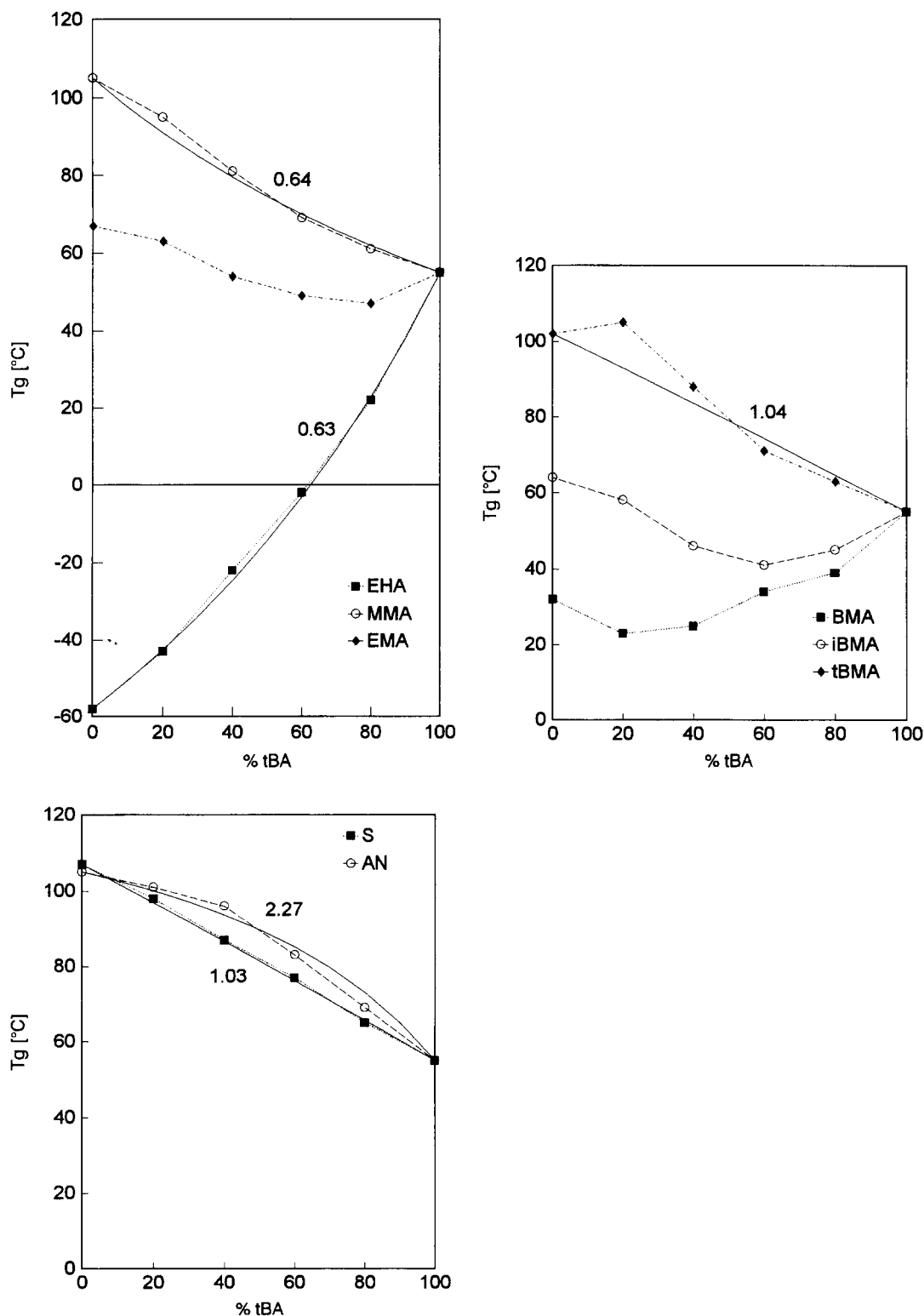


Figure 5 Glass transition temperatures of copolymers of tBA. Solid lines denote data from the Gordon–Taylor equation

the same explanation applies as for the 20BA/80AN copolymers.

Copolymers of tBA (Table 6 and Figure 5)

As is obvious from the data shown in Figure 5, a satisfactory description via the Gordon–Taylor equation is not feasible in the cases of the tBA copolymers with EMA, BMA and iBMA because these copolymers

exhibit glass transition temperatures outside of the temperature range delimited by the glass temperatures of the respective homopolymers.

