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Synthesis and characterization of copolymer resin derived from 4-methyl acetophenone, phenyl hydrazine and formaldehyde

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ABSTRACT

Copolymer resin (4-MAPHF) was synthesized by the condensation of 4-methyl acetophenone (4-MA) and phenyl hydrazine (PH) with formaldehyde (F) in the presence of hydrochloric acid catalyst and using varied molar ratios of reacting monomers. Copolymer resin compositions have been determined on the basis of their elemental analysis and the number average molecular weights of resin were determined by conductometric titration in non-aqueous medium. Viscometric measurements in dimethyl formamide (DMF) have been carried out with a view to ascertain the characteristic functions and constants. The UV-visible, FTIR and proton nuclear magnetic resonance (¹H NMR) spectra were studied to elucidate the structure. The surface features and crystalline behaviour of the copolymer resin have been analyzed by scanning electron microscope (SEM).

Keywords: Synthesis, polycondensation, resin, structure, degree of polymerization, Characterization, spectral analysis.

INTRODUCTION

Copolymer find very useful applications as adhesives, high temperature flame resistant, fibers, coating materials, semiconductors, catalysis and ion exchange resins [1-2]. The synthesis of polymers containing reactive functional groups has been an active field of research in polymer science, because it provides an approach to a subsequent modification of the polymer for the required applications. Coordination polymers are applied in the fields such as organic and inorganic chemistry, biology, materials science, electrochemistry, and pharmacology having many potential applications [3-4]. This interdisciplinary nature has led to extensive study of these materials for the past few decades [5]. Recently, different types of polymeric ligands have been prepared as a support for the preparation of transition metal complexes which is an active field of research [6-7]. In areas such as medical devices, healthcare products, hospital and dental office equipment, water purification systems, food storage and packaging, etc., the contamination by microorganisms is of great concern nowadays. One possible way to avoid such microbial contamination is to develop materials with antimicrobial activity [8].

In order to synthesize polymers possessing numerous practical applications, there is a need to investigate the effect of temperature on the polymers in order to establish their thermal stability. The degradation of polymer under air or inert atmosphere at increasing temperatures provides useful information about the nature of the species produced. The measurement of the thermal stability of solid complex compounds is usually carried out by the estimation of the heat of reaction from the metal salts with the ligands. Nowadays, the thermal analysis techniques play an important role in studying the structure and properties of metal complexes. The different factors affecting the thermal stability of transition metal complexes were discussed and reported by Donia [9].

In continuation of our interest in synthesis of various copolymer resin, we describe herein the synthesis of copolymer resin involving 4-methyl acetophenone and phenyl hydrazine with formaldehyde (4-MAPHF). The spectral, morphology and the physico-chemical methods have been used to characterize the copolymer resin.

MATERIALS AND METHODS

Materials

4-Methyl acetophenone (Ranbaxy Fine Chemicals, Mumbai) purified by rectified spirit. Formaldehyde (37%) (Qualigens Fine Chemicals, Mumbai) was used as received. Phenyl hydrazine (Loba, Mumbai, extra pure) was used as received. The solvents and monomers were purified by the conventional methods[10].

Preparation of 4-MAPHF copolymer resin

A mixture of 4-methyl acetophenone (0.1mol), phenyl hydrazine (0.1mol) and formaldehyde (0.3 mol) in the presence of 2M hydrochloric acid (200 ml) was heated in an oil bath at $124^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 5 h with occasional shaking [10-12]. The separated resinous product (4-MAPHF) was washed with hot water to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitated by dropwise addition of 1:1 (v/v) HCl / water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of the copolymer resin was found to be 86%. The reaction taking place is as shown in Fig. 1.

