Preparation and Properties of Ethylene/POSS Copolymer with *rac*-Et(Ind)$_2$ZrCl$_2$ Catalyst

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ABSTRACT: The various monovinyl-functional polyhedral oligomeric silsesquioxane (POSS) monomers had been copolymerized with ethylene (E) using *rac*-Et(Ind)$_2$ZrCl$_2$ and a modified methylaluminoxane (MMAO) cocatalyst. The unreacted POSS monomer could be removed completely by washing the copolymerization product with *n*-hexane. And the copolymers were characterized with ^{1}H NMR, TEM, DSC, TGA, and GPC to know the composition, thermal properties, molecular weight and its distribution, respectively. According to ^{1}H NMR data, the monomer reactivity ratios of various POSS monomers were calculated by the Fineman-Ross and Kelen-Tudos methods. Thermogravimetric analysis of E/POSS copolymers exhibited an improved thermal stability with a higher degradation temperature and char yields, demonstrating that the inclusion of inorganic POSS nanoparticles made the organic polymer matrix more thermally robust. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2697–2702, 2009

Key words: copolymerization; nanocomposite; ethylene; POSS; hybrid

INTRODUCTION

Synthetic polymers have played an increasingly important role in daily life because of their favorable processability and lower cost than those of other materials such as metals or ceramics. However, pure polymeric materials frequently face application limitations because of their low modulus and low thermal stability.[1] Organic–inorganic nanocomposite materials have been regarded as a new generation of high performance materials since they combine the advantages of the inorganic materials (rigidity, high stability) and the organic polymers (flexibility, dielectric, ductility, and processability).[2] Moreover, in the past few years, hybrid organic–inorganic nanocomposites based on the incorporation of POSS units into polymeric matrices have received a considerable amount of attention.[3] The cage-shaped POSS molecules have an empirical formula (RSiO$_{1.5}$)$_n$ with R groups that can be hydrogen or an organic group. A typical POSS nanoparticle contains an inorganic Si$_8$O$_{12}$ nanostructured skeleton surrounded by seven unreactive organic groups (e.g., isobutyl, cyclopentyl) on the corners to promote solubility in conventional solvents and one reactive group for polymerization.[4,5] POSS can be dispersed on a molecular level (1–3 nm), or as crystalline or amorphous aggregates, which can be in the order of microns in size.[6]

Because POSS has one reactive group for polymerization, it has afforded the opportunity to incorporate inorganic POSS cages into organic matrices through copolymerization. Monofunctional POSS has been incorporated into a variety of conventional polymers by a variety of polymerization techniques such as radical,[7] condensation,[8] and ring-opening polymerization.[9] The POSS derivatives have been shown to increase the glass transition temperature,[10,11] modulus,[12] decomposition temperature,[11] and oxygen permeability[13–15] while reducing flammability[14] when incorporated into polymer matrices.

Preliminary results[16] showed that POSS monomers of seven cyclopentyl or cyclohexyl groups and one alkenyl group did not undergo Ziegler-Natta catalyzed copolymerization with olefin. In an earlier report,[17] the E/POSS copolymers have been synthesized using a two-step procedure: ring-opening metathesis polymerization followed by hydrogenation.