Copolymers of EHA (Table 7 and Figure 6)

The Gordon–Taylor fitting approach yields a good representation of the experimental T_g data except for the glass temperature of the 60EHA/40MMA copolymer

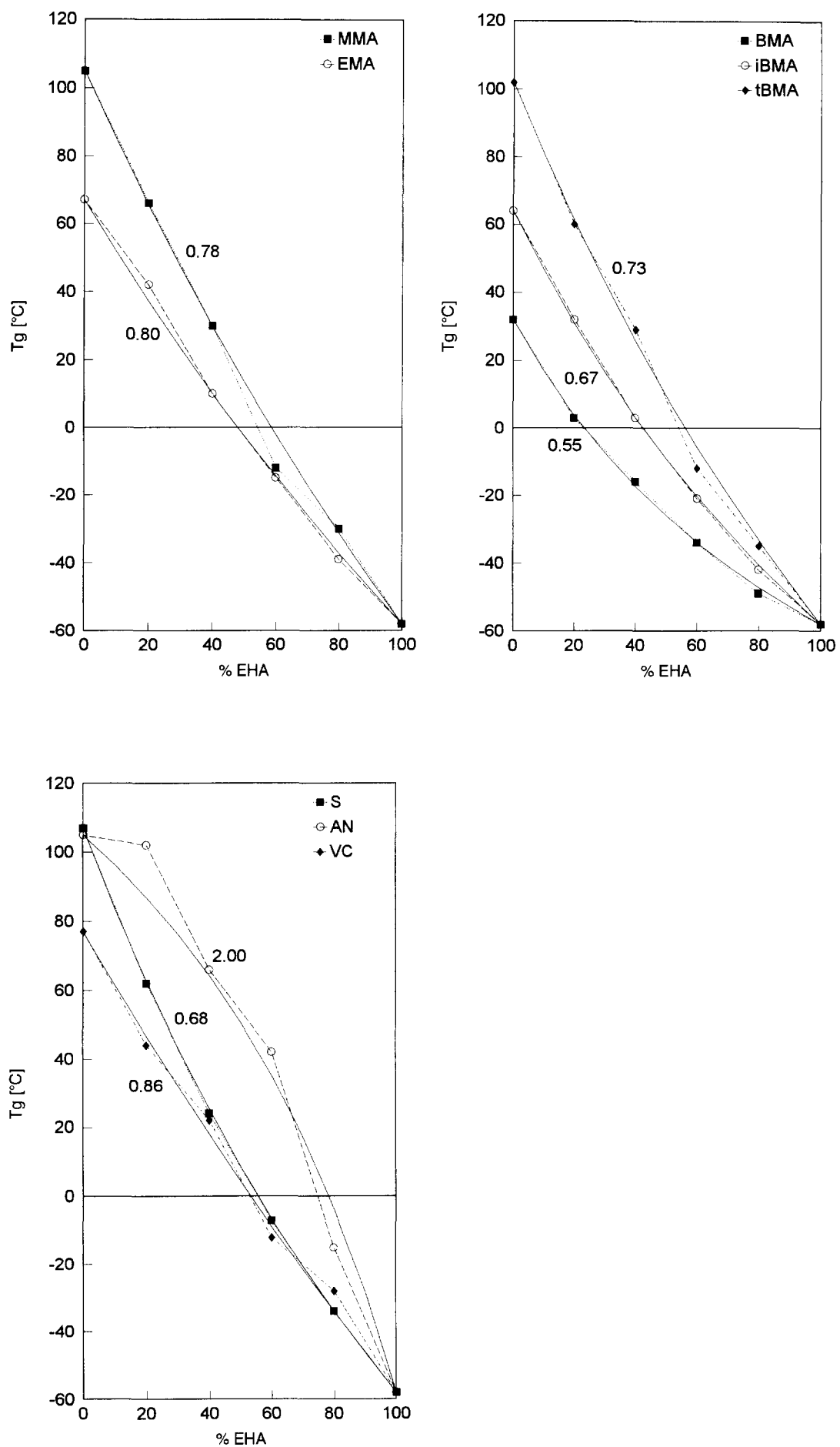


Figure 6 Glass transition temperatures of copolymers of EHA. Solid lines denote data from the Gordon-Taylor equation

