

Characterization of New Hindered Amine Light Stabilizers

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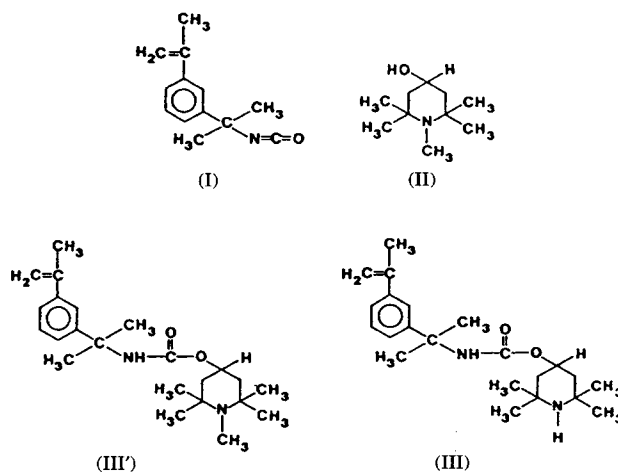
SYNOPSIS

New polymerizable urethane functional monomers containing hindered amine (III, III') and their copolymers with styrene (S) and methyl methacrylate (MMA) are characterized and tested as hindered amine light stabilizers (HALS). Experimental results indicated that the monomers possess high photostabilizing effectiveness comparable to that of Tinuvin 770 and Tinuvin 765. Their copolymers with S and MMA showed lower photostabilizing effectiveness mainly due to the low hindered amine content in the copolymers. The copolymers, however, showed very high resistance to liquid extraction. UV and ESR analyses indicate that the photostabilizing mechanism of these HALS is through the scavenging action of nitroxyl radicals on alkyl radicals formed from degradation of the substrate polymer.

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INTRODUCTION

Ever since *m*-isopropenyl- α,α -dimethylbenzyl isocyanate (*m*-TMI) (I) became available in about 1985, a number of new materials have been made using I as a starting material. For example, among the many polymerizable monomers made from I by Colvin and Cottman¹ was 2,2,6,6-tetramethyl-4-piperidinyl *m*-isopropenyl- α,α -dimethylbenzyl carbamate (III) which carries a secondary hindered amine group. New siloxanes have been made by hydrosilylation of I by Zhou and Smid.² Recently we reported the synthesis of a new polymerizable monomer carrying a tertiary hindered amine, 1,2,2,6,6-pentamethyl-4-piperidinyl-*m*-isopropenyl- α,α -dimethylbenzyl carbamate (III'),³ in which I was used as a starting material. Polymerization behaviour of this new carbamate III' will be reported elsewhere.⁴ In this paper we report our work on the characterization of III, III', and their copolymers with styrene (S) and with methyl methacrylate (MMA) as hindered amine light stabilizers (HALS).



EXPERIMENTAL

Materials

III' was prepared by reacting I and II using dibutyltin dilaurate as catalyst at 80°C. Detailed synthesis of III' and its characterization had been reported.³ Copolymerization of III' with S and with MMA using AIBN as initiator will be reported elsewhere.⁴

In this study the following copolymers were tested:

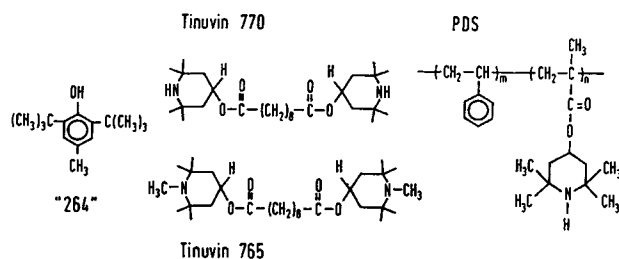
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Table I IR Absorption Groups in HALS (cm^{-1})

Sample	Carbamate	Styrene	MMA
III-St	1720 3400 3060	3020 700, 760	—
III'-St	1720 3400 3060	3020 700, 760	—
III-MMA	1720 3400 3060	—	1720-1735 2995
III'-MMA	1720 3400 3060	—	1720-1735 2995

Copolymer	III-S	III'-S	III-MMA	III'-MMA
Mole fraction of III or III'	0.0521	0.1205	0.1032	0.1295
% N	0.63	1.21	1.14	1.34

where % N is the weight percentage of piperidine nitrogen in the copolymer. The above copolymers are in the molecular weight range of 66000-74000. These higher molecular weight copolymers were used because we were interested in a study of their extractability as well as their photostabilizing effectiveness in comparison to that of the lower molecular weight HALS III, III', Tinuvin 770 (T770), and Tinuvin 765 (T765) by Ciba Geigy, PDS and phenol antioxidant 264 by Beijing 3rd Chemical Works.



