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Polymer Communication

Novel multi-alicyclic polymers for enhancing plasma etch resistance in 193 nm lithography

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Abstract

Fully multi-alicylic polymers designed for use as 193 nm photoresist materials have been synthesized by vinyl addition polymerization of tetracarbocyclic norbornene derivatives, *t*-butyl tetracyclo[4.4.0.1.^{2,5} 1^{7,10}]dodec-8-ene-3-carboxylate (*t*-BDN) and 3-acetoxytetracyclo-[4.4.0.1.^{2,5} 1^{7,10}]dodec-8-ene (AcODN). The alicyclic polymer backbones of these polymers provide plasma etch resistance and mechanical properties. Two pendant groups were introduced to provide the desired lithographic functions: the *t*-butyl carboxylate group as a carboxylic acid functionality masked by a protecting group undergoes acid-catalyzed thermolysis; and the acetoxy polar group influences adhesion, wettability and dissolution properties of the polymers. The polymer showed an acceptable high transmittance at 193 nm and good adhesion property. The plasma etch rates of the copolymer poly(*t*-BDN-*co*-AcODN) (85:15) using CF_4/CHF_3 mixed gas were 1.01 times with respect to a novolac based resist. The 0.2 μm line-and-space patterns were obtained with a dose of 45 mJ cm^{-2} using a KrF excimer laser stepper. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: 193 nm (ArF) resist materials; Muliti-alicyclic polymers; Norbornene polymers

1. Introduction

The successful design of single-layer positive photoresist materials for 193 nm (ArF laser) microlithography is a current challenge that must be solved to meet the requisite properties such as high sensitivity and transparency at the 193 nm exposure wavelength, and high resistance to reactive ion etching (RIE) [1,2]. The major research results over the last few years have led to the development of alicyclic or cycloaliphatic polymers which have alicyclic moieties in the side-chains or backbones for enhancing the plasma etch resistance [3,4].

Current research efforts have focused on alicyclic polymers based on norbornene polymers because such alicyclic main-chains provide effective plasma etch resistance as well as low absorbance at 193 nm [5,6]. To improve the adhesion and solubility properties, in addition to chemical amplication capability, polar substituents have been incorporated into the alicyclic polymers by electron donor–acceptor type radical polymerizations of the corresponding norbornene monomers and maleic anhydride [7,8]. Multiple alicyclic polymers based on the tetracarbocyclic olefin monomers having a *t*-butyl ester substituent to facilitate chemical amplification were also studied for enhancing the plasma etch resistance even further [9–11]. However, it is known that fully multi-alicyclic polymers are difficult to obtain by radical polymerization except by the ring-opening metathesis polymerization of norbornene type monomers [12,13].

We have synthesized the fully multi-alicyclic structural polymers by Pd(II)-catalyzed addition polymerization. They possess the acid-labile *t*-butyl carboxylic ester (*t*-BOC) groups along with useful acetoxy groups for improving adhesion and solubility as well as the multi-alicyclic structures for enhancing the plasma etch resistance. In this communication, synthesis, physical properties and lithographic performance of the novel multi-alicyclic polymers are described.

2. Experimental

2.1. Materials

Dicyclopentadien (DCP), *t*-butyl acrylate, and vinyl

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acetate were purchased from Aldrich Chemical Co. and purified by distillation under reduced pressure. Cyclopentadiene was obtained by cracking DCP and used immediately in a Diels–Alder reaction. Bis-tetrafluoroborate tetrakis(cyanomethan)palladium $[Pd(CH_3CN)_4](BF_4)_2$ was prepared according to the procedure published by Schramm and Wayland [14]. Triphenylsulfonium triflate (TPSOTf) used as a photoacid generator (PAG) was kindly donated by Korea Kumho Chemical Lab.

