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Acenaphthylene Copolymers. II. Glass Transition Temperatures

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ABSTRACT

Glass transition temperatures are reported for copolymers of acenaphthylene with the following comonomers: methyl methacrylate, styrene, maleic anhydride, diethyl maleate, N-vinylpyrrolidone, α-methylstyrene, and trans-stilbene. The data are discussed in terms of previously published treatments of the dependence of glass transition temperature on copolymer composition. The drop in glass transition temperature consequent upon incorporation of small quantities of comonomer is not related to the glass transition temperature of the corresponding homopolymer.

INTRODUCTION

The glass transition temperature T_g of a binary statistical copolymer normally falls between the transition temperatures of the corresponding homopolymers (T_1 and T_2), although there are important exceptions to this generalization. A number of equations have been proposed which relate T_g to the copolymer composition via T_1 and T_2. Thus, according to DiMarzio and Gibbs [1]

$$T_g = F_1'T_1 + (1 - F_1')T_2 \tag{1}$$

where F_1' is the mole fraction of comonomer 1 (F_1) weighted by its fraction of rotatable bonds. In the case where both monomers are alike in this respect, Eq. (1) reverts to a linear relationship between T_g and mole fraction:

$$T_g = F_1T_1 + (1 - F_1)T_2 \tag{2}$$

Equations (1) and (2) relate the glass transition temperature to the copolymer composition via T_1 and T_2 without the necessity of an adjustable parameter. The equation of Wood [2] which may be written in the form

$$T_g = \Phi_1T_1 + (1 - \Phi_1)T_2 \tag{3}$$

where

$$\Phi_1 = F_1/[F_1 + \alpha(1 - F_1)]$$

is a generalized equation which also represents the proposal of Gordon and Taylor [3] and the equation of Mandelkern et al. [4],

$$\frac{W_1 + B(1 - W_1)}{T_g} = \frac{W_1}{T_1} + \frac{B(1 - W_1)}{T_2} \tag{4}$$

which was based on an explicit free volume analysis. In Eq. (4), W_1 is the weight fraction of comonomer 1.

It must be appreciated that Eq. (3) contains an adjustable parameter α, the value of which is located by fitting the copolymer T_g/F_1 data to a suitably linearized form of the equation. Insofar as the direct representation of copolymer transition temperatures as a function of composition is concerned, use of Eq (3) is a curve-fitting operation. Barton [5] has extended the DiMarzio and Gibbs treatment in terms of diad sequences in the copolymer and writes

$$T_g = F_{11}'T_1 + F_{22}'T_2 + (F_{12}' + F_{21}')T_{12} \qquad (5)$$

where F_{11}' is the fraction of rotatable bonds in 1,1 diads etc., and T_{12} is the glass transition temperature of the alternating copolymer. In principle, the equation is free of adjustable parameters, although it requires a knowledge of the monomer reactivity ratios r_1 and r_2: in practice, as T_{12} is not generally available, the copolymer T_g values have to be used to locate a value for T_{12} and so give a best fit to the raw data. The equations reported by Ellerstein [6] and Kanig [7] may be considered as special cases of Eq. (5) and share one important feature not shown by Eqs. (1)-(4): because of the introduction of the third term in the right-hand side to Eq. (5), the equation is not restricted to those cases where $T_1 > T_g > T_2$ (or $T_1 < T_g < T_2$) but may also be used where a maximum or minimum T_g is shown at a particular copolymer composition. It might also be noted that Ham [8] has extended Barton's approach to consider triad sequences.

The availability of some series of copolymers of acenaphthylene with other monomers [9] has prompted us to test the applicability of various T_g-composition equations. The stiff polyacenaphthylene molecule has a high glass transition temperature, and we were interested to see how the incorporation of minor quantities of a comonomer would alter T_g and whether such alteration could be related to the comonomer structure.

EXPERIMENTAL

The copolymers were selected from the series described previously [9]. The glass transition temperature was measured on a Perkin-Elmer differential scanning calorimeter (DSC-1) at a heating rate of 32°C/min or by differential thermal analysis (DuPont 900) at 20°C/min. In the series where both methods were employed (thermally polymerized copolymers of acenaphthylene with styrene) the agreement of T_g values was good. In both techniques, the sample was taken to a temperature slightly in excess of T_g, briefly annealed, cooled and then rerun; thus, we follow the recommendations of Martin and Rose [10]. The transition temperature recorded is that of the first deviation from the baseline of the scan.