Since tertiary hindered amines have been shown by Kurumada et al.⁵ to have a greater photostabilizing effect than secondary ones, we also prepared III

(by method of Colvin¹), and its copolymers with S and MMA, to be tested against the others mentioned above.

Method

IR spectra were obtained using a Perkin-Elmer 782 spectrophotometer. NMR measurement was carried out on a JEOL FX-900 FT-NMR spectrometer (90 MHz) and a Bruker ACS300 NMR spectrometer (300 MHz) at 25°C with TMS as internal standard and CDCl_3 as solvent. Thermal stability test of HALS was carried out using a DuPont TGA-951 at a heating rate of 20°C/min under nitrogen. Solubility parameters of the HALS were calculated using the group contribution method.⁶ ESR measurement was carried out on a Bruker EPR-300 at 22°C. UV spectra were generated using a Unicam-1750 UV spectrophotometer with CHCl_3 as solvent. Thermooxidation of a sample was carried out at 120°C in an oven. The embrittlement time of the samples after thermooxidation was then determined. The HALS were tested by (1) photo-oxidation in a weather-o-meter using UV irradiation and (2) liquid extraction of the HALS additive from polypropylene films.

Additive, 0.3% by weight, based on the weight of dry polypropylene powder (PP), was dissolved together with a calculated amount of PP in chloroform. The mixture was thoroughly agitated so that the additive distributed itself evenly in the PP. The solvent was then removed under reduced pressure. This treated PP was dried and pressed at 190°C for 30 s into a 110- μ thick film. A blank PP film without additive was also similarly prepared for control.

Both the test films and blank control film were mounted inside a weather-o-meter in which two 1000 W high pressure mercury lamps were used as the UV light source. A Pyrex glass filter was used to cut off light of wavelength shorter than 2900 Å. The distance between the light source and test samples was set at 24 cm and test temperature was set at 50°C. A test sample and a blank sample were removed at selected time intervals for determination of carbonyl concentration in the samples using a Perkin-Elmer 782 IR spectrophotometer at a wave-

Table II Elemental Analysis of HALS

Sample (%)	III	III'	III-S	III'-S	III-MMA	III'-MMA
C	73.74	74.06	90.41	87.34	64.15	64.17
H	9.50	9.83	8.08	8.38	8.58	8.7
N	7.82	7.45	1.25	2.42	2.28	2.68