2.2. Measurements

Chemical structures were determined by IR spectroscopy (Mattson Geness series FT-IR) and ^1H and ^{13}C NMR spectroscopy (200 MHz Varian Gemini) in $CDCl_3$. Molecular weights of the polymers were measured by gel permeation chromatography (GPC) with a Waters Model 150-C ALG system calibrated with polystyrene standards at room temperature using THF as a solvent. The absorbance of the films was recorded on a UV/VIS/NIR Lambda 19 spectrophotometer (Perkin–Elmer) scanning from 170 nm wavelength. Elemental analysis data were obtained on a GmbH Vario EL. Differential scanning calorimetry (DSC) and themogravimetric analysis (TGA) data were obtained on a Perkin–Elmer TA7 series system at a heating rate of 20°C min^{-1}. Lithographic exposure was carried out on a Micro Scan II DUV (KrF) exposure system with 0.6 NA (numerical aperture). Conventional UV exposure at 250 nm was carried out with a UI 502Q exposure system of Ushio Inc. Plasma etch resistance were evaluated on an Advanced Materials model P5000 RIE system.

2.3. Synthesis of norbornene type monomers

Norbornene-derived monomers were prepared by a Diels–Alder reaction of cyclopentadiene and the corresponding dienophiles, *t*-butyl acrylate and vinyl acetate. *t*-Butyl tetracyclo[4.4.0.1.^{2,5} 1^{7,10}]dodec-8-ene-3-carboxylate (*t*-BDN) was prepared as follows. A mixture of 59.40 g (0.45 mol) of DCP, 57.67 g (0.45 mol) of *t*-butyl acrylate and 0.10 g of hydroquinone in 200 ml of diethyl ether was heated at 180°C for 24 h in a pressure reactor. After the reaction, diethyl ether was stripped off and *t*-BDN was separated from the crude product by distillation under reduced pressure followed by column chromatography on silica with hexane-ethyl acetate (20:1 by volume) as an eluent.

t-BDN was isolated as colorless oil in 33% yield (38.63 g): bp135–138°C/0.4 mmHg. ^1H NMR ($CDCl_3$): δ (ppm) 0.6–0.8 (m, 1H), 1.1–1.3 (m, 2H), 1.4 (s, 9H,(*t*-Bu), 1.7 (m, 1H), 2.0 (m, 4H), 2.1–2.4 (m, 2H), 2.5 (m, 1H), 2.8 (s, 2H), 5.9 (s, 2H, olefinic protons). ^{13}C NMR ($CDCl_3$): δ (ppm) 28.3 ($C(CH_3)_3$), 31.8, 34.0, 35.6, 36.3, 37.7, 38.9, 42.3, 42.5, 42.7, 43.0, 43.3, 46.5, 46.7, 46.9, 48.3, 48.6, 48.7, 49.7, 53.0, 79.6, 135.4, 135.5, 135.7, 135.8, 135.9, 174.1 and 175.2 (carbonyl). FT-IR: ν (cm^{-1}) 2961 (–CH), 1727 (C=O), 1367 (*t*-butyl), 1153 (C–O–C). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.46; H, 9.23. Found: C, 78.51; H, 9.28.

3-Acetoxytetracyclo[4.4.0.1.^{2,5} 1^{7,10}]dodec-8-ene (AcODN):-colorless oil in 36% yield (35.33 g): bp130–134°C/4 mmHg. ^1H NMR ($CDCl_3$): δ (ppm) 0.5 (m, 1H), 0.8 (m, 1H), 1.3 (m, 2H), 1.6 (bm, 1H), 1.8 (bm, 1H), 2.0 (s, 3H, acetoxy), 2.2 (m, 2H), 2.3 (m, 1H), 2.45(m, 1H,), 2.80 (s, 2H), 4.4 and 4.7 (m, 1H), 6.0 (m, 2H, olefinic protons). ^{13}C NMR ($CDCl_3$): δ (ppm) 21.3, 30.8, 32.6, 37.0, 38.6, 39.0, 39.6, 41.9, 42.2, 43.3, 46.3, 47.0, 48.1, 48.8, 53.3, 75.9, 78.7, 135.5, 135.8, 136.3, 171.0 and 171.3 (carbonyl). FT-IR: ν (cm^{-1}) 2976 (–CH), 1736 (C=O), 1115. Anal. Calcd for $C_{14}H_{18}O_2$:C, 77.06; H, 8.26. Found: C, 77.24; H, 8.61.