In this article, a direct synthetic route to prepare E/POSS copolymers was proposed. E was directly copolymerized with three derivatives of POSS monomer containing seven cyclopentyl or isobutyl groups and one polymerizable group initiated with a typical metallocene catalyst. After copolymerization, the copolymer products were purified completely, and were analyzed with ^{1}H NMR, TEM, DSC, TGA, and GPC.
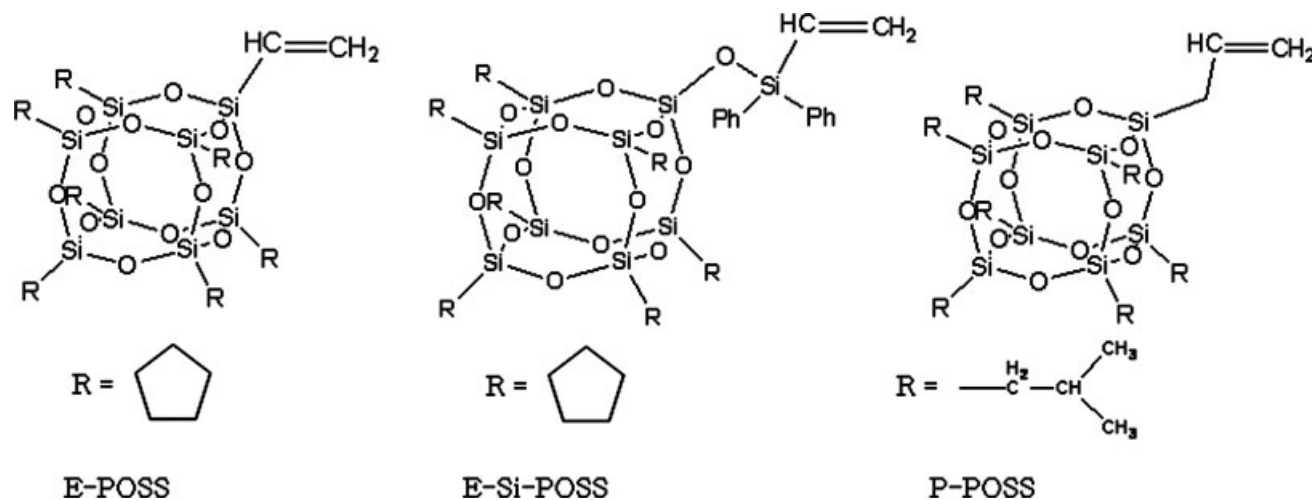
Scheme 1 POSS derivatives.

EXPERIMENTAL

Materials

The various POSS monomers such as 1,3,5,7,9,11,13-heptacyclopentyl-15-vinylpentacyclo-[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}] octasiloxane (E-POSS), 1,3,5,7,9,11,13-heptacyclopentyl-15-diphenylvinyl-silyl-oxyheptacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxane (E-Si-POSS) and 1-allyl-3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxane (P-POSS) were purchased from Aldrich, USA and their structure is shown in Scheme 1. Polymer grade E was provided by Korea Petrochemical Ind. Co., Korea and passed through two columns of P_2O_5 and $CaSO_4$. The rac-[ethylenebis(indenyl)]-zirconium dichloride catalyst (Strem Chemical, USA) and modified methylaluminoxane (MMAO, Tosoh Finechem Corporation, Japan, 6.9 wt % Al in toluene) were obtained and used directly.

Polymerization procedure

The E/POSS copolymerizations were carried out in the glass reactors equipped with a magnetic stirring bar. The reactors were evacuated and refilled with N_2 three times and charged with E gas, and then POSS (dissolved in toluene) was injected into the reactors. After the POSS was introduced, an MMAO solution was injected followed by a toluene solution of rac-Et(Ind)$_2$ZrCl$_2$ catalyst and then the polymerization started with a continuous flow of E. After a fixed period of time, polymerization was terminated by the addition of methanol, and then the copolymers were fully precipitated in a 10% HCl/methanol solution. The copolymer was recovered by filtering and washed with a sufficient amount of n-hexane to remove the unreacted POSS monomer and dried overnight in a vacuum at 60°C.

Polymer characterization

The ^{1}H NMR spectra were taken on a 500 MHz NMR spectrometer (Varian, Unity 500) at 120°C with 1,2,4-trichlorobenzen/benzene-d_6 (9/1) as a solvent.

The dispersion of POSS in nanocomposites was observed with transmission electron microscopy (TEM, H-7600, Hitachi, Japan) at 100 kV. The specimens for this measurement were microtomed to an approximate thickness of 60 nm. Subsequently, these slices were placed on a 200 mesh copper net for TEM observation.

The melting temperatures were determined by differential scanning calorimetry (DSC, DuPont TA 4000, TA Instruments) operating at a heating rate of 10°C/min. The materials were cooled down from a melt state (200°C) to 30°C at a rate of 10°C/min, and the melting point was determined in the second scan. Thermogravimetric analysis (TGA, TGA-50, Shimazhu) was carried out at a heating rate of 10°C/min from 30 to 700°C under a continuous nitrogen purge (20 mL/min).