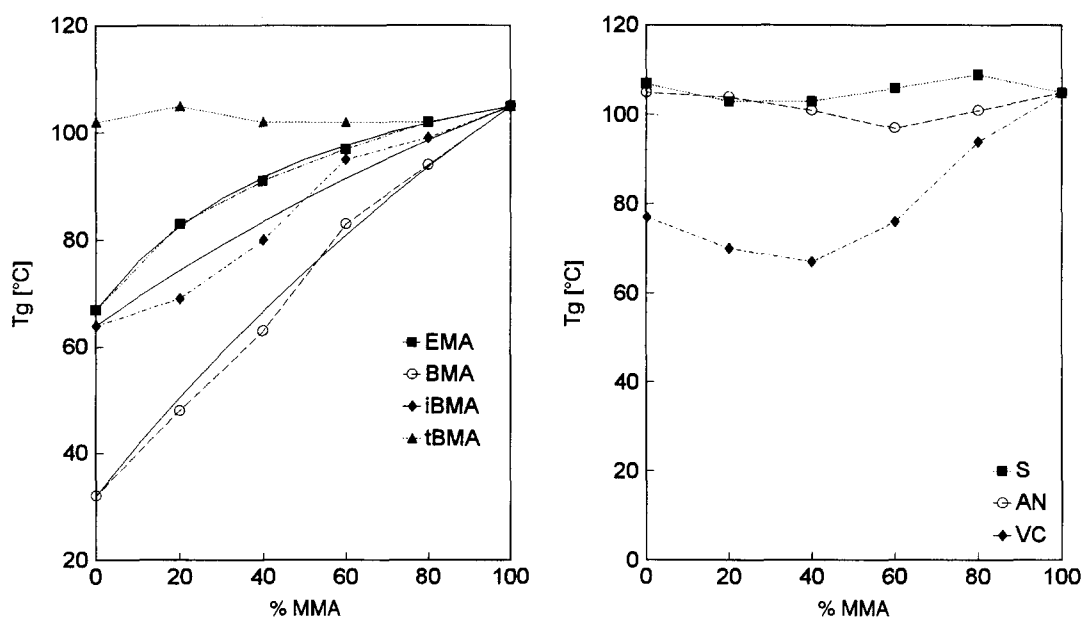


Figure 7 Glass transition temperatures of copolymers of MMA. Solid lines denote data from the Gordon-Taylor equation

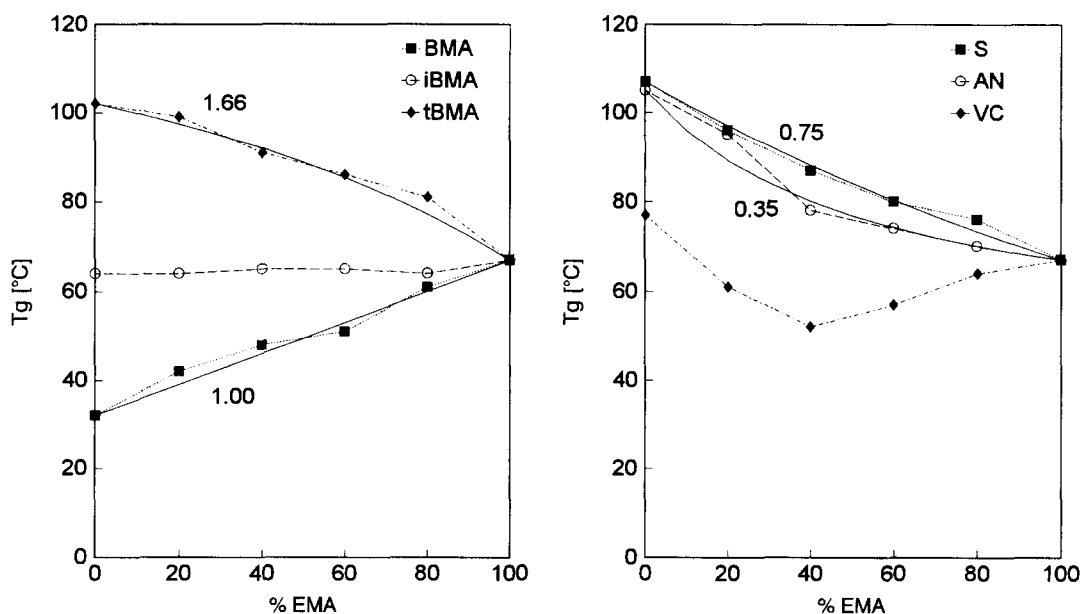


Figure 8 Glass transition temperatures of copolymers of EMA. Solid lines denote data from the Gordon-Taylor equation

and for the case of the EHA/AN copolymers, where the data are scattered around the interpolating curve.

