

Effect of Cardinyl Acrylate on Thermal Behavior of Methyl Methacrylate Copolymers

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SYNOPSIS

Cardinyl acrylate (CA), prepared by the reaction of acryloyl chloride and cardinol, was copolymerized with methyl methacrylate (MMA) in bulk at 80°C using 2% benzoyl peroxide as an initiator. The copolymer composition was determined by ¹H-NMR spectroscopy. Three copolymer samples containing 0.0048–0.0838 mol fraction of cardinyl acrylate were obtained. A significant improvement in the thermal stability of MMA was observed by incorporating 0.0048–0.0838 mol fraction of CA in the backbone. The activation energy for decomposition in the temperature range 350–480°C for copolymers was higher than PMMA. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Attempts have been made in the past to improve the elevated temperature performance of poly (methyl methacrylate) by incorporating low mol fraction of N-arylmaleimide in its backbone.^{1–4} An increase in T_g and initial decomposition temperature was observed by incorporation of 0.1–0.9 mol fraction of these comonomers in the backbone. In our attempt to increase the decomposition temperature of PMMA, we decided to examine the effect of acrylate derivative of cardinol on the thermal behavior of PMMA. Cardinol, a relatively low-cost material, is 3-pentadecyl phenol, having 1, 2, or 3 double bonds in the side chain. Its uses in the polymer industry as a stabilizer for PVC,^{5–6} molding powder,⁷ surface coating, paints and primers,⁸ varnishes, lacquers, and speciality coatings⁹ are well documented. The long alkyl side chain of cardinol or its derivatives may act as an internal plasticizer, thereby imparting flexibility to otherwise brittle PMMA. It was therefore considered of interest to study the copolymers

of MMA with low mol fraction of cardinyl acrylate. In the present article we report the synthesis and characterization of cardinyl acrylate (CA) and its copolymerisation with MMA using benzoyl peroxide as an initiator. Thermal behavior of copolymers was studied by thermogravimetric technique.

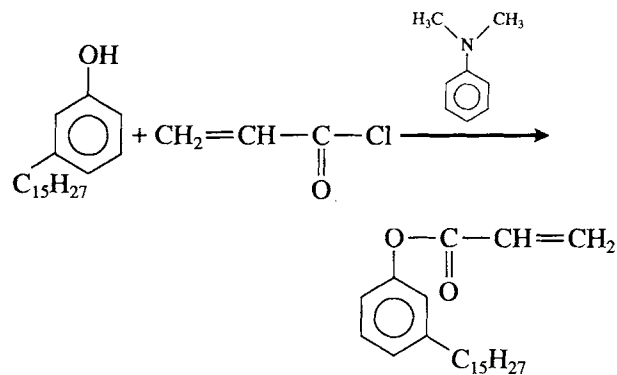
EXPERIMENTAL

Acryloyl chloride (Fluka AG) was used as such. N,N-dimethylaniline and cardinol were purified by distillation. Benzoyl peroxide (Loba Chemie) was recrystallized from chloroform. Methyl methacrylate (Merck) was freed from inhibitor by washing several times with a 10% solution of sodium hydroxide. The monomer was then washed with distilled water and was dried over anhydrous Na₂SO₄ and distilled under reduced pressure.

Preparation of Cardinyl Acrylate (CA)

Cardinyl acrylate was prepared by reacting cardinol (0.1 mol) with acryloyl chloride (0.1 mol) in the presence of a base [N,N-dimethylaniline (0.2 mol)], according to the Schotten Bauman reaction, as depicted in the following scheme:

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The monomer prepared was purified by passing through column packed with active alumina (yield = 70%).

Copolymerization of Cardinyl Acrylate and Methyl Methacrylate

Bulk copolymerization of cardinyl acrylate with methyl methacrylate was carried out at 80°C using benzoyl peroxide as an initiator. In a three necked flask, fitted with a water condenser, a nitrogen inlet tube, and a magnetic stirrer, required amounts of monomers were placed. Whole assembly was placed in an oil bath maintained at 80°C. Nitrogen was passed through the flask for 10 min and then 2% benzoyl peroxide (w/w) was added and the reaction was continued until the percentage conversion was around 10%. The solution was then poured in excess methanol with continuous stirring. The precipitated

polymer was purified by dissolving and reprecipitating in chloroform/methanol two times. Precipitated polymer was then dried in a vacuum oven at 80°C for 24 h.