2.4. Vinyl addition polymerization

Polymerization involving air- and/or moisture-sensitive compounds was carried out under standard high-vacuum or in a dry box. Into a 250 ml round bottom flask equipped with gas inlet–outlet tubes was charged a monomer solution which contained 19.28 g (74.2 mmol) of *t*-BDN, and 1.79 g (8.2 mmol) of AcODN in 30 ml of nitromethane. A solution of 368 mg (0.8 mmol, 1 mol%) of $[Pd(CH_3CN)_4](BF_4)_2$ in 30 ml of nitromethane was then introduced by means of a syringe. The mixture was reacted for 72 h at room temperature under a steady stream of dry nitrogen. The polymer was precipitated by pouring into methanol and purified further by reprecipitation from THF into methanol, and dried in vacuo at 50°C. Palladium-containing end groups were removed by reduction; hydrogen gas was bubbled through a polymer solution in THF for 5 h. The solution was kept standing for 24 h as the black Pd(0) particles coagulated, and then the black residue was removed by filtration through a celite pad. The volume of the solution was reduced by evaporation under reduced pressure to approximately one-fourth of its volume and then the polymer was precipitated into methanol, filtered, and dried in vacuo at 50°C. Poly(*t*-BDN-*co*-AcODN) was obtained in a yield of 8.85 g (42%) as a white powder.

2.5. Lithographic evaluation

A photoresist solution was prepared by dissolving 4.00 g of poly(*t*-BDN-*co*-AcODN) and 0.08 g (2%) of TPSOTf in 24 g of propylene glycol methyl ether acetate. The solution was filtered twice through a 0.2 μm Teflon membrane filter prior to the application to silicon wafers. A resist film was prepared by spin-coating the photoresist solution on a hexamethyldisilazane-treated silicon wafer followed by soft-baking (SB) at 90°C for 90 s. The resist film was exposed at 248 nm through a photomask with a KrF excimer laser stepper with 0.6 NA and post-exposure-baked (PEB) at 130°C for 2 min. The resist image patterns were developed by dipping in a commercial 2.38 wt% tetramethylammonium hydroxide (TMAH) solution for 30 s. The film thickness was measured with an Alpha-Step 500 profiler (Tencor

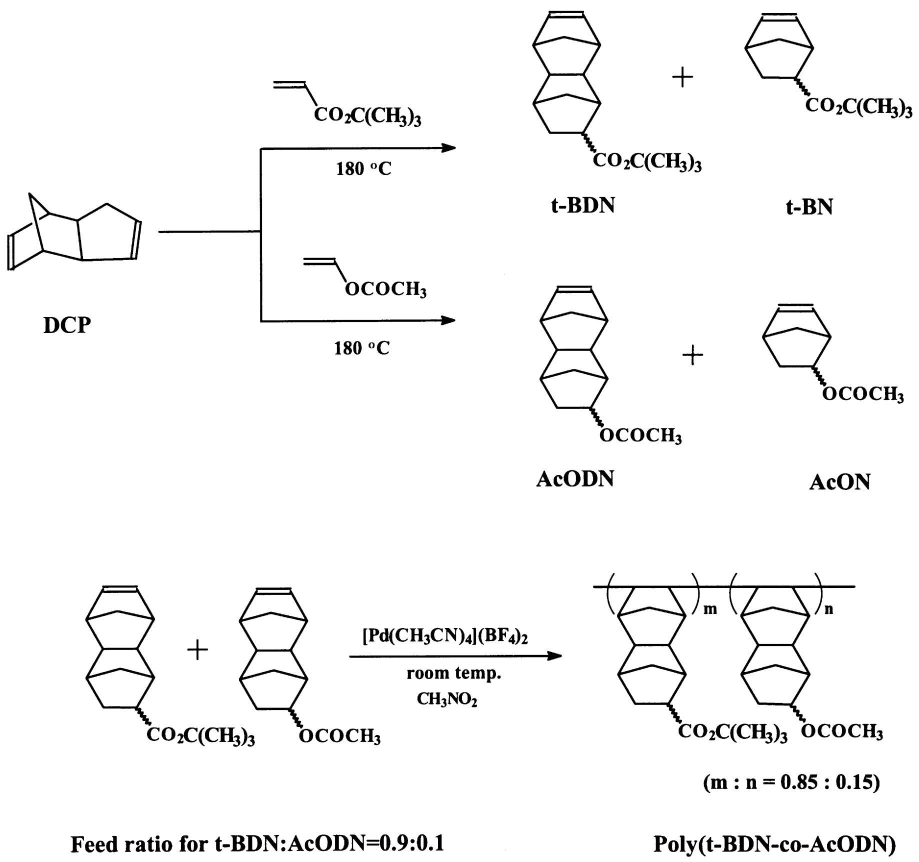

Fig. 1. Synthesis and polymerization of *t*-BDN and AcODN.

