Hydroxymethylation and Alkoxymethylation of Methacryloguanamine

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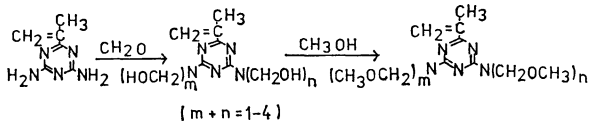
The reaction of 2-amino-4-(substituted amino)-6-isopropenyl-1,3,5-triazines (methacryloguanamine) with formaldehyde gave several new monomers having hydroxymethyl groups in satisfactory yields. These monomers were easily converted into the corresponding alkyl ethers with methanol. Their melting points and solubilities were affected considerably by the species and the number of substituted groups. Especially, tetrakis(hydroxymethyl)methacryloguanamine and its methoxymethyl derivative were readily soluble in water and nonpolar solvents, respectively. The former was polymerized and crosslinked smoothly to yield a insoluble polymer. Copolymerization of the latter with methyl methacrylate, however, gave soluble polymers, formed flexible and tough films. Similarly, the reactive polymers were prepared from polymers containing guanamine structure by hydroxymethylation followed by etherification.

Poymers containing amino-1,3,5-triazinyl groups have been investigated as industrial materials and heat-stable polymers. Furthermore, the polymers with aminotriazine units in the side or main chain are expected to have a variety of other properties, such as rigidity, intermolecular interaction, thermal stability and basicity.[1-3]

Recently, 2-amino-4-(substituted amino)-6-isopropenyl-1,3,5-triazines (methacryloguanamine) were readily prepared from methacrylic active esters and biguanides.[4] The syntheses and properties of copolymers of these monomers with styrene, unsaturated carboxylic acid, and their alkyl esters have been studied previously:[1,5] Softening and glass transition temperature rose, specific gravity increased, and solubilities markedly changed with the content of triazine units; copolymers with methacrylic acid were ampholytes.

This paper describes the syntheses of new reactive monomers with hydroxymethyl and methoxymethyl groups, starting from *N*-substituted methacryloguanamines by hydroxymethylation followed by etherification as given below; their polymerization and some properties of both the monomers and the polymers further were investigated. Similarly, the preparation of polymers having pendant highly reactive groups by polymer side reaction will be reported.



Experimental

Materials. Biguanides were prepared by the method of Kono and Odo[6] or Cohn[7] from dicyanodiamide and the corresponding amines. Formalin (*ca.* 37 wt%), paraformaldehyde, benzoyl peroxide, and DMSO-d_6 were commercial materials. All other reagents and solvents were commercially available and were used after purification if necessary. 2,4-Diamino-(AIPT), 2-amino-4-dimethylamino-(DMAIPT)-, and 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT) were prepared from phenyl methacrylate and biguanides by the procedure described previously.[4]

Procedure. Hydroxymethylation and etherification of *N*-substituted methacryloguanamine were as described below.

2,4-Bis[bis(hydroxymethyl)amino]-6-isopropenyl-1,3,5-triazine (4F-AIPT): A mixture of 2.79 g (18.5 mmol) of AIPT and 12 cm^3 of formalin which was adjusted to pH 9.0 with aqueous sodium hydroxide solution, was stirred at 50 °C. This mixture became homogeneous after 2 h and was stirred for another hour. The solution was allowed to stand at room temperature, and concentrated at 5—10 °C using evaporator. To the resulting solution was added 100 cm^3 of ether, and colorless crystals (mp 122—124 °C) was obtained in 67.8% yield.

Found: C, 44.07; H, 6.29; N, 26.08%. Calcd for $C_{10}H_{17}N_5O_4$: C, 44.28; H, 6.27; N, 25.83%.

2,4-Bis[bis(methoxymethyl)amino]-6-isopropenyl-1,3,5-triazine (4M-AIPT): A mixture of 2.57 g of 4F-AIPT and 1 cm^3 of concd HCl (*ca.* 35 wt%) in 30 cm^3 of methanol was stirred at room temperature for 30 min and became clear. After the solution had been neutralized with a methanol solution of potassium hydroxide, and it was concentrated under reduced pressure at 10—20 °C. To the remaining product was added 75 cm^3 of water, and the crude product obtained were recrystallized from ether to afford collorless needles (mp 46—47 °C) in 80.0% yield.