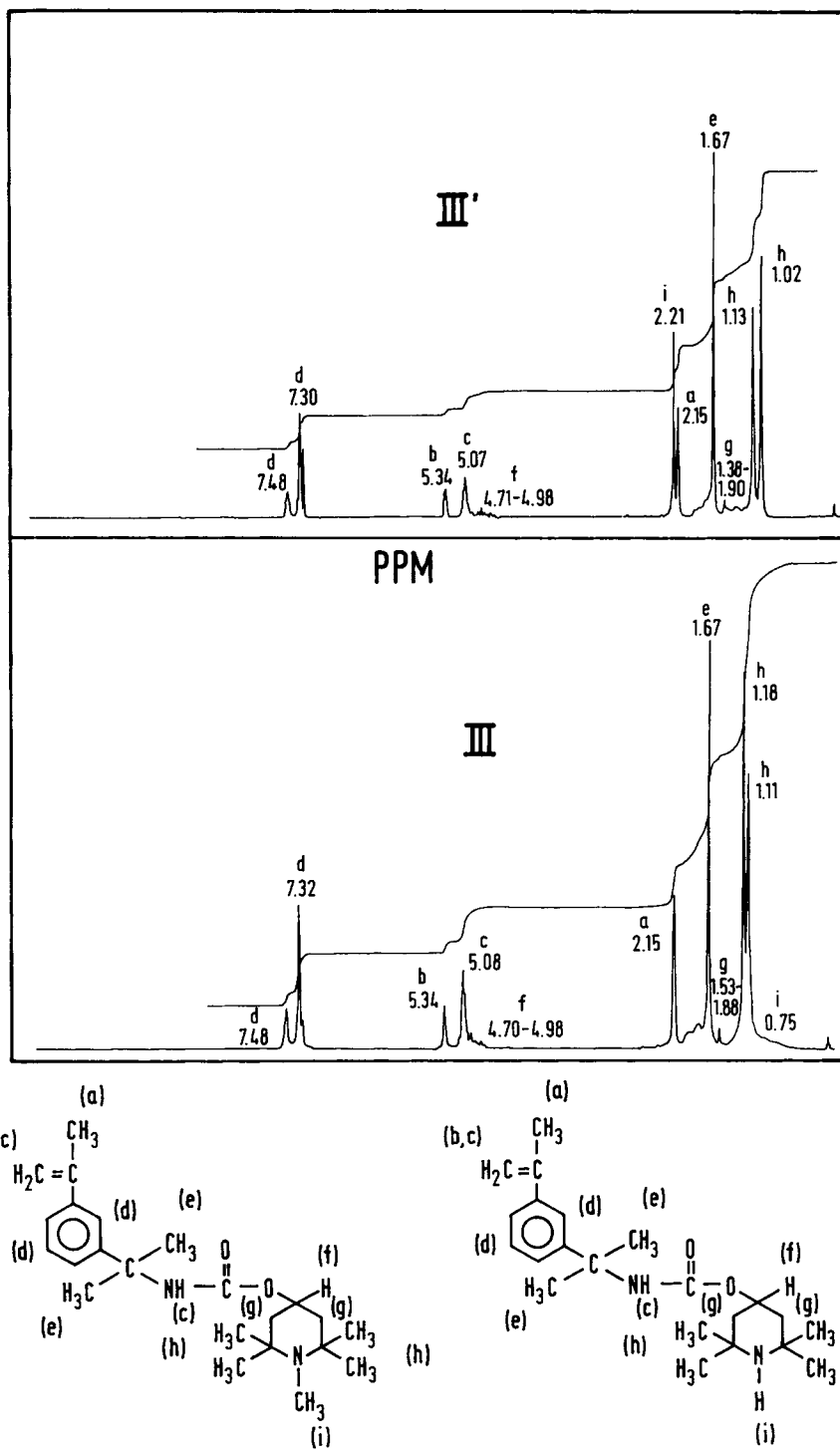


Figure 1 (a) NMR spectra of urethane functional HALS.