Gel permeation chromatography (GPC) was conducted on a PL-220 (Polymer Laboratories Model) equipped with refractive-index detector at 135°C, using 1,2,4-trichlorobenzene (TCB) as a solvent.

RESULTS AND DISCUSSION

Preparation and purification of copolymer

The copolymerization of E and three derivatives of POSS monomer were carried out with rac-Et(Ind)$_2$ZrCl$_2$ in conjunction with MMAO. The pressure was kept constant throughout the polymerization process by using a bubbler, and the experimental results were given in Table I.

TABLE I
Copolymerization of E and POSS Derivatives[a]

Monomer	POSS feed mole ratio (E/POSS)	Activity[b]	POSS content mol %	wt %	T_m (°C)	ΔH (J/g)	T_{dm} (°C)	M_w ($\times 10^{-3}$ g/mol)	PDI
E	–	2315	–	–	132	148	463	103	2.8
E/E-POSS	1/0.04	2537	0.04	1.3	132	150	473	173	3.5
	1/0.08	1290	0.07	2.3	132	140	472	143	2.7
	1/0.12	967	0.16	5.0	126	135	470	115	3.0
	1/0.16	389	0.18	5.6	123	124	470	103	3.1
	1/0.32	154	0.32	9.6	122	118	480	136	3.2
E/E-Si-POSS	1/0.04	2825	0.06	2.4	133	150	473	223	3.7
	1/0.08	1545	0.11	4.2	132	142	470	177	3.4
	1/0.12	1015	0.20	7.5	132	137	470	118	2.6
	1/0.16	954	0.27	9.8	131	126	472	109	3.8
	1/0.32	186	0.47	16.0	125	119	486	130	2.5
E/P-POSS	1/0.04	3190	0.08	2.4	132	134	479	314	3.7
	1/0.08	1504	0.15	4.4	128	127	472	261	3.4
	1/0.12	1070	0.27	7.7	127	124	473	210	3.0
	1/0.16	757	0.45	12.2	125	113	468	183	3.0
	1/0.32	357	0.62	16.0	124	103	480	132	3.5

[a] Experimental conditions: [catalyst] = 2×10^{-5} mol/L and [Al]/[Zr] = 3000, reaction time: 1 h (PE: 15 min), 1 atm, 40°C.

[b] Activity: kg-polymer/(mol-Zr h).

For the exact physical characterization of polymeric material, the purification procedure of any polymer product is critical in the removal of the unreacted monomers and other impurities.[15]

The POSS monomer could be dissolved in *n*-hexane and THF, so the copolymers were washed with *n*-hexane to remove the unreacted POSS monomer which remained with the copolymerization product. To confirm the complete removal of unreacted POSS for copolymerization of E and POSS, the GPC chromatograms of pure POSS, copolymerization products before and after washing with *n*-hexane are shown in Figure 1.

In Figure 1(a), the three peaks of retention time (24, 22, and 21 min) were corresponding to those of the TCB eluent, antioxidant (2,6-di-*t*-butyl-*p*-cresol) and E-POSS monomer, respectively. Before washing
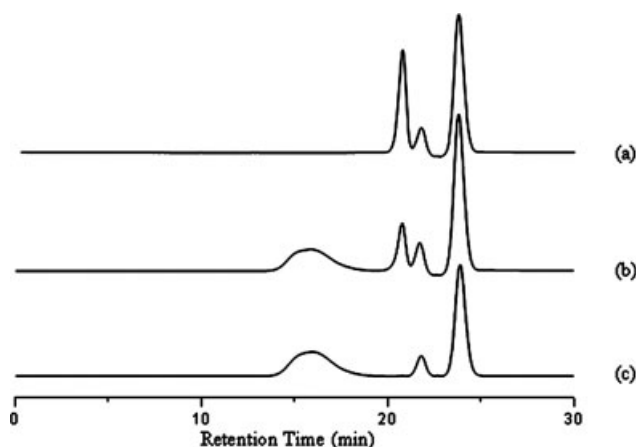

Figure 1 GPC chromatograms of E-POSS (a), copolymerization product before (b), and after (c) washing with *n*-hexane.

with *n*-hexane, the copolymer product was found to contain the E-POSS monomer as well as the copolymer itself of a broad peak at a lower retention time (16 min) as shown in (b). For copolymer products after treating with *n*-hexane shown in (c), no peak of E-POSS monomer was observed indicating that the unreacted E-POSS monomer was removed completely by washing with *n*-hexane. Naturally, the broaden peak with low retention time was attributed to the E/E-POSS copolymer.