Copolymers of MMA (Table 8 and Figure 7)

For the MMA/BMA and the MMA/iBMA copolymers a sigmoidal shape of the T_g versus composition dependence is found. An interesting behaviour is observed for the MMA/VC system: the glass temperature of the 40MMA/60VC copolymer is as far as 10 K below the glass temperature of pure PVC. This effect is even more pronounced for the EMA/VC copolymers, where the difference in the respective glass temperatures amounts to 15 K. MMA copolymers with tBMA, S and AN exhibit variations of the glass temperatures which are in the range of experimental uncertainty.

Copolymers of EMA (Table 9 and Figure 8)

The glass temperatures of the EMA and iBMA homopolymers coincide within experimental error, i.e. it is not meaningful to apply the Gordon-Taylor equation. The T_g curve of the EMA/VC copolymers exhibits a pronounced minimum below the glass transitions of the respective homopolymers.

Copolymers of BMA (Table 10 and Figure 9)

As in the case of EMA/VC copolymers, a minimum in the T_g curve is found for the BMA/VC copolymers. But, in contrast to EMA/VC, the composition where this minimum occurs is shifted to a BMA content of 80%.

Copolymers of iBMA (Table 11 and Figure 10)

In principle, the data can be described according to the

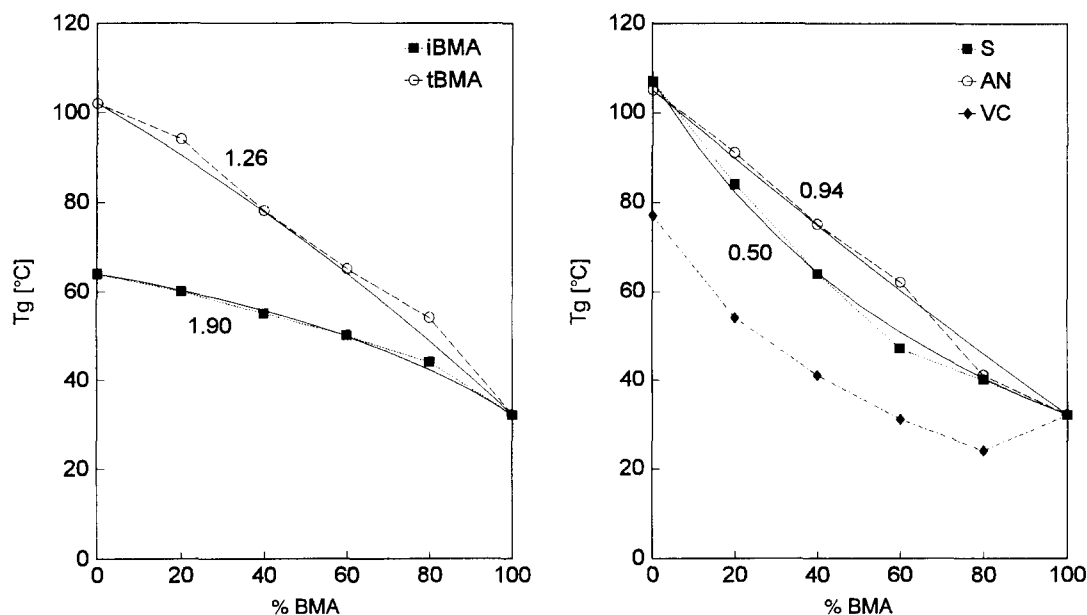


Figure 9 Glass transition temperatures of copolymers of BMA. Solid lines denote data from the Gordon–Taylor equation