Characterization

Structural characterization of cardinyl acrylate in thin film form was done by using Nicolet 5D-X FTIR spectrophotometer.

¹H-NMR spectra of monomer and copolymers were recorded in CDCl₃, using a Jeol JNM-FX100 spectrophotometer and tetramethylsilane as an internal standard.

The intrinsic viscosity of the polymer samples was determined in chloroform at 30 ± 1°C, using an Ubbelohde suspension level viscometer.

Thermal stability of polymer samples in nitrogen atmosphere was evaluated by using a DuPont 1090 thermal analyzer having a 951 TG module. A sample size of 11 ± 1 mg was used in each experiment.

RESULTS AND DISCUSSION

Monomer Characterization

The IR spectrum of cardinyl acrylate is shown in Figure 1. The characteristic peaks, due to ester group, were observed at 1750 cm⁻¹ (ν_{C=O}), 1220, and 1041 cm⁻¹ (asym. and sym. C—O—C stretch). Other prominent absorption peaks, at 2937 and 2854

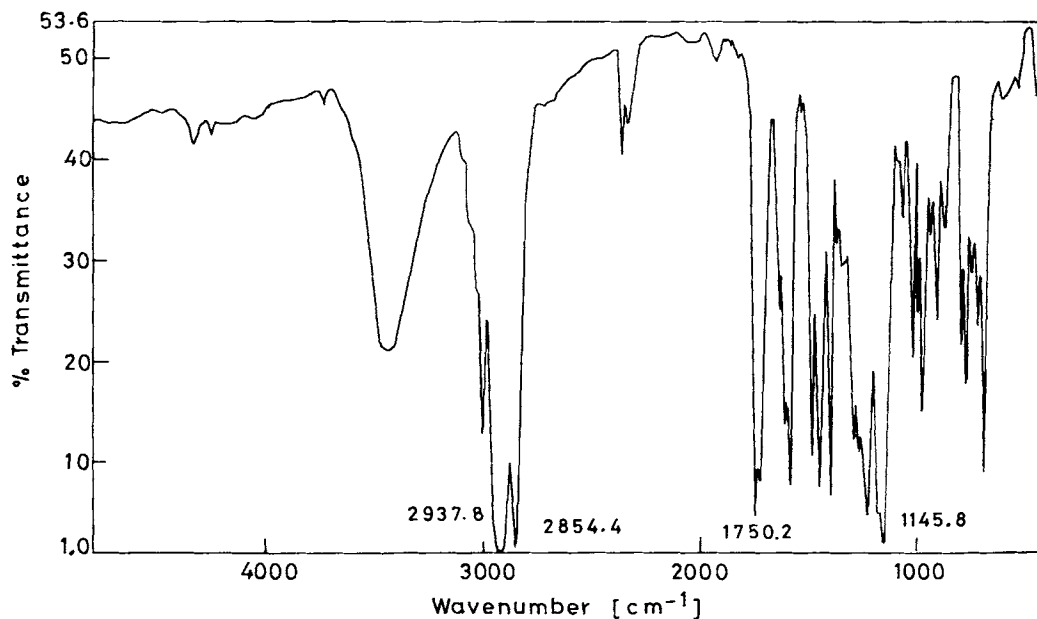


Figure 1 FTIR spectrum of cardinyl acrylate.