Catalyst activity and copolymer composition

To know the copolymer composition, the purified copolymers were characterized with ^{1}H NMR and the spectra are shown in Figure 2.

The POSS contents were calculated by the monitoring of resonances regarding the cyclopentyl groups or isobutyl groups of POSS cage. With regards to E/E-POSS and E/E-Si-POSS copolymers, the incorporated amounts of POSS were obtained with the 2, 3 H peaks of cyclopentyl group[17] and the 4 H peak of main-chain from the spectra of Figure 2(a). With respect to the E/P-POSS copolymers, the 1 H peak of isobutyl group[18] and the 4 H peak of main chain were used to calculate the incorporated POSS with the spectra of Figure 2(b).

As given in Table I, the activity for the E/POSS copolymers decreased continuously and the incorporated POSS increased with higher POSS feed ratio. For E/POSS copolymerization, E-Si-POSS and P-POSS comonomers exhibited higher activity and more POSS contents than E-POSS because the polymerizable vinyl group of the previous ones has a
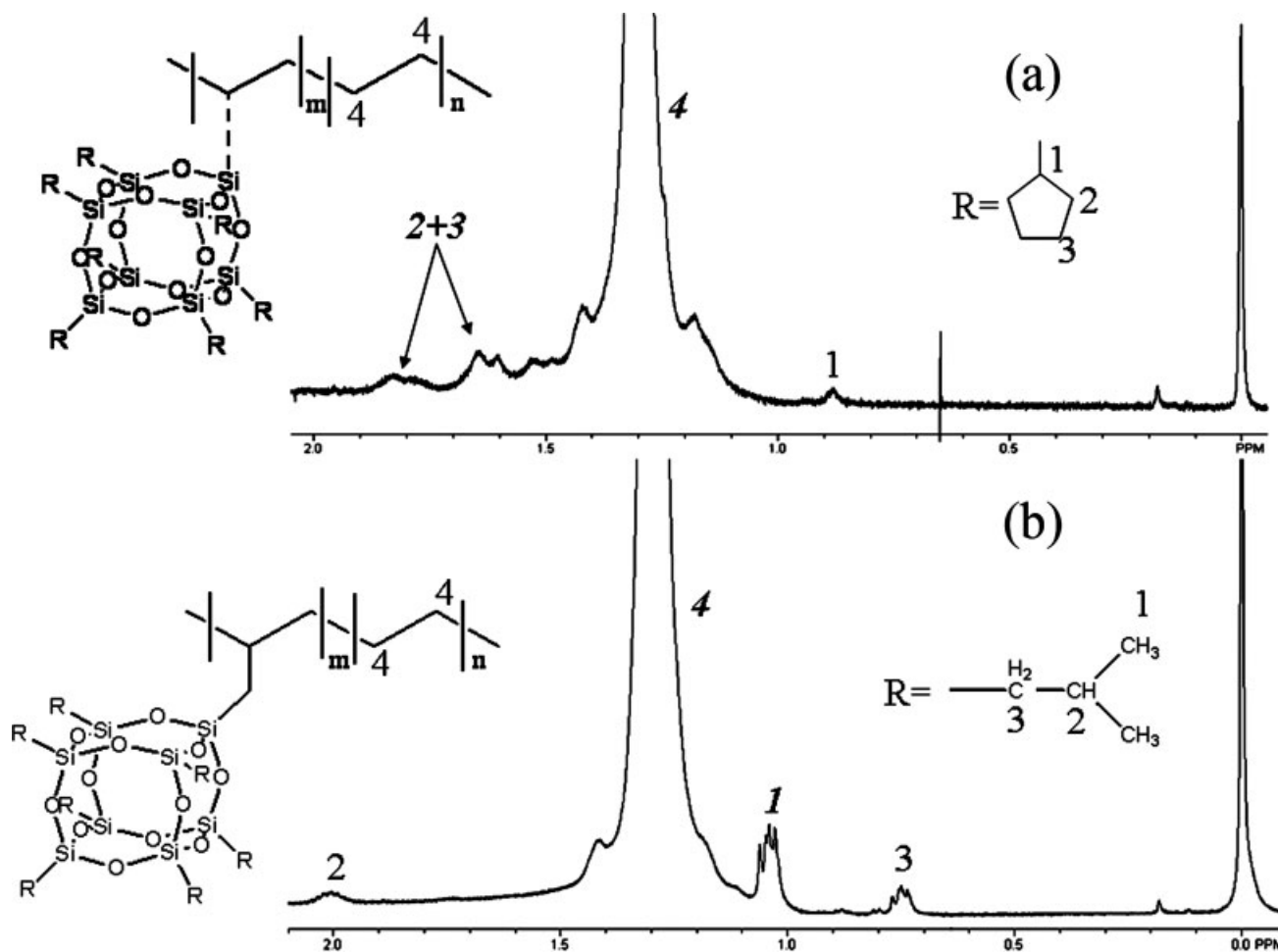
Figure 2 ^{1}H NMR spectra of E/E-POSS and E/E-Si-POSS copolymers (a), and E/P-POSS copolymer (b).