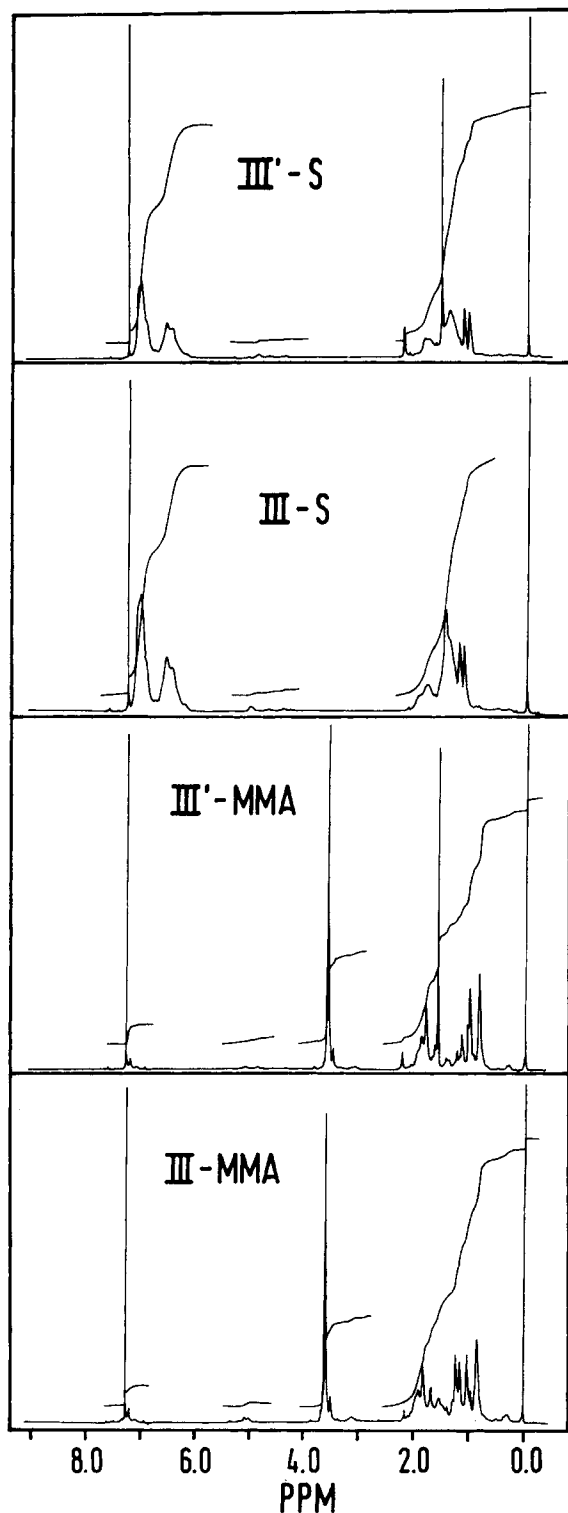


Figure 1 (b) NMR spectra of urethane functional HALS.

number of 1710 cm^{-1} . Induction period was determined from a plot of carbonyl absorption vs. UV exposure time.

PP films, as prepared above, were leached by hot water at 90°C . Carbonyl concentration in the leached films was monitored vs. leaching time. Polystyrene (PS) film containing III'-S and PMMA film containing III'-MMA were made by solution casting, using chloroform as solvent. These PS and PMMA films were leached by methanol in a Soxhlet apparatus. Nitrogen content in these PS and PMMA test samples was monitored using a CHN analyzer.

RESULTS AND DISCUSSION

Copolymers of the urethane functional HALS were characterized by IR, NMR, and elemental analysis and their results are summarized in Tables I and II and Figure 1.

As polymers are usually processed at relatively high temperatures ($220\text{--}260^{\circ}\text{C}$), the thermostability of stabilizers used in these polymers should be considered. For example, Murayama⁷ synthesized over 1000 piperidiny compounds of which only 2 were found usable as photostabilizers because all the others showed a very low thermostability. Table III shows the temperatures at which the HALS began to show a loss of weight in a TGA run.

The copolymer HALS have a much higher thermostability over their precursors III and III' and thus can withstand the usual processing temperature. Their MMA copolymers show a lower decomposition temperature than their S-copolymers due to the inherently lower thermostability of the MMA units.

The compatibility of HALS with their substrate polymer is another important factor to consider because low compatibility would make it difficult for an additive to disperse uniformly in a substrate and eventually an incompatible additive would migrate away from the substrate polymer. The substrate/additive compatibility is indicated by similar solubility parameter δ values of the substrate and of the additive. δ values of these HALS were calculated by the method of group contribution.⁶ Density of HALS were determined using density gradient columns (ASTM D-1505-68) and a comparative method in which a test sample was dispersed in a series of organic liquids of different, known density. The one in which the test sample neither sank nor floated to the top of the liquid was of the same density as the test sample. Results are listed in Table IV. It can be expected that these HALS are compatible with polypropylene which has a δ of $9.2\text{--}9.4\text{ cal}^{1/2}/\text{cm}^{3/2}$.

The photostabilizing effectiveness of these HALS was gauged by the induction period estimated from

Table III ThermoStability of HALS

HALS	III	III'	III-S	III'-S	III-MMA	III'-MMA	II
Decomposition temp. (°C)	159	148	271	271	225	214	118

Table IV Solubility Parameter of HALS

HALS	III	III'	III-S	III'-S	III-MMA	III'-MMA	T770	T765	PDS	PP
Density (g/cm ³)	1.06	1.11	0.99	0.96	1.08	1.05	1.09	0.96	1.02	0.90
δ (cal ^{1/2} /cm ^{3/2})	9.1	9.3	8.7	8.4	8.9	8.4	9.2	7.8	8.8	9.2

