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Preparation and properties of nylon 66 copolymers with 2,2-dialkyl-1,3-propanediols

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Nylon 66 copolymers were prepared by melt polycondensation of nylon 66 salt with 10–30 mol% (in feed) of 1,3-propanediol and 2,2-dialkyl-1,3-propanediols, where the alkyl groups are dimethyl, diethyl and butyl-ethyl. Reduced specific viscosity was decreased by the copolymerization. Comonomer contents in copolymers were considerably smaller than those in the feed. Crystallinities and densities of melt-pressed films as well as heat-treated films decreased with increasing content of comonomer and length of alkyl side chain in the comonomer. Glass transition temperature and melting temperature were decreased by the copolymerization, and an increase in the length of the alkyl side chain reduced the melting-temperature depression of heat-treated films. Dye uptake and thermal shrinkage were increased and alkali resistance, water absorption and Young's modulus were decreased by the incorporation of comonomer having an alkyl side chain. These results are discussed and compared with those for the previously reported poly(ethylene terephthalate) copolymers.

(Keywords: nylon 66 copolymers; dialkyl propanediols; characterization)

INTRODUCTION

In a previous paper[1] we described the preparation of poly(ethylene terephthalate) (PET) copolymers copolymerized with 1,3-propanediol and 2,2-dialkyl-1,3-propanediols, where the alkyl groups are dimethyl, diethyl and butyl-ethyl, and studied the effect of varying length and amount of alkyl side chain on the structure and properties of copolymers. It was found that crystallinity, density, glass transition temperature and melting temperature were decreased and alkali resistance, dye uptake and thermal shrinkage were remarkably increased by the incorporation of comonomer having an alkyl side chain.

In this paper, we report on the preparation and characterization of nylon 66 copolymers copolymerized with the same 1,3-propanediol and 2,2-dialkyl-1,3-propanediols as used in ref. 1. The thermal, physicochemical and mechanical properties of these nylon 66 copolymers are studied and are compared with those of the PET copolymers[1]. This type of nylon 66 copolymerized with glycol by melt polycondensation has the chemical structure of random aliphatic copolyesteramide. There have been few studies of similar nylon 66 copolymers with hexamethylene adipamide/hexamethylene adipate copolymers in relation to their isomorphic replacement[2] and biodegradability[3].

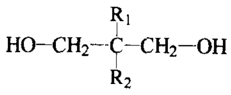
EXPERIMENTAL

Monomers

Scheme 1 shows structural formulae and codes of the comonomers. 2,2-Diethyl-1,3-propanediol (C_2C_2) and 2-butyl-2-ethyl-1,3-propanediol (C_2C_4), donated by Chisso Corp., were used without further purification. 1,3-Propanediol (HH), 2,2-dimethyl-1,3-propanediol (CC) and adipic acid were used as received. Hexamethylenediamine was distilled under reduced pressure.

Preparation of copolymers

Copolymers were prepared by a melt polycondensation method. A mixture of comonomer and equimolar adipic acid with a small amount of titanium tetraisopropoxide as a catalyst was heated at 200–205°C for 1 h in a stream of nitrogen gas. A given amount of nylon 66 salt was added, then the temperature was increased to 270–275°C for 1 h followed by heating at the same temperature for 2–3 h in a vacuum of 0.3–1.0 torr.


$$HO{-}CH_2{-}\overset{R_1}{\underset{R_2}{C}}{-}CH_2{-}OH$$

Code	R_1	R_2
HH	H	H
CC	CH_3	CH_3
C_2C_2	C_2H_5	C_2H_5
C_2C_4	C_2H_5	C_4H_9

Scheme 1 Structural formulae and comonomer codes

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Table 1 Reduced specific viscosities of copolymers. Numbers in the polymer code represent the comonomer content (mol%) in the feed

Code	η_{sp}/C (dl g^{-1})	Code	η_{sp}/C (dl g^{-1})
Ny66	2.10		
HH-10	1.24	C_2C_2-10	1.32
HH-20	1.17	C_2C_2-20	1.19
HH-30	1.39	C_2C_2-30	1.32
CC-10	1.25	C_2C_4-10	1.46
CC-20	1.14	C_2C_4-20	1.43
CC-30	1.55	C_2C_4-30	0.92