The intrinsic viscosities of selected samples were determined to verify that polymer molecular weights were sufficiently high to minimize any molecular weight dependence of glass transition temperature.

RESULTS AND DISCUSSION

Copolymers of Acenaphthylene with Methyl Methacrylate

This is the most extensive set of data and combines samples prepared by radical initiation at 60° C with those made by thermal polymerization at 110° C. First we list the homopolymer data in Table 1. For calculation purposes we take $T_1 = 640°K$ and $T_2 = 392°K$; both values are rather higher than the literature [13] values, which may be a consequence of the rather high rates of temperature increase employed in the thermal analysis. Reported values for

TABLE 1. Glass Transition Temperatures of Polyacenaphthylene and Poly(methyl Methacrylate)

Polymer	Sample	Polymerization	T_g (°K)	$[\eta]$ (dl/g)[a]	$\overline{M}_v$[b]
Polyacenaphthylene	LT/24	Thermal	649	0.323	370,000
	LT/46	Radical	649	0.108	70,000
	AC/5	Thermal	628	0.336	392,000
	AC/11	Radical	632	0.081	45,000
Poly(methyl methacrylate	LT/21	Radical	400	0.405	140,000[c]
	MM/21	Thermal	392	–	–

[a] In toluene, 25° C.

[b] From the equation of Barrales-Rienda and Pepper [11] unless otherwise noted.

[c] From the equation of Chinai et al. [12].

TABLE 2. Glass Transition Temperatures of Acenaphthylene-Methyl Methacrylate Copolymers

F_1 (mole fraction acenaphthylene)	Polymerization	T_g (°K)	[η] (dl/g)[a]
0.129	Thermal	419	
0.189	Radical	426	0.255
0.254	Thermal	446	
0.300	Radical	448	0.154
0.336	Thermal	457	
0.388	Thermal	473	
0.451	Radical	471	0.135
0.530	Radical	501	0.134
0.600	Radical	529	0.128
0.608	Thermal	513	
0.688	Thermal	523	
0.779	Radical	562	0.124
0.819	Radical	585	0.120
0.866	Thermal	548	
0.917	Radical	617	0.129
0.980	Radical	626	0.110

[a] In toluene, 25°C.

polyacenaphthylene vary considerably, from 487 to 618°K, whereas the T_g of poly(methyl methacrylate) is normally quoted as about 378°K.

The glass transition temperatures of the copolymers are listed in Table 2 and shown in Fig. 1.

With the exception of one datum point, the thermally polymerized samples fit in well with the radically polymerized samples. Also shown in Fig. 1 are the curves predicted from Eqs. (1)-(3); for Eq. (1) it was assumed that acenaphthylene residues have one rotatable bond