Instrument). The line-width of the resist patterns was measured on a Hithachi S-800 CD-SEM and the cross-section profile micrographs were obtained with a Hithachi S-8820 SEM.

2.6. Evaluation of plasma etch resistance

The plasma etch rates were calculated by measuring the thickness variation of the polymer films on silicon substrates before and after reactive ion etching against CF_4/CHF_3 mixed gas using an Advanced Materials model P5000 RIE system. The average etch rates were calculated based on four times of sample tests with about 1.0 μm thick resist films.

3. Results and discussion

Two norbornene-derived, multi-alicyclic monomers, *t*-butyl tetracyclo[4.4.0.1.^{2,5} 1^{7,10}] dodec-8-ene-3-carboxylate (*trivial name*, *t*-BOC-dinorbornene) (*t*-BDN) and 3-acetoxy- tetracyclo[4.4.0.1.^{2,5} 1^{7,10}]dodec-8-ene (*trivial name*, acetoxydinorbornene) (AcODN), were prepared by a Diels–Alder reaction of the commercially available dicyclopentadiene and corresponding dieneophiles as described in Fig. 1. *t*-Butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (*t*-BOC-norbornene, *t*-BN) and 2-acetoxy-bicyclo[2.2.1]hept-5-ene (acetoxy norbornene, AcON) were also obtained as byproducts in the reactions [7,11]. In this study *t*-BDN and AcODN were adopted in polymerization only for improving the plasma etch resistance. Their chemical structures were identified by NMR and IR spectra. ^{1}H NMR spectra of two the norbornene monomers, *t*-BDN and AcODN, are shown in Fig. 2 along with their copolymer poly(*t*-BDN-*co*-AcODN) (85:15). *t*-BDN has a singlet peak for two olefinic protons at 5.9 ppm and two strong singlet peaks for nine *t*-Bu protons at 1.4 ppm while AcODN has a multiplet for two olefinic protons at 6.0 ppm and two strong singlet peaks for three acetoxy protons at 2.0 ppm. The splitting of the two strong singlet peaks for *t*-Bu ester and acetoxy groups in the NMR spectra is ascribable to the *exo* and *endo*-isomeric norbornene monomers. *t*-BDN was employed to provide an acid-cleavable *t*-Bu carboxylate side group which is responsible for creating radiation-induced solubility changes based on the chemical amplification. The multi-alicyclic structure and the acetoxy group of AcODN in the polymer chains provide the plasma etch resistance and adhesion capability to the silicon substrate, respectively.

Vinyl addition copolymerizations of two norbornene-derived monomers were carried out according to the procedures adapted from Risse and coworkers [14–17] by using a Pd(II) catalyst ($[Pd(CH_3CN)_4](BF_4)_2$) in nitromethane at