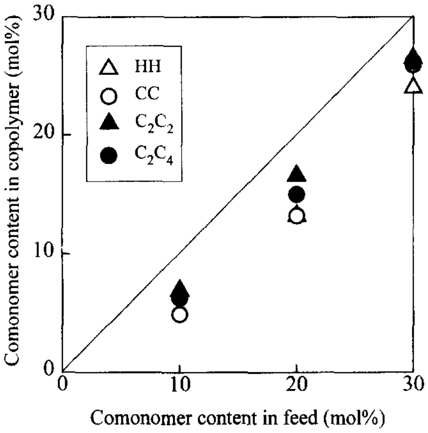


Figure 1 Change of copolymer composition by polymerization

Film preparation

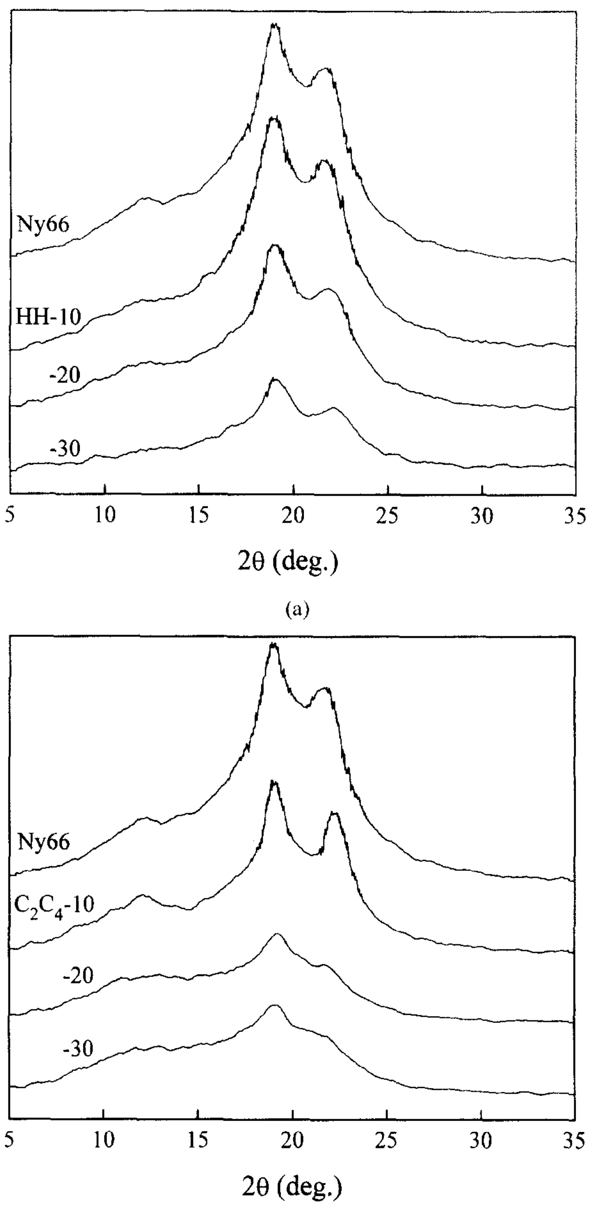
The film was melt pressed between aluminium plates with an aluminium spacing plate of 100 μm thickness, and then quenched into ice water. After dissolving off the aluminium plates in 10% NaOH aqueous solution, the film was washed with water and dried overnight at room temperature *in vacuo* and then stored in a desiccator.

Characterization

Reduced specific viscosity (η_{sp}/C) was determined with a 1% polymer concentration in *m*-cresol at 30°C. ^{1}H nuclear magnetic resonance (n.m.r.) was performed in CF_3COOD at 50°C. Wide-angle X-ray scattering (WAXS) was performed with nickel-filtered CuKα radiation. The density was measured in a heptane-tetrachloromethane density gradient column at 30°C. Differential thermal analysis (d.t.a.), differential scanning calorimetry (d.s.c.) and thermogravimetry (t.g.) were performed at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Dyeing was carried out in a dye bath with 1 g of 1,4-diaminoanthraquinone (disperse dye) in 300 ml water at 80°C for 24 h. Alkali hydrolysis was carried out in 10% NaOH aqueous solution at 70°C for 4 h. Water absorption was measured by immersing the film in water at 30°C for 24 h, then removing surplus surface water with a filter paper and weighing immediately. Tensile testing was performed with a strain rate of 125% min^{-1}. Thermal shrinkage was carried out in silicon oil at 200°C for 2 min.