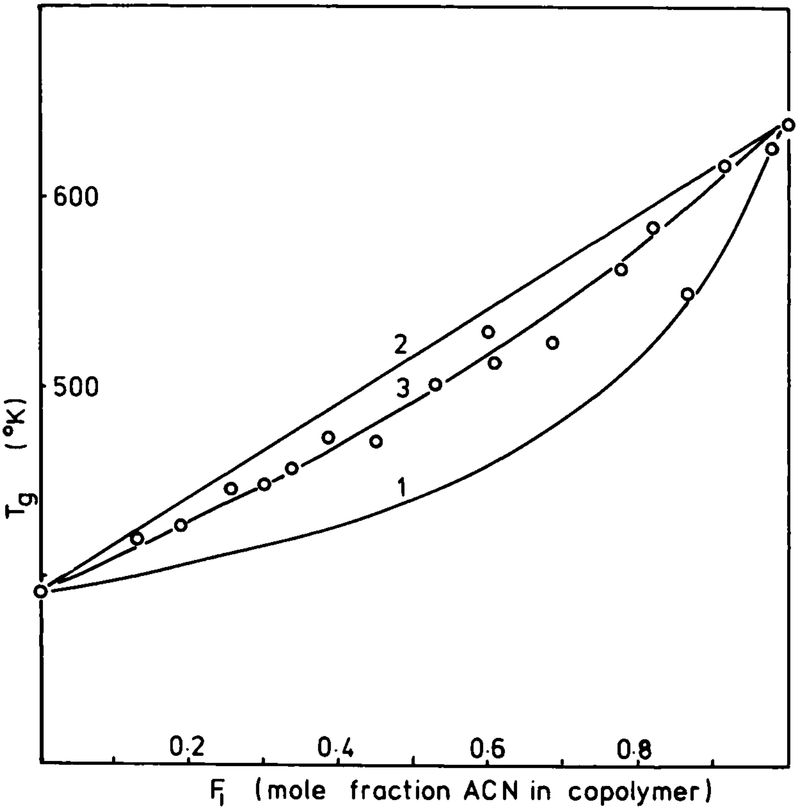

FIG. 1. Glass transition temperatures of acenaphthylene-methyl methacrylate copolymers: (o) experiment; (1) Eq. (1); (2) Eq. (2); (3) Eq. (3).

while methyl methacrylate has four. Equations (1) and (2) are unsuitable, whereas Eq. (3) fits the data well.

We have also taken the opportunity to test the Barton equation, Eq. (5) against the transition temperature-composition data. The following procedure was adopted: the monomer reactivity ratios $r_1 = 1.05$, $r_2 = 0.38$ as found previously [9] were used to relate F_1 to the corresponding feed composition f_1. The mole fraction of 1,1 diads, F_{11} was then calculated from F_1, f_1, and r_1, and F_{22} found similarly; the sum of these two quantities is equal to unity less

(F_{12} + F_{21}). The number of rotatable bonds in 1,1 diads was placed equal to 2 and in 2,2 diads to 8 and the F_{ij} terms converted to F_{ij}'. Calculation was also made by omitting consideration of the numbers of rotatable bonds by replacing F_{ij}' terms in Eq. (5) by F_{ij}. Although the two sets of copolymers give a common curve (Fig. 1) they do not give a common pair of reactivity ratios [9]. Therefore, the calculations based on Eq. (5) were repeated with r_1 = 1.73, r_2 = 1.04, both with and without the rotatable bond fraction contribution. The data are given in Table 3.

It is strikingly apparent that, by using T_{12} of Eq. (5) as an adjustable parameter, perfectly adequate representations of the data are made possible, despite changes in the values of the composition terms F_{ij}'; none of the four cases is superior to Eq. (3). The reason for this insensitivity is readily seen on inspection of Eq. (5). Since T_{12} is now a curve-fitting parameter, without an established physical significance, we will rewrite it as T* and replace Eq. (5) by Eq. (6):

$$T_g = pT_1 + qT_2 + rT^* \tag{6}$$

where p + q = 1 - r and p is a function of F_1, such that as $F_1 \rightarrow 1$, $p \rightarrow 1$ and $q \rightarrow 0$; whereas, as $F_1 \rightarrow 0$, $p \rightarrow 0$ and $q \rightarrow 1$. A number of arbitrary functions might fit this requirement. Putting p = F_1 is unsuitable, since it makes r zero, and Eq. (6) reverts to Eq. (2). Putting p = F_1^2 gives Ellerstein's [6] equation, and the calculations for this case and also for p = F_1^3 are detailed in Table 3. Although the latter plot is less satisfactory, the Ellerstein equation is an excellent representation of the data; furthermore, the case of p_1 = $F_1^{3/2}$ is also adequate for curve-fitting purposes.

Copolymers of Acenaphthylene with Styrene

The glass transition temperatures are recorded in Table 4; the curves through the data of Fig. 2 are those derived from Eqs. (1) and (3), respectively. Again, the adjustable parameter of Eq. (3) is required to give an adequate representation of the experimental findings. In view of the discussion in the preceding section, the other curve-fitting equations were not calculated.