Found: C, 50.93; H, 7.89; N, 21.75%. Calcd for $C_{14}H_{25}O_4$: C, 51.38; H, 7.65; N, 21.41%.

Polymerization was carried out in vacuum-sealed ampoules. Methanol or methanol–water solution was used as a precipitant. The composition of compounds were evaluated from the carbon and nitrogen contents.

Measurement. IR, UV, and ^{1}H-NMR spectra were recorded on a Hitachi 285 spectrometer, a Hitachi 139 spectrometer, and a Hitachi R-24B (60 MHz) spectrometer, respectively. DTA experiments were carried out on a Shimadzu thermal analyzer DT-20. Softening temperature was measured with a Shimadzu MM-2 micro-softening apparatus.

Results and Discussion

Hydroxymethylation and Alkoxymethylation of Methacryloguanamines. As shown in Table 1, the reaction of 2,4-diamino-6-isopropenyl-1,3,5-triazine(AIPT) with formaldehyde was carried out at 50 °C for 3 h in the presence of basic catalyst. The observed molar ratio of hydroxymethyl group to AIPT increased with increasing initial molar ratio. Especially, for the molar ratio of 3.0 and 8.0, di- and tetrakis(hydroxymethyl) derivatives were obtained in adequate purity and satisfactory yield, respectively. Moreover, these monomers were easily converted into the corresponding derivatives with a large excess of methanol at room

Table 1. Hydroxymethylation[a] and alkoxymethylation[b] of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT)

Monomer No.	Formalin (cm^3)	Solvent (cm^3)	Ratio F/AIPT	Yield %	Observed[c] F or M / AIPT ratio	N (%)[d] Found (Calcd)
F-AIPT	3.0	Water (6)	2.0	83.4	1.3	36.63
2F-AIPT	4.5	Water (5)	3.0	85.6	2.0	32.40 (33.18)
3F-AIPT	6.0	—	4.0	73.1	3.3	27.40
4F-AIPT	12.0	—	8.0	67.8	4.0	26.08 (25.83)
2M-AIPT	—	Methanol (30)	—	55.6	2.0	29.10 (29.29)
4M-AIPT	—	Methanol (30)	—	80.0	4.0	21.75 (21.41)

a) Conditions; AIPT: 2.79 g (18.5 mmol), at pH 9.0, at 50 °C, for 3 h, F: formaldehyde or hydroxymethyl group. b) Conditions; 2F-AIPT or 4F-AIPT: 9.5 mmol, concd HCl: 1.0 cm^3, at room temp, for 30 min, M: methoxymethyl group. c) Calculated from the carbon and the nitrogen content. d) Calcd % of N are for pure bis- and tetrakis(hydroymethyl), and its methoxy derivatives.

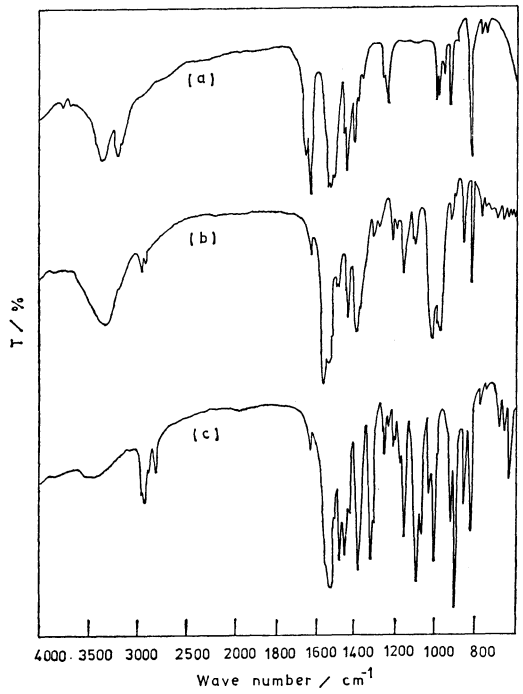


Fig. 1. IR spectra of (a) 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT), (b) the tetrakis(hydroxymethyl) derivative (4F-AIPT), and (c) the tetrakis(methoxymethyl) derivative (4F-AIPT).