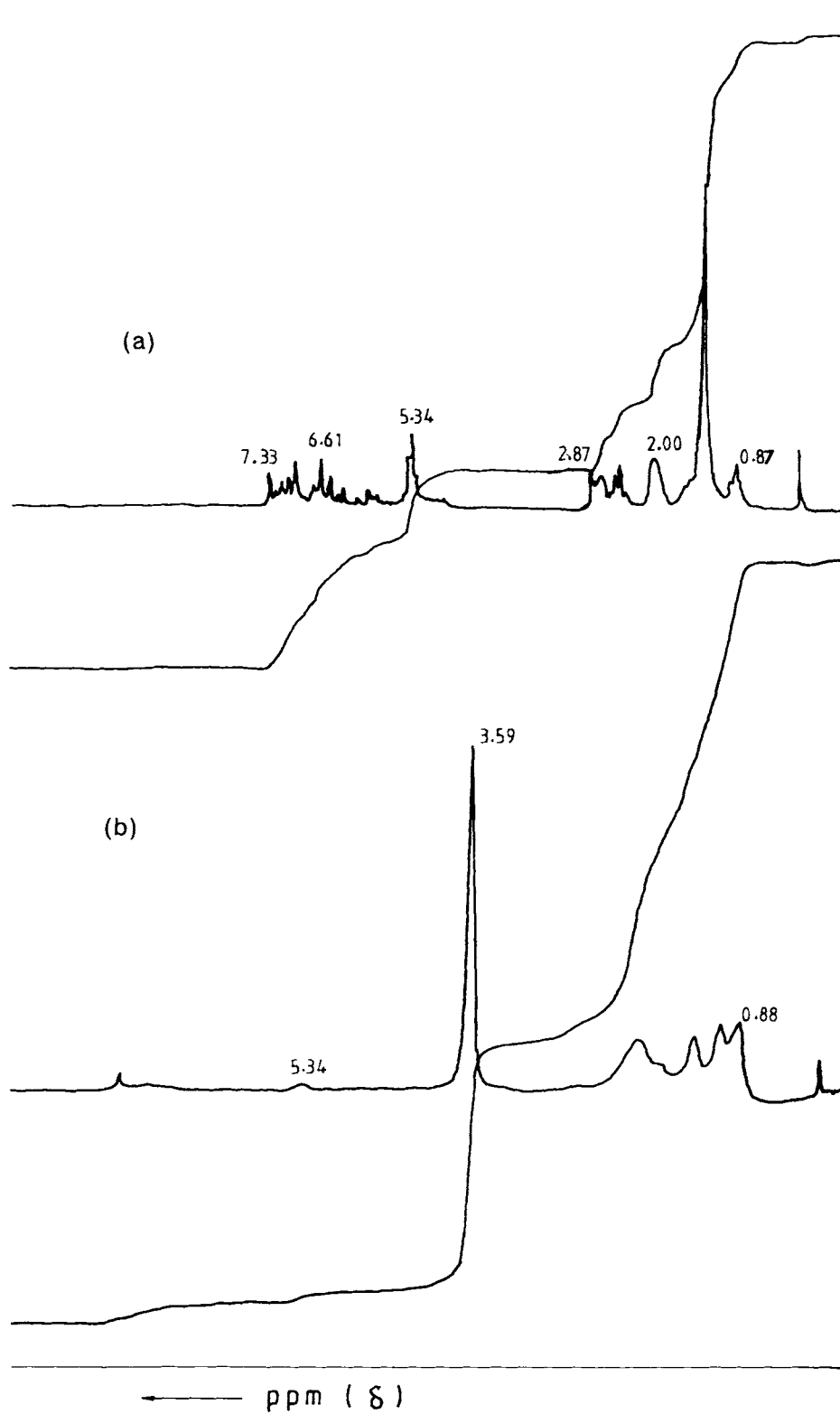


Figure 2 $^1\text{H-NMR}$ spectra of (a) CA monomer and (b) CA-5 copolymer.

cm^{-1} ($\gamma_{\text{C-H}}$), 720–750 cm^{-1} [$(\text{CH}_2)_n$], and 1604–1640 cm^{-1} ($\gamma_{\text{C=C}}$), were also observed.