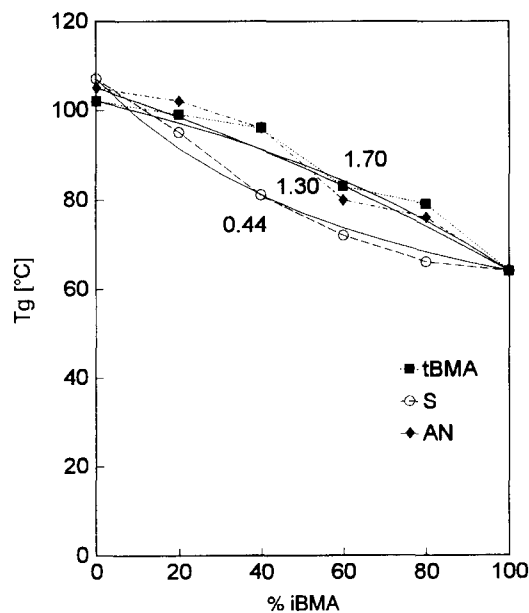


Figure 10 Glass transition temperatures of copolymers of iBMA. Solid lines denote data from the Gordon–Taylor equation

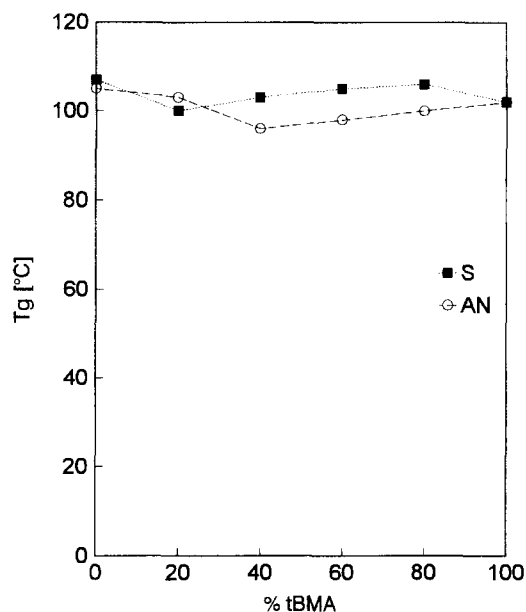


Figure 11 Glass transition temperatures of copolymers of tBMA

Gordon–Taylor equation. But the large scatter in the cases of the copolymers with tBMA and AN precludes any further interpretation.

Copolymers of tBMA (Table 12 and Figure 11)

The glass temperatures of the tBMA, S and AN homopolymers coincide within experimental error, i.e. it is—as in the case of the EMA/iBMA copolymers—not meaningful to apply the Gordon–Taylor equation.

Copolymers of S/AN (Table 13 and Figure 12)

A maximum of the T_g curve above the glass temperatures of the respective homopolymers is observed, i.e. the

Gordon–Taylor equation cannot be used for an adequate description of the data. Besides, only for the 40S/60AN copolymer is the change in T_g outside the range of experimental uncertainty.

CONCLUSION

It was found that the Gordon–Taylor equation describes the dependence of the glass transition temperature from the composition of the copolymers very well—apart from some exceptions discussed above. A thorough discussion of the relationship between a theoretical description of the data and structural aspects of the monomers is given in the second part of this study³. The aim of the present report is mainly to offer a

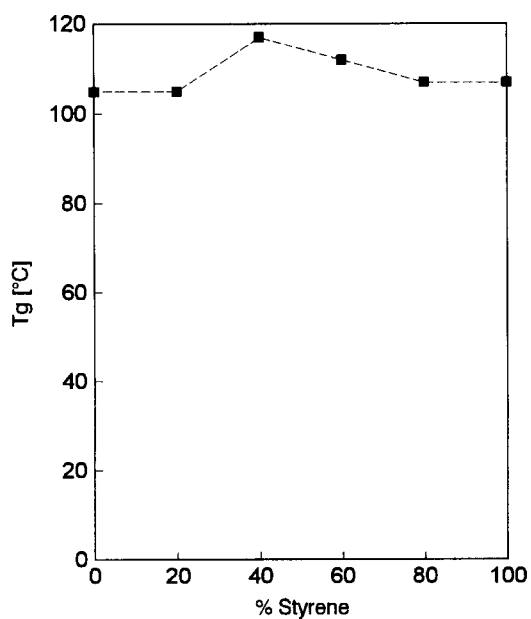


Figure 12 Glass transition temperature of S/AN copolymers

reliable database as a starting point for the testing of models concerning the glass temperature of random copolymers^{7,8}.

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