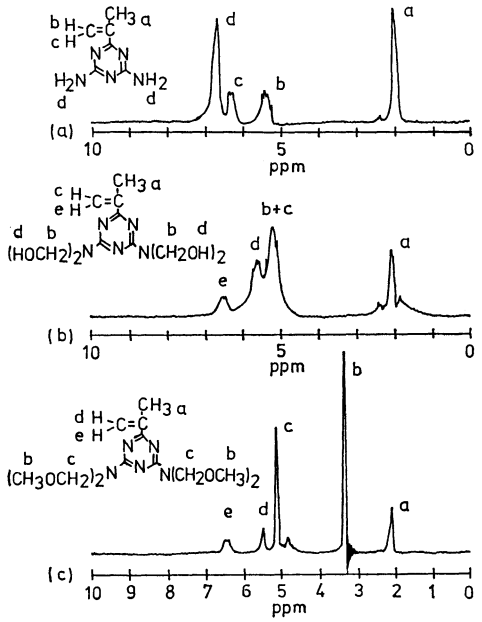


Fig. 2. ^{1}H-NMR spectra of (a) 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) in DMSO-d_6, and (b) the tetrakis(hydroxymethyl) derivative (4F-AIPT) in DMSO-d_6, and (c) the tetrakis(methoxymethyl) derivative (4M-AIPT) in CCl_4.

temperature in the presence of acid catalyst.

The new monomers were identified by elemental analyses, IR, ^{1}H-NMR, and UV spectra. For example, the IR spectra of tetrakis(hydroxymethyl) and tetramethoxy derivatives are shown in Fig. 1. The characteristic bands of isopropenyl-1,3,5-triazine were observed at 830 (the triazine ring), 1640 (the C=C stretching), and 930 cm^{-1} (the C–H bending), whereas the absorption near 1640—1660 cm^{-1} due to the N–H scissoring was rarely detected. In Fig. 1(b) the absorption at 1000 cm^{-1} due to C–O stretching indicates the presence of hydroxymethyl group;[8] the strong absorptions near 2950 and 1110 cm^{-1} are assigned to the C–H stretching and the C–O–C stretching of methoxymethyl group, respectively.

In the NMR spectrum given in Fig. 2(b), the signal at 6.68 ppm due to the protons of NH_2 group is rarely observed, and the appearance of the absorption in the region of 5.1 to 5.5 ppm may be attributed to the methylene protons and the hydroxyl group protons on $N(CH_2OH)_2$; in Fig. 2(c) the singlet signals at 3.35 and 5.16 ppm are due to the absorptions for the methoxyl and methylene protons on $N(CH_2OCH_3)_2$,[8] and the characteristic signals of isopropenyl group are also found at 2.11(CH_3), 5.49 and 6.49 ppm (CH_2=C). The ratio of the absorption intensities of the signals is recognized to be in agreement with the calculated one for pure hydroxymethyl or methoxymethyl derivative.

Table 2 shows that the solubilities of the reactive monomers obtained increased generally with the reduction of melting point (T_m). T_m of the hydroxymethyl derivatives rose 90 to 124 °C with the number of substituents, but became much lower than that of

Table 2. Properties of hydroxymethyl and methoxymethyl derivatives of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT)

Monomer No.	Observed[a] F or M / AIPT ratio	Mp θ_m/°C (Lit)[5]	Solubilities[b] δ 7.4 Hex	7.7 Et_2O	9.1 Bz	9.3 MEK	9.7 DOX	14.5 MeOH	23.4 H_2O	UV (MeOH) λ_{max}/nm ($\varepsilon \times 10^{-3}$)
4M-AIPT	4.0	46—47	++	++	++	++	++	++	+	277 (3.54)
2F-AIPT	2.0	87—90	−	−	+	++	++	++	+	275 (3.05)
F-AIPT	1.3	91—93	−	−	+	++	++	++	+	274 (2.94)
3F-AIPT	3.3	107—108	−	−	±	++	++	++	++	277 (3.18)
4F-AIPT	4.0	122—124	−	−	−	++	++	++	++	278 (3.40)
2M-AIPT	2.0	223—226	−	−	−	−	++	+	−	276 (3.20)
AIPT	—	247—248 (247—248)	−	−	−	−	+	+	±	271 (2.58)

a) F: Hydroxymethyl group, M: methoxymethyl group. b) ++: Readily soluble, +: soluble, ±: soluble at heating, −: insoluble, Hex: hexane, Et_2O: diethyl ether, Bz: benzene, MEK: ethyl methyl ketone, DOX: dioxane, MeOH: methanol, δ: solubility parameter.