RESULTS AND DISCUSSION

Table 1 shows the reduced specific viscosity (η_{sp}/C) of the copolymers. It was observed for the PET copolymers that the copolymerization does not provide significant depression of η_{sp}/C, suggesting the small effect of the alkyl side group on the reactivity of polymerization[1]. This is also seen among these nylon copolymers, but the η_{sp}/C values of the nylon copolymers are considerably lower than that of nylon 66 homopolymer, probably due to the lower reactivity of diols than of diamine with adipic acid.



(a)

(b)

Figure 2 WAXS curves of (a) HH and (b) C_2C_4 melt-pressed films

The comonomer contents in copolymers measured by ^{1}H n.m.r. are plotted against the comonomer contents in the feeds in *Figure 1*. The comonomer contents in the copolymers are considerably smaller than those in the feeds. Similar behaviour was also observed for the PET copolymers; this could be ascribed to the cyclization of glycol comonomers due to the steric strain of the alkyl substituents forcing them apart, in addition to the increased volatility of comonomers with smaller molecular weight[1].

Figure 2 shows WAXS curves of the melt-pressed HH and C_2C_4 films. The intensities of the WAXS curves decreased with increasing the comonomer content and

Table 2 Glass transition temperatures of copolymers measured by d.s.c. for melt-quenched samples

Comonomer content (mol%)	T_g (°C)			
	HH	CC	C_2C_2	C_2C_4
0	41	41	41	41
10	29	31	37	33
20	22	24	27	29
30	–	17	20	21

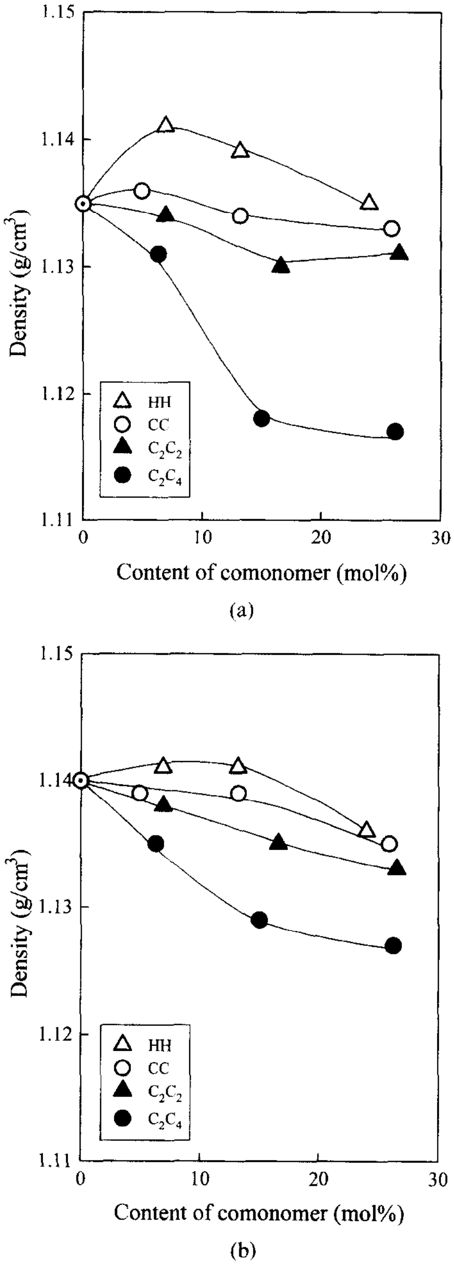


Figure 3 Densities of (a) melt-pressed and (b) heat-treated films at 170°C for 2 h