Cardinol is 3-pentadecylphenol having 1, 2, or 3 double bonds in the side chain. In order to assign the structure of cardinyl acrylate, the $^1\text{H-NMR}$ spectrum of monomer was recorded. The aromatic protons appeared as a multiplet at $\delta = 6.7\text{--}7.3$ (Fig. 2). The integration in this region was equivalent to 4 H. The proton content of olefinic, vinylic, and other methylene and methyl groups was calculated using the integration of the aromatic region. Olefinic protons (3.78 H) appeared as a multiplet at $\delta = 4.86\text{--}5.34$. The signals that occurred at $\delta = 5.9\text{--}6.6$ were due to vinylic protons (3 H). The resonance signal at 2.47 ppm was attributed to the benzylic protons (2 H), while that at 2.87 ppm was due to methylene protons flanked by double bonds. The signal due to methylene protons of monoene component $-\text{CH}_2-\text{CH}=\text{CH}$ (4 H) appeared at $\delta = 2$. ($-\text{CH}_2$)_n (14 H) appeared as a singlet of sharp intensity at 1.29 ppm. The terminal $-\text{CH}_3$ group (3H) in the side chain gave a triplet centered at 0.87 ppm.

Copolymerization Studies

Since the main objective in the present studies was to improve the high temperature capabilities of PMMA without sacrificing its useful properties, copolymer samples containing low mol fraction of CA in the backbone were prepared. The details of feed composition and polymer designations are given in Table I.

The copolymerization may proceed by (a) reaction of acrylate group of CA with MMA, or (b) reaction of olefinic groups of pentadecyl side chain of CA with MMA.

Therefore, in order to assess the relative contribution of these two possible reactions, the copolymer composition was determined from $^1\text{H-NMR}$ (Fig. 2) by:

Table I Copolymerization of Methyl Methacrylate with Cardinyl Acrylate

Sample Designation	Mol Fraction of CA in Feed	Conversion (%)	Time (min)	Intrinsic Viscosity (dL/g)
CA-2	0.0224	11.2	180	0.36
CA-5	0.0526	9.8	255	0.31
CA-10	0.1088	10.5	360	0.31

Table II Copolymerization of CA and MMA: Effect of Monomer Feed on Copolymer Composition

Sample Designation	Mol Fraction of CA in Copolymer From		
	$\frac{I_{\text{OCH}_3}}{I_{\text{CH}=\text{CH}}}$	$\frac{I_{\text{OCH}_3}}{I_{\text{CH}_2+\text{CH}_3}}$	$\frac{I_{\text{OCH}_3}}{I_{\text{Ar}}}$
CA-2	0.0048	—	0.0183
CA-5	0.0393	0.0457	0.0606
CA-10	0.0838	0.2304	0.1679

1. Taking the ratio of $-\text{OCH}_3$ protons of MMA and olefinic protons of side chain of CA ($I_{\text{OCH}_3}/I_{\text{CH}=\text{CH}}$),
2. Ratio of $-\text{OCH}_3$ protons to total aliphatic protons ($I_{\text{OCH}_3}/I_{\text{CH}_2+\text{CH}_3}$),
3. Ratio of $-\text{OCH}_3$ protons to aromatic protons ($I_{\text{OCH}_3}/I_{\text{Ar}}$).

The results are tabulated in Table II.

Mol fraction of CA in copolymer was found to be greater when the calculations were based on the ratio of peak areas under the methoxy and aliphatic protons ($I_{\text{OCH}_3}/I_{\text{CH}_2+\text{CH}_3}$) or methoxy and aromatic protons ($I_{\text{OCH}_3}/I_{\text{Ar}}$), as compared to the peak areas under methoxy and olefinic protons of side chain ($I_{\text{OCH}_3}/I_{\text{CH}=\text{CH}}$). This indicates the possibilities of participation of side chain unsaturation in copolymer formation. The reactivity of these olefinic groups, which are 1,2-disubstituted, is expected to

Table III Results of Thermogravimetric Analysis of PMMA and its Copolymers in N_2 Atmosphere (Heating Rate = $10^\circ\text{C}/\text{min}$)