Table 3. Hydroxymethylation[b] and alkoxylation[c] of 2-amino-4-(substituted amino)-6-isopropenyl-1,3,5-triazines

Monomer[a] No.	Ratio F/Triazine	Solvent (cm^3)	Yield/%	Observed[d] F or M / Triazine ratio	N (%)[e] Found (Calcd)
F-DMAIPT	8	Water (5)	88.2	1.0	33.17 (33.65)
M-DMAIPT	—	Methanol (30)	98.0	1.0	30.91 (31.53)
F-AAIPT	8	Water (20) / Dioxane (30)	85.1	1.4	26.12
M-AAIPT	—	Methanol (30)	63.0	1.4	24.31

a) Substituent; DMAIPT: 4-dimethylamino, AAIPT: 4-anilino. b) Conditions; DMAIPT or AAIPT: 15.0 mmol, at pH 9.0, at 50 °C, for 8 h, F: formaldehyde or hydroxymethyl group. c) Conditions; F-DMAIPT or F-AAIPT: 12.0 mmol, concd HCl: 1.0 cm^3, at room temp, for 30 min, M: methoxymethyl group. d) Calculated from the carbon and the nitrogen content. e) Calcd % of N are for pure mono(hydroxymethyl) and mono(methoxymethyl) derivatives.

AIPT (248 °C). Then, these derivatives became more soluble in MEK, alcohols and water compared to AIPT; these properties could be related to not only the decrease of intermolecular interaction between aminotriazine rings, but also the increase of intra- and intermolecular hydrogen bonding of hydroxymethyl group to nitrogen atom on the triazine ring.

On the other hand, upon introducing methoxyl groups into the bis(hydroxymethyl) derivative, T_m rose markedly and the solubilities decreased; this may be due to the increase of modelately strong interaction between triazine rings with NH groups.

The tetramethoxy derivative, however, showed noticeable properties: This monomer melts at a very low temperature (47 °C), soluble not only in alchols and water, but also readily soluble in nonpolar solvents such as hexane, benzene, and carbon tetrachloride; this suggests that introduction of four methoxyl groups to AIPT reduces the rigidity of the triazine ring, decreases extremely its intra- and intermolecular interaction,[5] and increases the hydrophobicity as well as the hydrophilicity.

In addition, in the UV spectra, the electron-releasing effect of hydroxymethyl and methoxymethyl groups resulted in a bathochromic shift compared with AIPT; ε values also increased.

Subsequently, as shown Table 3, the reaction of *N*-dimethylamino- (DMAIPT) or *N*-phenylmethacryloguanamine (AAIPT) with excess formaldehyde was performed at 50 °C for 8 h; the molar number of the combined formaldehyde to guanamine, however, was 1.0 and 1.4, respectively. Then, the almost complete conversion of these monomers to their methoxy derivatives occurred during a rapid lapse of time.

Table 4 shows that the reduction of T_m occurred remarkably with hydroxymethylation, and T_m rises significantly again with etherification. The mono(hydroxymethyl) derivative of DMAIPT as well as the tetramethoxy derivative of AIPT exhibited high solubilities in water and nonpolar solvents, in which the corresponding methoxy derivative was insoluble. The hydroxymethyl derivative of AAIPT was more readily soluble in benzene and alcohols than the methoxy derivative, but insoluble in water.