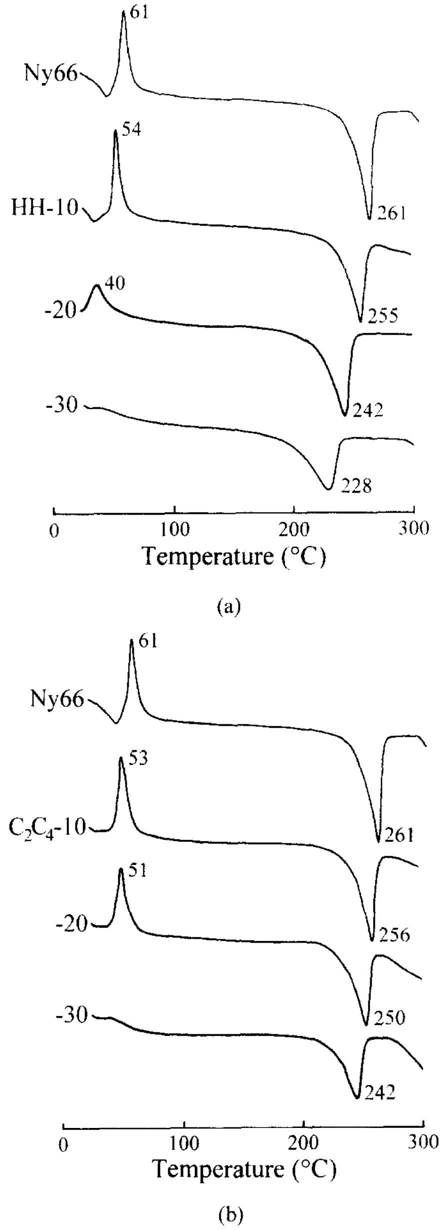


Figure 4 D.t.a. curves of (a) HH and (b) C_2C_4 melt-quenched samples

the length of alkyl side chain in the comonomer, suggesting that the increase of steric hindrance due to the longer alkyl side chains suppresses the crystallization of nylon chains. It is noted that these melt-pressed nylon copolymer films show crystalline patterns, while the melt-pressed PET copolymer films showed broad amorphous patterns[1]. This means that the nylon copolymers could crystallize during the film preparation, probably due to their lower glass transition temperatures (T_g) near or below room temperature, which were measured by d.s.c. for melt-quenched samples and are shown in *Table 2*.

The comonomer contents in copolymers are plotted against densities of melt-pressed and heat-treated films in *Figure 3*. The density of melt-pressed film (*Figure 3a*) decreases with increasing the length of alkyl side chain in comonomer and the content of comonomer, which corresponds well to the results of WAXS described above. The higher densities of HH copolymers than of nylon 66 homopolymer may be ascribed to the higher crystallinities of HH copolymers due to the lower T_g, as shown in *Table 2*. The heat treatment increases the density a little (*Figure 3b*), and thus the degrees of crystallinity calculated from the density of nylon 66 homopolymer are 33 and 36% for melt-pressed and heat-treated films, respectively.

Figure 4 shows d.t.a. curves of melt-quenched samples for HH and C_2C_4 copolymers. The d.t.a. curves of CC and C_2C_2 copolymers were similar to those of HH and