Sample Designation	PMMA	CA-2	CA-5	CA-10
Property				
$T_{\text{max-1}}^\circ\text{C}$	311.4	—	—	—
$T_{\text{f-1}}^\circ\text{C}$	350	—	—	—
$T_{\text{max-2}}^\circ\text{C}$	396.8	393.0	421.2	435.1
$T_{\text{f-2}}^\circ\text{C}$	420.9	437.8	448.6	477.8
Wt. loss % in temp. range				
240–350 $^\circ\text{C}$	29.39	20	8	14
350–480 $^\circ\text{C}$	67.65	76.82	87.32	78
Char yield at 500 $^\circ\text{C}$	2	3	4	9

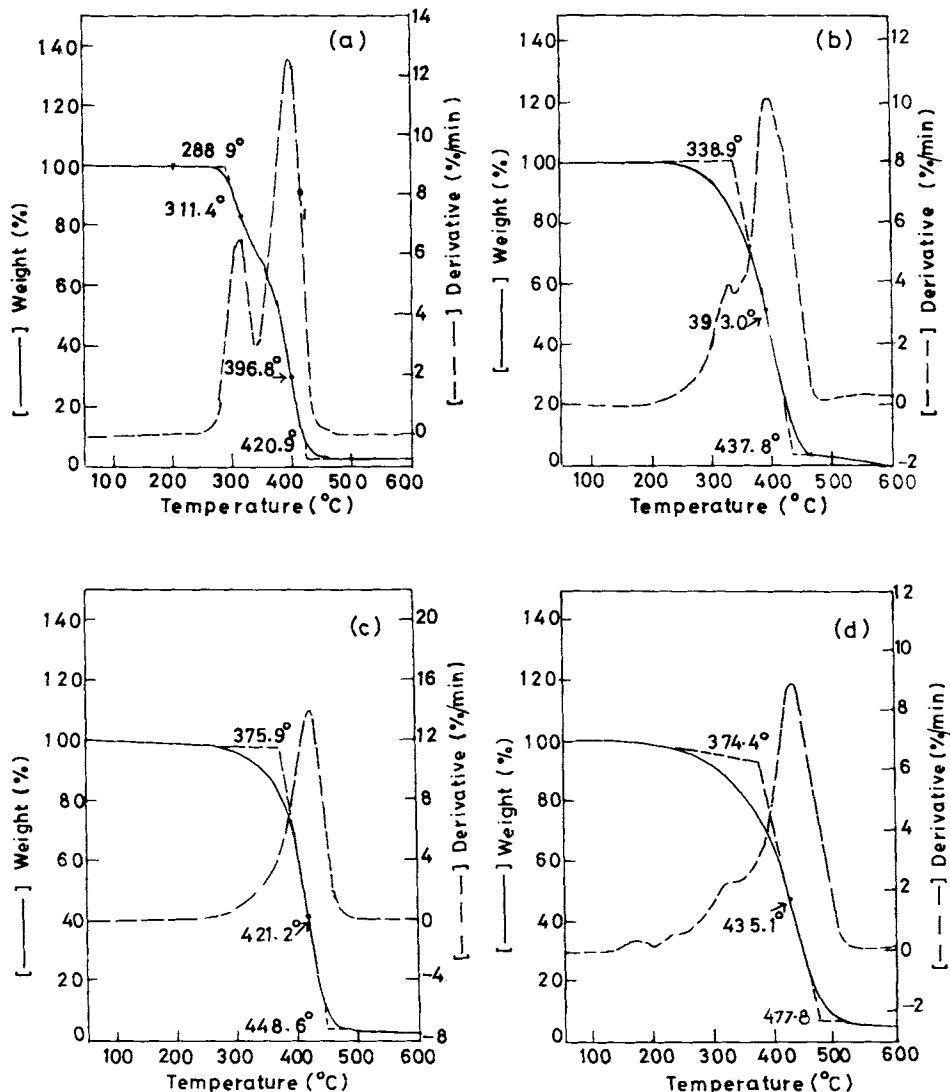


Figure 3 TG and DTG traces of (a) PMMA, (b) CA-2, (c) CA-5, and (d) CA-10, in N_2 atmosphere at a heating rate of $10^\circ C/min$.

be lower than that of the acrylic group in CA. Still, the copolymerization of MMA with 1,2-disubstituted derivatives is well documented in the literature.