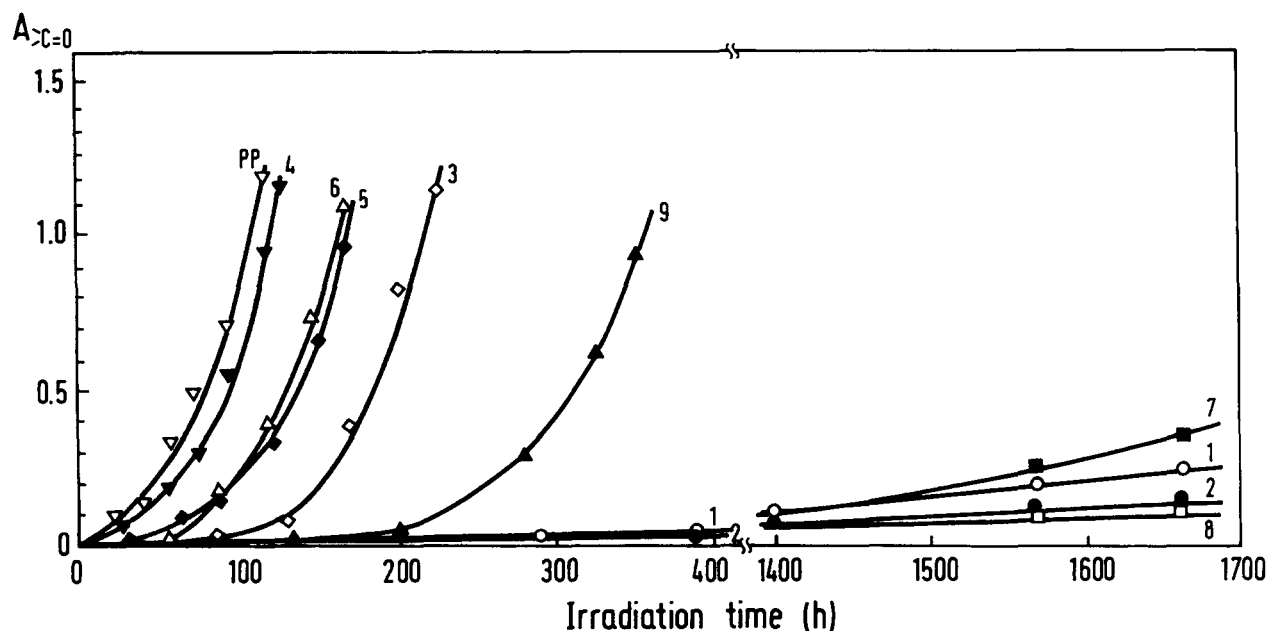
Table V Induction Period and Embrittlement Time of PP Films Containing HALS

HALS	Blank	III	III'	III-S	III'-S	III-MMA	III'-MMA	T765	T770	PDS	"264"
I.P. (h)	25.5	1385	1480	122	44	80	76	1412	1660	216	/
t_{em} (h)	22.5	85	110	62	62	134	156.5	540	540	465	41
% N	0.00	3.73	3.91	0.63	1.21	1.14	1.34	5.5	5.8	2.2	/

I.P., induction period; t_{em} , embrittlement time; % N content of nitrogen in piperidine ring of HALS. The concentration of additive in PP was 0.3%.

a plot of change in carbonyl content in the PP film vs. UV exposure time in a weather-o-meter. Results are presented in Figure 2 and Table V. Both monomers III and III' show a very high photostabilizing effectiveness, comparable to that of T770 and T765.

Their copolymers with S and MMA, however, appear to have a lower photoprotecting power, mainly due to their low hindered amine content in the substrate as only 0.3% by weight of the copolymers were used. Table V also gives the embrittlement time of the

**Figure 2** Induction time of urethane functional HALS in photooxidation.

test PP samples. It can be seen that all the HALS possess antioxidant activity higher than that of phenol antioxidant 264 prepared by Beijing 3rd Chemical Works. T765, T770, and PDS show a higher antioxidant effectiveness, probably due to their higher hindered amine content on a per unit mass basis.