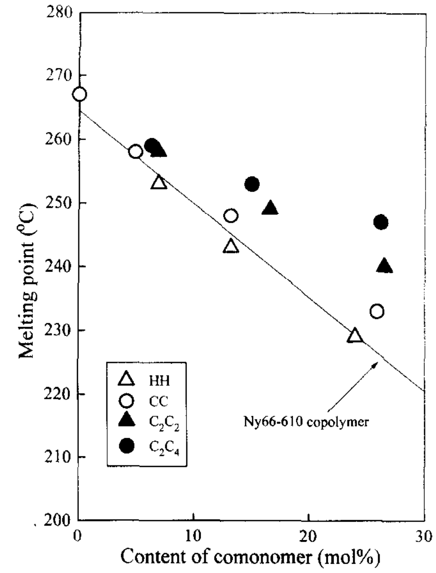


Figure 5 Melting-temperature depression of copolymers

C_2C_4 copolymers, respectively, with small variations. Cold crystallization temperature (T_{cc}) and melting temperature (T_m) decrease with increasing comonomer content. This result suggests that the mobility of polymer chains is increased while the crystal growth of nylon 66 chains is decreased by the incorporation of glycol comonomers. For the PET copolymers, T_{cc} increased with increasing content of glycol comonomers[1] due to the decrease of the sequence length of PET chains, which disturbs the crystallization. For the nylon copolymers, T_{cc} decreases with increasing content of glycol comonomers, probably due to the decrease in the number of intermolecular hydrogen bonds which enhances the mobility of polymer chains in spite of the decrease in sequence length of nylon chains. The T_m values were increased a little by heat-treatment for 2 h at 170°C. These T_m values of heat-treated samples are plotted against the comonomer contents in copolymers in *Figure 5*. The T_m depression of HH copolymer is well fitted to the solid line which was obtained for the nylon 66-610 copolymer[4]. It is noted that T_m increases with increasing length of alkyl side chain in the comonomer. For the PET copolymers, T_m was decreased by the incorporation of glycol comonomers having alkyl side chains, and the length of alkyl side chain hardly affected the T_m depression of the copolymers[1]. The increase of T_m for the nylon copolymers having side chains suggests the formation of block-type copolymer due to the lower compatibility of the glycol or polyester component with the nylon component, which was observed as phase separation at the initial stage of polycondensation. Similar block-type copolymers were also obtained for the PET copolymers copolymerized with poly(ethylene glycol) (PEG) or poly(butylene glycol) (PBG) due to the lower compatibility of PET component with PEG and PBG[5].

Table 3 Weight loss temperatures of copolymers measured by thermogravimetry

Code	5% weight loss temperature (°C)	50% weight loss temperature (°C)
Ny66	388	430
HH-10	383	413
HH-20	370	421
HH-30	351	409
CC-10	390	446
CC-20	373	435
CC-30	374	440
C_2C_2-10	386	445
C_2C_2-20	378	438
C_2C_2-30	365	430
C_2C_4-10	380	443
C_2C_4-20	367	427
C_2C_4-30	368	427

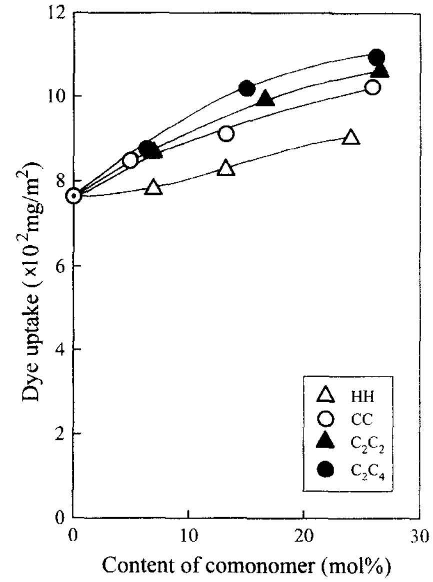


Figure 6 Dye uptake of melt-pressed films for disperse dye at 80°C for 24 h

Table 3 shows 5% and 50% weight loss temperatures of copolymers measured by t.g. It was observed for the PET copolymers that thermal stability was slightly increased by the copolymerization[1]. A similar result was obtained for some nylon copolymers, but because nylon 66 homopolymer is more thermally stable than PET homopolymer, the other copolymers showed lower thermal stability than nylon 66 homopolymer.

Figure 6 shows the dye uptakes of melt-pressed films against the comonomer contents in copolymers. The dye uptake increases with increasing comonomer content and the length of alkyl side chain in the comonomer. The increase of the dye uptake for disperse dye may be ascribed to the decrease in crystallinity and the increase in hydrophobicity due to the alkyl side chain. The dye uptakes of the PET copolymers were up to five times larger than that of PET homopolymer[1], while the increase in dye uptake for the nylon copolymers is much smaller, probably due to the much higher crystallinity of nylon copolymers which decreases the dyeable amorphous region.