TABLE 3. Predicted Glass Transition Temperatures for Acenaphthylene-Methyl Methacrylate Copolymers

F_1 (mole fraction acenaphthylene in copolymer)	Glass transition temperature (°K)[a]						
	Case 1 $T_{12} = 526$	Case 2, $T_{12} = 468$	Case 3, $T_{12} = 567$	Case 4, $T_{12} = 472$	Case 5, $T^* = 461$	Case 6, $T^* = 479$	Case 7 $T^* = 422$
0.1	408	406	413	409	407	416	403
0.2	428	424	433	429	424	436	420
0.3	449	442	453	450	443	454	440
0.4	472	464	474	473	465	471	463
0.5	494	487	495	497	489	488	489
0.6	515	513	518	522	514	508	516
0.7	537	541	543	549	543	532	545
0.8	561	571	573	578	573	561	575
0.9	594	606	604	608	605	596	607

[a] Case 1: $r_1 = 1.05$, $r_2 = 0.38$ with allowance for rotatable bonds; case 2: $r_1 = 1.05$, $r_2 = 0.38$ without allowance for rotatable bonds; case 3: $r_1 = 1.73$, $r_2 = 1.04$ with allowance for rotatable bonds; case 4: $r_1 = 1.73$, $r_2 = 1.04$ without allowance for rotatable bonds; case 5: $p = F_1^2$, etc.; case 6: $p = F_1^3$, etc.; case 7: $p = F_1^{3/2}$, etc.

TABLE 4. Glass Transition Temperature of Acenaphthylene- Styrene Copolymers

F_1 (mole fraction acenaphthylene in copolymer)	Polymerization	T_g (°K)	$[\eta]$ (dl/g)[a]	$\overline{M}_v$[b]
0	Thermal	368	0.845	228,000
0	Radical	370	0.716	179,000
0	Thermal	371	0.826	220,000
0.253	Thermal	421	–	–
0.275	Radical	426	–	–
0.443	Radical	450	–	–
0.452	Thermal	433	–	–
0.681	Radical	499	–	–
0.733	Thermal	495	–	–
0.822	Radical	534	–	–
0.892	Thermal	571	–	–

[a] In toluene, 25° C.

[b] From the equation of Outer, Carr, and Zimm [14].

Copolymers of Acenaphthylene with Maleic Anhydride

This set of copolymers is interesting, in that no direct measurement of T_2 may be made, since maleic anhydride does not homopolymerize. Equation (3) may be used, however, to solve for both α and T_2, and the curve shown in Fig. 3 is that so obtained, with the hypothetical $T_2 = 530°$ K. Application of Eq. (3) does, of course, imply that $T_2 < T_g$ at all copolymer compositions. Barton's equation [Eq. (5)] could not be used successfully; as r_2 is zero or very small, the term in T_2 is negligible, but a plot of $(T_g - F_{11}T_1)$ against $(1 - F_{11})$ is not linear through the origin. A similar result obtains if, in Eq. (6) $p = (F_1)^2$ and $q = 0$. An alternative approach would be to assume that the glass transition temperature of the copolymers made at low feed contents of acenaphthylene approximated to T_{12} and then to solve