As a result, new reactive monomers were readily prepared from *N*-substituted methacryloguanamine, by hydroxymethylation followed by methoxymethylation; then these monomers differ in the melting points and the solubilities, which are affected markedly by the species and the number of substituents attached to triazine ring.[4]

Table 4. Properties of hydroxymethyl and methoxymethyl derivatives of 2-amino-4-(substituted amino)-6-isopropenyl-1,3,5-triazines

Monomer[a] No.	Observed[b] F or M / Triazine ratio	Mp θ_m/°C (Lit)[5]	Solubilities[c] δ 7.4 Hex	7.7 Et_2O	9.1 Bz	9.3 MEK	9.7 DOX	14.5 MeOH	23.4 H_2O	UV (MeOH) λ_{max}/nm ($\varepsilon \times 10^{-3}$)
F-DMAIPT	1.0	118—119	+	++	++	++	++	++	+	287 (3.07)
M-DMAIPT	1.0	149—151	−	−	−	−	−	++	+	280 (3.19)
DMAIPT	—	191—192 (191—192)	−	+	++	+	++	++	±	288 (2.74)
F-AAIPT	1.4	63— 68	−	−	++	−	++	++	−	252 (18.3)
M-AAIPT	1.4	184—186	−	−	−	−	−	++	−	251 (17.1)
AAIPT	—	174—175 (174—174.5)	−	+	++	+	++	++	−	252 (22.7)

a) Substituent; DMAIPT: 4-dimethylamino, AAIPT: 4-anilino. b) F: Hydroxymethyl group, M: methoxymethyl group. c) ++: Readily soluble, +: soluble, ±: soluble at heating, −: insoluble, δ: solubility parameter.

Table 5. Copolymerization[a] of 2,4-bis[bis(methoxymethyl)amino]-6-isopropenyl-1,3,5-triazine (4M-AIPT) with methyl methacrylate (MMA)

Polymer	4M-AIPT or AIPT in monomer (mol%)	Conversion wt%	4M-AIPT or AIPT in copolymer (mol%)	η_{sp}/C[c] dl g^{-1}	Solubilities[e] δ 9.0 IPA	Bz	10.0 DOX	MCS	12.0 AcA	DMSO	14.5 MeOH	Softening temperature °C
P(4M-AIPT -MMA)	10.4	39.5	24.7	0.48	+	++	++	++	++	++	+	92—97
	20.0	37.8	50.3	0.51	+	++	++	++	++	++	+	118—123
P(AIPT-[b] -MMA)	18.9	48.1	26.7	1.21[d]	−	−	−	±	+	++	−	255—265
	58.3	43.0	52.6	—	−	−	−	−	+	±	−	>300
Poly(MMA)	—	50.2	—	0.63	+	++	++	+	++	+	−	145—155

a) Conditions; [4M-AIPT]+[MMA]=0.40 mol dm^{-3}, [*N*,*N*-dimethylaniline]=[BPO]=2×10^{-3} mol dm^{-3}, in dioxane at 30 °C, for 24 h. b) AIPT: 2,4-Diamino-6-isopropenyl-1,3,5-triazine. c) C=0.30 g/dl, in benzene at 30 °C. d) C=0.30 g/dl, in DMSO at 30 °C. e) ++: Readily soluble, +: soluble, ±: soluble at heating, −: insoluble, IPA: isopropyl alcohol, MCS: Methyl cellosolve, DMSO: dimethyl sulfoxide, δ: solubility parameter.

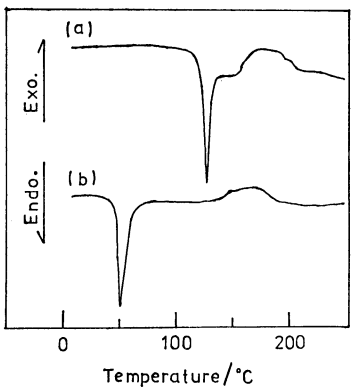


Fig. 3. DTA curves of (a) the tetrakis(hydroxymethyl) derivative (4F-AIPT) and (b) the tetrakis(methoxymethyl) derivative (4M-AIPT), derived from 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) at heating rate of 10 °C/min.