Table 4 shows weight losses of melt-pressed films in alkali solution against the comonomer contents in copolymers. Nylon 66 homopolymer does not show weight loss, while the weight losses of the C_2C_4 copolymers increase with increasing comonomer content due to the increase in ester linkage concentration caused by copolymerization. It was observed that the C_2C_4-30 copolymer film already fragmented at the small weight

Table 4 Alkali resistances of melt-pressed films in 10% NaOH aqueous solution at 70°C for 4 h

	Weight loss	
Code	(%)	($g m^{-2}$)
Ny66	0	0
C_2C_4-10	5	3.1
C_2C_4-10	13	8.8
C_2C_4-30	24	14.5 (fragmented)

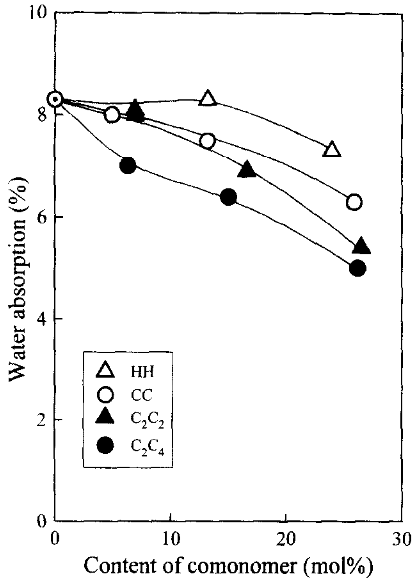


Figure 7 Water absoprtions of melt-pressed films

Table 5 Young's moduli of melt-pressed films in dry and wet conditions

	Young's modulus ($kg mm^{-2}$)		
Code	Dry	Wet	Dry – Wet
Ny66	162	44	118
C_2C_4-10	141	32	109
C_2C_4-20	114	19	95
C_2C_4-30	91	22	69

loss of $14.5 g m^{-2}$, whereas the PET homopolymer film showing weight loss of $15 g m^{-2}$ did not fragment and the weight loss was decreased by the copolymerization of comonomer having the alkyl side chain[1]. The fragmentation of film at the early stage of alkali hydrolysis of nylon copolymers could be attributed to the higher hydrophilicity of the nylon component, which enables the degradation of more of the inner part of a film leading to fragmentation. Similar fragmentation at the early stage of alkali hydrolysis was observed for the nylon 66 copolymers copolymerized with hexamethylene glycol[3].

Figure 7 shows water absorptions of melt-pressed films against the comonomer contents in copolymers. The water absorption decreases with increasing comonomer content and the length of alkyl side chain in comonomer. The decrease of the water absorption, in spite of the increase of water-absorbable amorphous region shown by the decrease of crystallinity for these copolymers, could be ascribed to the decrease of the hydrophilic amide groups as well as to the increase of the hydrophobic alkyl side groups in comonomers.

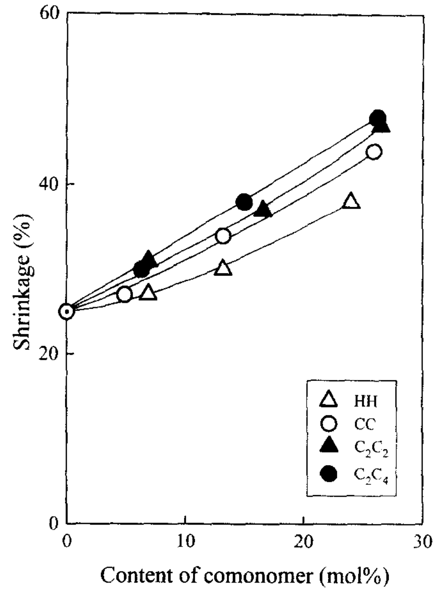


Figure 8 Shrinkage of drawn (3×) films in silicone oil at 200°C for 2 min

Table 5 shows the Young's moduli of nylon 66 homopolymer and metl-pressed C_2C_4 copolymer films. The Young's modulus decreases with increasing comonomer content, which was also observed for the PET copolymers[1]. The decrease of the Young's modulus could be attributed to the decrease of the crystallinity and the intermolecular hydrogen bonds. The Young's moduli are decreased remarkably by the absorption of water, and the degree of their decrease given by dry – wet values decreases with increasing the comonomer content, probably due to the decrease of the water absorption shown in *Figure 7*.

Figure 8 shows thermal shrinkage of drawn (3×) films against the comonomer contents in copolymers. The shrinkage increases with increasing comonomer content and the length of alkyl side chain in comonomer, but the degree of increase is much smaller than at PET copolymer films, which showed the shrinkage of 100% for copolymers with higher comonomer content[1]. The much smaller shrinkages of nylon copolymer films could be ascribed to their higher crystallinities, which decrease the shrinkable amorphous chains.

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