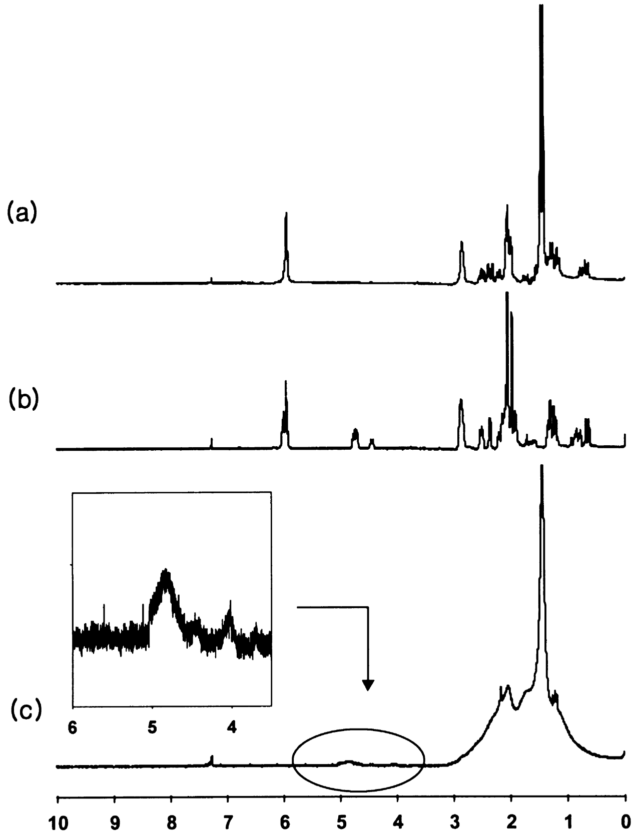

Fig. 2. ^{1}H spectra of monomers and polymer: (a) *t*-BDN; (b) AcODN; and (c) poly(*t*-BDN-*co*-AcODN) (85:15).

room temperature for a prolonged period of time. In the copolymerization the molar feed ratio for *t*-BDN to AcODN was 90:10 and the polymerization yield was acceptable by 42% in this type of polymerization. The composition of the obtained copolymer, poly(*t*-BDN-*co*-AcODN), was found to be 85:15 for *t*-BDN to AcODN repeating units based on ^{1}H NMR spectra and TGA themogram analysis.

As summarized in Table 1, the weight average molecular weights ($\bar{M}_w$) and molecular weight distribution (MWD) of poly(*t*-BDN-*co*-AcODN) were 8800–9200 and 1.05–1.14, respectively, depending on the reaction conditions.

The copolymers revealed the much improved adhesion properties to silicon substrates in comparison with the previously known alicyclic norbornene polymers even in its high glass transition temperature over 200°C. The glass transition temperature of poly(*t*-BDN-*co*-AcODN) (85:15) was not detected until the deprotection temperature T_{dp} which was determined at 260°C owing to the liberation of isobutene from the *t*-butyl carboxylate (*t*-BOC) groups in TGA thermograms as shown in Fig. 3. After the first thermal deprotection of *t*-BOC groups, the deprotected copolymer having pendant carboxy groups exhibited onset decomposition around 400°C. Upon UV exposure, the polymer rendered T_{dp} of *t*-BOC groups at about 90°C in the presence of 2 wt% TPSOTf as PAG. The deprotection temperature that decreased significantly represents the catalytic deprotection of *t*-BOC groups in the polymer by photo-generated acid (TfOH). The observed mass loss of poly(*t*-BDN-*co*-AcODN) (85:15) was 18% in good agreement with the theoretically calculated value.

The absorbance of poly(*t*-BDN-*co*-AcODN) (85:15) and the copolymer containing 2 wt% TPSOTf was 0.56 and

Table 1
Vinyl addition polymerization of norbornene-derived monomers with Pd(II) catalyst (polymerization with 1 mol% [Pd(CH_3CN)$_4$](BF_4)$_2$ for 72 h)

No.	Monomer[a]	$\bar{M}_w$[b]	MWD[c]	Yield (%)
1	*t*-BDN	5800	1.12	36
2	AcODN	9800	1.04	44
3	*t*-BDN/AcODN (feed ratio, 7:3)	9200	1.05	42
4	*t*-BDN/AcODN (feed ratio, 9:1)	8800	1.14	42

[a] *t*-BDN = *t*-BOC-dinorbornene, AcODN = acetoxydinorbornene.

[b] Molecular weights, $\bar{M}_n$ and $\bar{M}_w$ were obtained by GPC in THF.

[c] MWD = $\bar{M}_w/\bar{M}_n$.