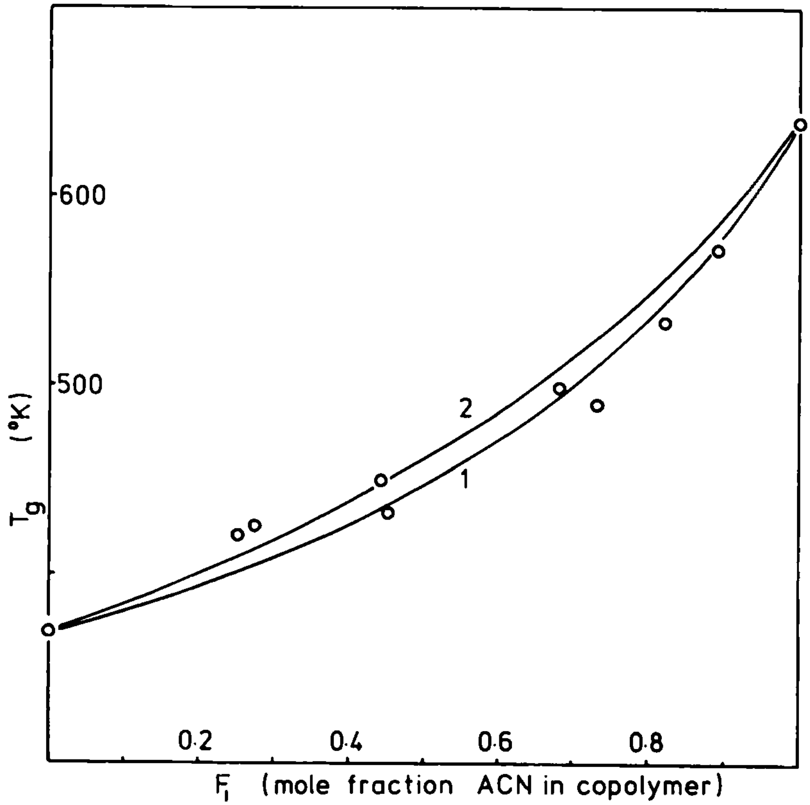

FIG. 2. Glass transition temperatures of acenaphthylene-styrene copolymers: (o) experiment; (1) Eq. (3); (2) Eq. (1).

Eq. (5) for T_2; however these calculations lead to impossible (i.e., negative) values for T_2.

The experimental data for the acenaphthylene-maleic anhydride polymers, all of which were radically polymerized at 60°C, are given in Fig. 3; the samples may have modest molecular weights, their intrinsic viscosities in dimethylformamide at 25°C falling in the range 0.078-0.128.

Copolymers of Acenaphthylene with Diethyl Maleate

These copolymers are analogous to the acenaphthylene-maleic anhydride copolymers, in that no T_2 value is known. Equation (3) was

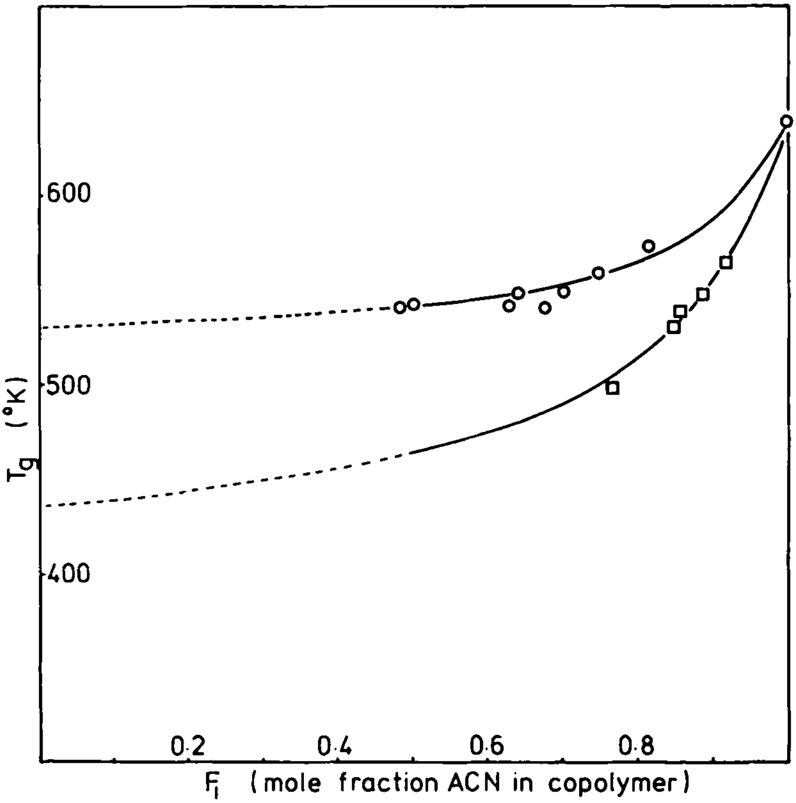

FIG. 3. Glass transition temperatures of acenaphthylene copolymers: (○) copolymers with maleic anhydride; (□) copolymers with diethyl maleate; (—) Eq. (3).

found applicable but, again, Eq. (5) with $F_{22}' = 0$, failed to represent the data, which are shown in Fig. 3. The hypothetical T_2 value from Eq. (3) is 435° K.