longer distance from the POSS inorganic cage than the latter one, meaning that they have different steric effect from each other. Although E-Si-POSS has a longer distance from the POSS inorganic cage than P-POSS, the former has two phenyl groups near the carbon–carbon double bond of the vinyl group to exhibit more steric effect[19] than the latter.

According to the initial E/POSS feed ratio and POSS contents, the monomer reactivity ratio was calculated by means of Fineman-Ross and Kelen-Tudos methods[20] as shown in Table II.

For the case where the two monomer reactivity ratios are different such as $r_1 > 1$ and $r_2 < 1$, one of the monomers was more reactive than the other toward both propagating species. This copolymer contains a larger proportion of the more reactive monomer (E) and the copolymer chain has a random structure.[20] With the calculation from the data for Norbornylen-POSS comonomer,[19] a similar result was found ($r_1 > 1$ and $r_2 < 1$) and it was considered that E/Norborny-len-POSS copolymer also had a random structure.

To further elucidate the microstructure of the copolymer, the dispersion of the POSS cage in the copolymer films obtained with copolymerization of

E/POSS derivatives was probed using TEM as given in Figure 3.

The POSS unit because of its silicon content has higher mass contrast than PE chains, which are comprised solely of carbon and hydrogen. In addition, POSS linkage has a higher electron density than the PE chains. Both of these above effects render POSS darker in TEM imaging without any chemical treatment.[21] The aggregation of POSS was observed by means of TEM analysis at the same magnification (30,000×). With more POSS content, the color of the TEM micrograph became darker as shown in

TABLE II
Monomer Reactivity Ratio of Ethylene (M$_1$) and POSS (M$_2$)