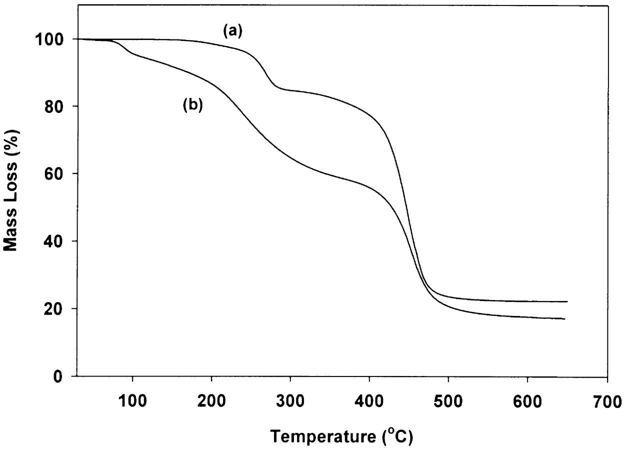

Fig. 3. TGA thermograms of poly(*t*-BDN-*co*-AcODN) (85:15) containing 2 wt% TPSOTf: (a) before exposure; and (b) after 250 nm DUV exposure (45 mJ cm^{-2}).

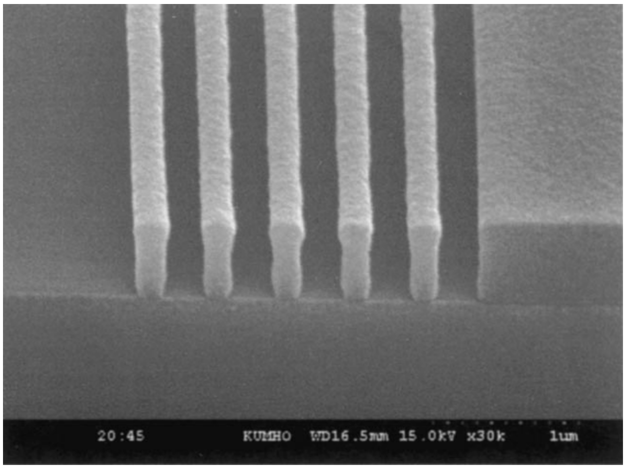

Fig. 4. A SEM micrograph of 0.2 μm line-and-space patterns: film thickness, 0.48 μm; SB, 90° for 90 s; PEB, 130°C for 120 s; dose, 45 mJ cm^{-2}.

Table 2
Plasma etch rates of polymers (gas flow: $CF_4/CHF_3 = 15:25$ standard cubic centimeters per minute, 60 mTorr, 650 W, 100 s)

Polymer sample	Etch rate
Poly(*t*-BDN-*co*-AcODN) (85:15)	1.01
PMMA[a]	1.87
Novolac photoresist[b]	1.00

[a] Molecular weight $= 1 \times 10^5$.
[b] A commercial photoreist, AZ HTK-501 (Clariant).

0.75 μm at 193 nm, respectively. The surprisingly low absorbance at the wavelength of 193 nm corresponds to high transparency above 50% transmittance in a 0.5 μm thick film for the lithographic work. Lithographic performance of the polymer was evaluated using a KrF exposure system with 0.6 NA. The resist solution formulated with poly(*t*-BDN-*co*-AcODN) (85:15) and 2 wt% TPSOTf was spin-coated to give a 0.48 μm thick film. The resist film was exposed with a dose of 45 mJ cm^{-2} followed by the post-exposure bake (PEB) treatment at 130°C for 2 min. The SEM micrograph rendered clear the 0.2 μm line-and-space patterns as shown in Fig. 4 after being developed with a conventional 2.38% TMAH developer. As listed in Table 2, the plasma etch rate of poly(*t*-BDN-*co*-AcODN) (85:15) was comparable to the commercial novolac resist. The etch rates were the average values obtained more than four times of sample tests. The etch conditions were 60 mTorr mixed gases of CF_4/CHF_3 (15:25 sccm) with a RF power of 650 W for 100 s.

4. Conclusions

Multi-alicyclic polymers with a tetracarbocyclic structure having both *t*-BOC and acetoxy groups were prepared by the vinyl addition polymerization of norbornene-derived monomers, *t*-BDN and AcODN, with a Pd catalyst. The polymer formulated with 2 wt% PAG gave a clear 0.2 μm line-and-space patterns with a KrF laser stepper. The multi-alicyclic polymer, poly(*t*-BDN-*co*-AcODN) (85:15), was found to have acceptable transparency at 193 nm and excellent plasma etch resistance comparable to a novolac based resist. The multi-alicyclic polymers are capable of high resolution photoresists with excellent plasma etch resistance in the 193 nm wavelength.

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