Preparation of Polymers Containing Hydroxymethylguanamines and/or Their Alkyl Ethers. As given in Fig. 3, the tetrakis(hydroxymethyl) derivative (4F-AIPT) melts at 125 °C and exhibited a broad peak near 130—180 °C, which probably corresponds to reaction (condensation and polymerization). Thus, by hot melt at 80—100 °C in aqueous solution, 4F-AIPT was polymerized and crosslinked smoothly to yield an insoluble polymer, having softening temperature (T_s) of over 300 °C; similarly, copolymerizations of 4F-AIPT with methyl methacrylate (MMA), using redox initiator at 30 °C, formed insoluble polymer films, which did not softened up to 300 °C.

On the other hand, the tetramethoxy derivative (4M-AIPT) was relatively stable below 100 °C, but polymerized at 140—160 °C to give a benzene-soluble polymer which softened at 150—155 °C. Moreover, as shown in Table 5, the redox copolymerizations of 4M-AIPT with MMA gave polymers having much lower softening temperature (90—120 °C) than both T_s of the polymer containing AIPT (over 250 °C) and T_s of poly(MMA) (145—155 °C); these polymers showed fair solubilities in not only benzene and dioxane, but also in alcohols and DMSO, and gave a more flexible, tough, and transparent film, compared with the polymer containing AIPT.

Finally, as shown in Table 6, AIPT–MMA copolymer (AIPT content 10.2 mol%) reacted with paraformaldehyde in DMF at 80 °C over basic catalyst to give a crosslinked insoluble polymer with hydroxymethyl groups, having T_s of over 300 °C. Subsequently, hydroxymethylation was carried out at pH 9 using a large excess of paraformaldehyde and butanol at 60 °C, followed by hydroxymethylation at pH 3 with maleic anhydride as acid catalyst. Then, the IR spectra of the product shows the strong absorptions

Table 6. Hydroxymethylation and alkoxymethylation of copolymer of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) with methyl methacrylate (MMA)

Starting[a] polymer (g)	Paraform-aldehyde (g)	DMF/Butyl alcohol (cm^3/cm^3)	Temp/pH/Time °C / h	Yield g	IR[d] $\tilde{\nu}/cm^{-1}$	Softening temperature °C	Solubilites
1.05	0.30	50/20	80/8/3[b]	1.14	1000, s	>300	Insoluble
1.13	1.70	20/20	60/9/9[b] 60/3/9[c]	1.32	1000, m (CH_2OH) 1100, s (CH_2OBu)	108—113	Readily soluble: IPA, Bz, MEK, DOX, MCS, DMSO
1.80	1.90	50/40	60/9/18[b] 60/3/18[c]	2.05	1000, m 1100, m	105—110	Soluble: DMSO, Acetic acid

a) AIPT-MMA copolymer (triazine content 10.2 mol%); softening temperature: 177—187 °C, soluble: DOX, MCS, DMSO, Acetic acid, Insoluble: IPA, Bz, MEK. b) Hydroxymethylation. c) Butoxymethylation using maleic anhydride as acid catalyst. d) s: Strong intensity, m: medium intensity.

near 1110 cm^{-1} (CH_2OBu) and 1000 cm^{-1} (CH_2OH), and the C(%)/N(%) value (10.4) became much larger than that of starting polymer (8.6); the polymer probably contains 10 mol% of triazine rings having two butoxymethyl groups and one hydroxymethyl group as pendants. The properties of this polymer, therefore, are very similar to that of the above-mentioned copolymers containing more than 25 mol% of triazine rings with four methoxyl groups; the polymer obtained, which softened at 108—113 °C, dissolved freely in 2-propanol, benzene, and MEK, whereas the starting polymer, having T_s of 177—187 °C, was insoluble in these solvents. A longer reaction period gave a flexible polymer, film, soluble only in DMSO or organic acid, maybe due to the intramolecular crosslinking reaction.

In conclusion, the reactive polymers containing hydroxymethyl and/or alkoxymethylguanamines were readily prepared both by polymerization of the suitable monomers and by polymer side reaction. Their properties were greatly affected by the species of substituents and the composition of the polymer;[5] these effects can be based upon not only the rigidity of triazine rings and the flexibility of substituents, but also their intra- and/or intermolecular interactions and reactivities.

In addition, these polymers are thermally crosslinkable with or without acid catalyst. Therefore, the above monomers and polymers having highly reactive groups may be utilized as a crosslinking agent for thermosetting resin or an adhesive as well as a modifier for improved properties of various polymers.

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