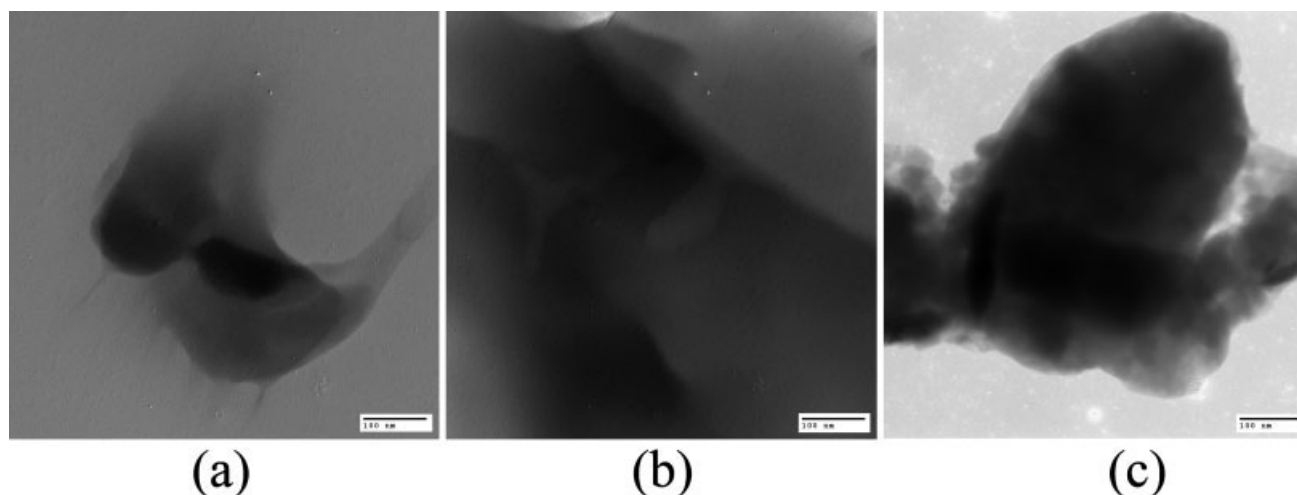| Copolymer	Fineman-Ross		Kelen-Tudos	
	r_1	r_2	r_1	r_2
E/E-POSS	101.3	0.57	97.9	0.22
E/E-Si-POSS	67.8	0.34	67.2	0.26
E/P-POSS	51.6	0.97	48.9	0.40
E/N-POSS[a]	288.0	0.23	279.3	0.16

[a] Calculated from Ref. 19.

Figure 3 TEM micrographs of E/E-POSS (a, 0.32 mol %), E/E-Si-POSS (b, 0.47 mol %), and E/P-POSS (c, 0.62 mol %) copolymers.

Figure 3. Uribe et al.[22] reported that both a cyclopentyl-POSS and a cyclohexyl-POSS pendent on the poly(4-methylstyrene) can aggregate to form nanocrystals when the POSS loading is increased to a critical content. Coughlin and coworkers[4,23] showed that pendant POSS moieties, randomly incorporated into PE, could aggregate during the solidification of copolymer melts or upon the precipitation of the copolymer from solutions. Highly ordered POSS domains formed in sizes and shapes that were restricted by the attached PE chains and the aggregation kinetics.

Thermal properties and molecular weight of copolymers

The thermal properties as well as molecular weight and its distribution of copolymers are given in Table I. The melting temperature (T_m) and heat of fusion ($\triangle H$) of E/POSS copolymers decreased with the increasing POSS content, which also indicated the presence of a random copolymer structure.[19] The T_m of copolymer was lower than that of pure PE due to the structural irregularities, which are caused by the incorporated spherosiloxane-bearing monomer.[24] The decrease of ΔH corresponding to the low degree of crystallinity have been caused by the random incorporation of POSS which disrupts the PE crystallization process.

The maximum degradation temperature (T_{dm}) of copolymer increased with the increasing POSS content, and was 5 ~ 23°C higher than that of PE. The residual part of copolymers was found to be 0.3–1.8 wt % because the POSS inclusive Si—O inorganic cage cannot be eliminated as an organic substance.

According to the GPC result, the E/POSS copolymer had a higher weight-average molecular weight (M_w) than pure PE and the M_w of copolymer decreased when the POSS content increased. No significant change or trend was observed for the polydispersity index (PDI), which was 2–4.

CONCLUSIONS

The hybrid E/POSS copolymer was synthesized via rac-Et(Ind)$_2$ZrCl$_2$ ansa-metallocene catalyst in conjunction with MMAO. By washing the copolymerization product with n-hexane, the unreacted POSS could be removed completely. The incorporation of POSS increased with the POSS feed ratio, and the ability of POSS to incorporate into PE was in the order of E-POSS < E-Si-POSS < P-POSS because of the steric effect. The monomer reactivity ratio was calculated from a copolymer composition in which the copolymer had a random structure. Aggregation of POSS was observed in the copolymer for a higher POSS content. With increasing POSS content, a gradual decrease in the melting temperature and heat of fusion of the copolymers was observed. With TGA analysis under nitrogen, the copolymer was found to improve the thermal stability with higher degradation temperatures compared to PE homopolymer. Generally, the molecular weight of the copolymer decreased with the addition of the POSS comonomer and the PDI of copolymer was found to be 2–4.

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