In order to investigate the effect of the comonomer (cardinyl acrylate) on the thermal stability of poly(methyl methacrylate), thermogravimetric analysis was carried out. From the differential thermogravimetric traces, the temperature of maximum rate of weight loss (T_{max}) was determined (Fig. 3) and from the TG traces, the final decomposition temperature (T_f) was obtained by extrapolation (Table III).

PMMA, prepared under similar conditions, showed a distinct two step degradation. The first step was in the temperature range of 288–350°C and

accounted for 29.4% weight loss, while major weight loss (67.5%) was observed in the temperature range 350–450°C. In CA-MMA copolymers, distinct two step degradation was not observed. Only the major decomposition step was observed above 335°C. However, for assessing relative thermal stability, the weight loss in 240–350°C range for PMMA and copolymers was noted from TG traces (Table III). As is obvious from these results, a decrease in weight loss is observed in copolymers (8–20%). Also, an increase in the concentration of CA in copolymers brought about an increase in T_f and T_{max} values, thereby showing the increased thermal stability of these copolymers. The presence of cardinyl acrylate units in PMMA backbone acted as sites of chain

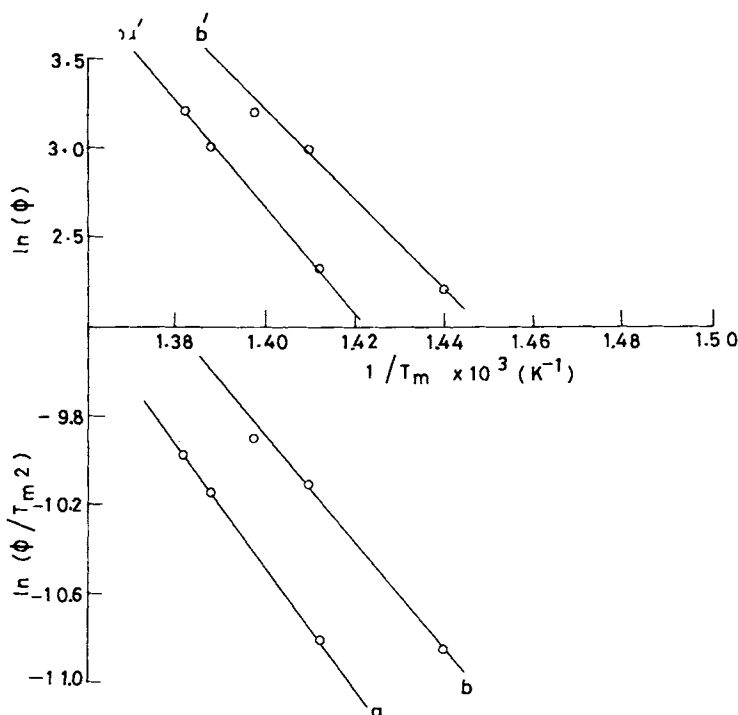


Figure 4 Kissinger plot of (a) CA-5, (b) CA-10, and Ozawa plot of (a') CA-5, (b') CA-10.

termination for the depropagation reaction. The alkyl side chain of CA is flexible and may degrade at a lower temperature. However, some of the olefinic double bonds may have participated in copolymerization, thereby making the side chain less flexible and more stable.

The activation energy for degradation was also determined for CA-5 and CA-10 by using Ozawa's and Kissinger's method.¹⁰ These plots for CA-5 and CA-10 are shown in Figure 4.

An activation energy of 184 kJ/mol has been reported in the literature for the random chain scission (DTG peak at 360°C) for PMMA.¹¹ The values observed in the present work are higher than PMMA (Table IV). Therefore, on the basis of the activation energy data and temperatures of degradation, it can be concluded that copolymerization of CA with

MMA leads to an increase in thermal stability of PMMA.

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Table IV Activation Energy for Degradation of CA-5 and CA-10 in Nitrogen Atmosphere

Sample Designation	Activation energy (E) kJ/mol	
	Kissinger Method	Ozawa Method
CA-5	201	211
CA-10	235	231

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