UV spectra of these urethane functional HALS are displayed in Figure 3, from which it can be seen that there is no UV absorption by these HALS beyond 300 nm. Therefore the photoprotection capability of these HALS is not by way of UV absorption. Figure 4 shows the ESR signals from PP films containing these HALS. They are standard signals of stable nitroxyl free radicals in solid state.⁸⁻¹¹ The "G" value of these HALS is 2.0064. It is expected that the photostabilizing mechanism of these HALS, like that of other low molecular weight HALS,⁹⁻¹² is also through the scavenging action of $>N-\dot{O}$ on alkyl radicals formed during the photooxidation of polymers.

The staying power of an additive in a polymer substrate is another important factor to consider. As expected all the low molecular weight HALS showed a high extractability and the higher molecular weight copolymer HALS showed a much higher resistance to liquid extraction.

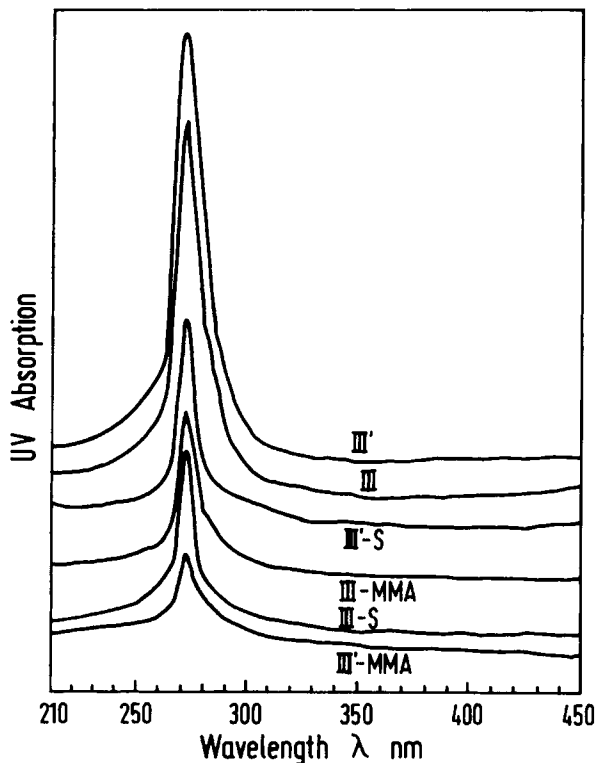


Figure 3 UV spectra of urethane functional HALS.

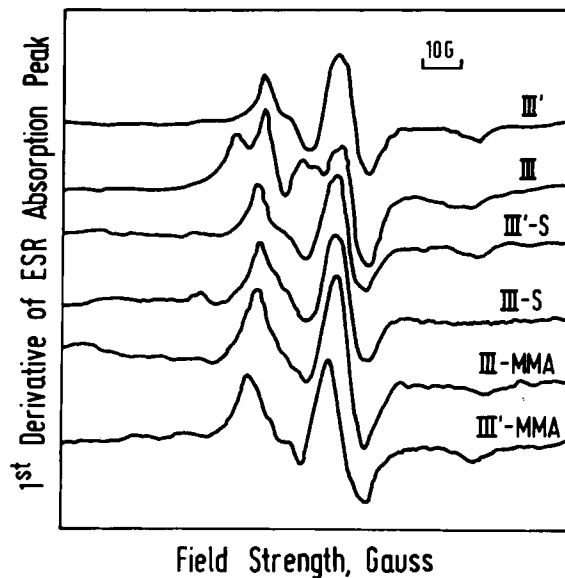


Figure 4 ESR spectra of urethane functional HALS.

CONCLUSIONS

1. Monomers III and III' of the urethane functional HALS show a high photostabilizing effectiveness comparable to that of Tinuvin 765 and Tinuvin 770. Their copolymers with styrene and with MMA showed a lower photostabilizing effectiveness probably due to low hindered amine content in the copolymer.
2. Of all the HALS tested, HALS of low molecular weight showed a high extractability and HALS of high molecular weight showed a high resistance to liquid extraction.
3. The monomers showed a much lower thermostability than their copolymers with styrene and MMA.
4. The photostabilizing mechanism of these urethane functional HALS is by way of scavenging alkyl radicals (formed from polymer degradation) by the formation of stable nitroxyl free radicals.

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