Other Polymers

The copolymers of acenaphthylene with N-vinylpyrrolidone which were available covered a rather narrow range of compositions. The

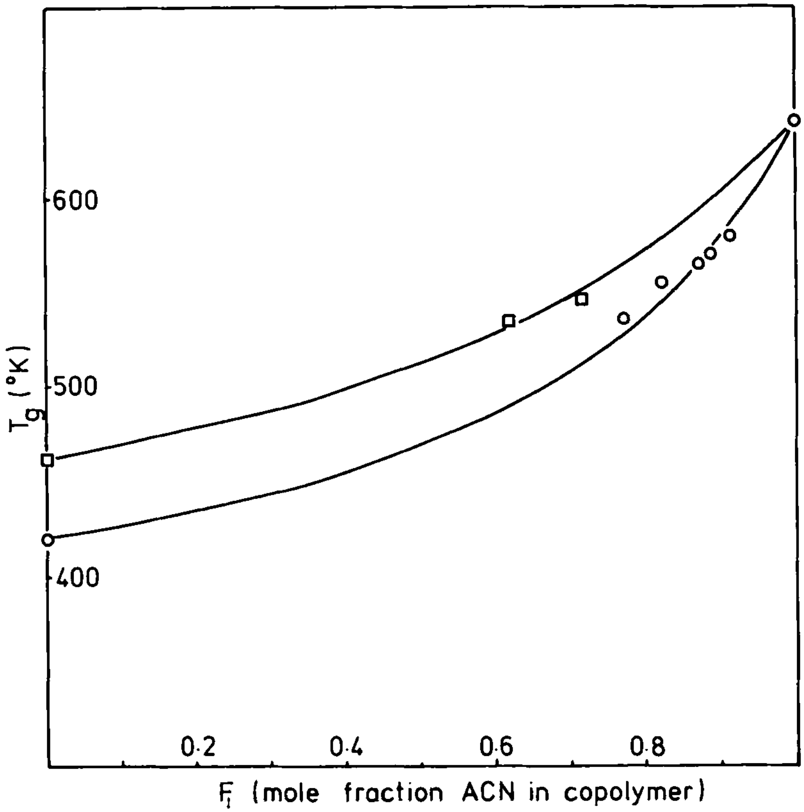

FIG. 4. Glass transition temperatures of acenaphthylene copolymers: (○) copolymers with N-vinylpyrrolidone; (□) copolymers with α-methylstyrene; (—) Eq. (3).

measured value of T_2 (420° K) is higher than literature values [13]. Figure 4 shows that Eq. (3) may be fitted with modest success. As reported [9], satisfactory reactivity ratios could not be attributed to this copolymerization, possibly because of penultimate group effects. Consequently, Eq. (5) may not be tested on these data. Furthermore, the Ellerstein [6] equation, a special case of Eq. (6), is not consistent with the T_g/F_1 values.

Only two copolymers with α-methylstyrene were measured, together with a cationically polymerized homopolymer whose glass transition temperature was 463° K, again rather higher than the previously reported [13] value. The curve shown in Fig. 4 is of Eq. (3) but must be regarded as speculative only. The T_g values of three copolymers with trans-stilbene were found, but as no reliable compositions are known the data cannot be treated in the same manner as those for other sets of copolymers. For completeness we give the monomer feed composition (f_1) and glass transition, which are: $f_1 = 0.149$, $T_g = 532$°K; $f_1 = 0.252$, $T_g = 558$° K; $f_1 = 0.542$, $T_g =$ 611° K. Thus incorporation of the hindered monomer leads to a significant drop in the transition temperature.

CONCLUSIONS

For these series of copolymers in which $T_1 > T_g > T_2$, the relation between glass transition temperature and copolymer composition is adequately represented by Eq. (3) and no advantage results from the use of Barton's equation or its generalized form [Eq. (6)]. We believe that the practical value of Eqs. (5) and (6) must be restricted to those less common cases where the T_g/F_1 curve shows a maximum or minimum.

Incorporation of small amounts of a comonomer into the polyacenaphthylene chain causes a significant drop in the glass transition temperature; thus 5 mole % of comonomer reduced T_g by between 17 and 51° K. Inspection of Figs. 1-4 shows, however, that the relative extent of this drop in glass transition temperature is not simply related to the structure of the comonomer as revealed by the glass transition temperature of the corresponding homopolymer. Thus the smallest reduction in T_g is brought about by incorporation of methyl methacrylate units, for which $T_2 = 392$° K, whereas the greatest drop is caused by copolymerization with diethyl maleate, which has a predicted T_2 of 435° K. Maleic anhydride units, which would be expected to be the least flexible comonomeric species, as evidenced by the predicted T_2 of 530° K, produce a considerable fall in T_g.

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