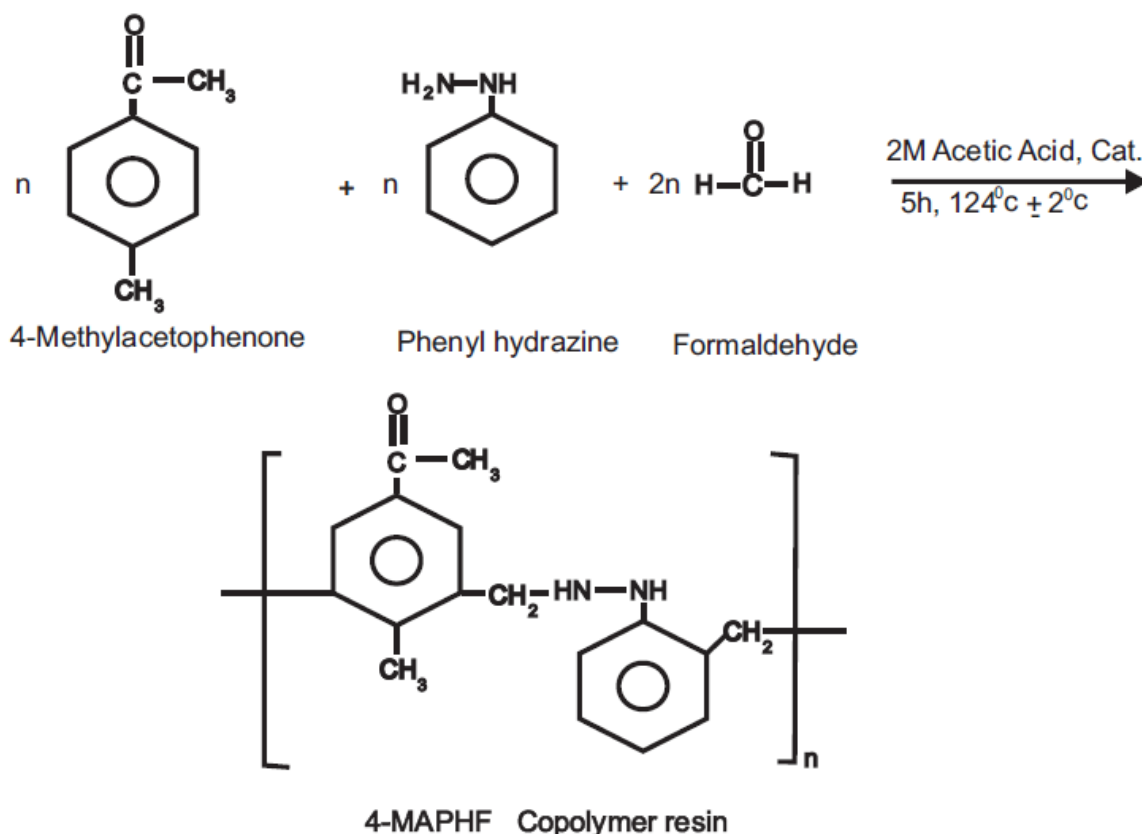


Fig.1. Synthesis of 4-MAPHF copolymer resin

Characterization of copolymer resin

The copolymer resin was subjected to microanalysis for carbon, hydrogen and nitrogen on Perkin Elmer C, H, N, S analyzer. The number average molecular weights (M_n) were determined by conductometric titration in DMF using KOH in a 50% (v/v) DMF/alcohol mixture as a titrant. The viscosities were determined using Tuan-Fuoss viscometer at six different (concentration ranging from 3.0 wt % to 0.5 wt % of resin in DMF at 33°C). The intrinsic viscosity η was calculated by the Huggins equation (1) and Kramer equation (2).

$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \quad \dots\dots\dots(1)$$

$$\ln \eta_{rel}/C = [\eta] - K_2 [\eta]^2 C \quad \dots\dots\dots(2)$$

Electronic absorption spectra of the copolymer in DMF were also recorded on Shimadzu UV-1800 double beam spectrophotometer in the range of 200-800 nm. Infrared spectra of 4-MAPHF copolymer resin was recorded, using a Shimadzu PR-Affinity spectrophotometer in KBr pellets in the number region of 4000-400 cm^{-1} at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. Proton NMR spectra of PTMF copolymer was recorded on Varian VXR – 300s 300 MHz proton NMR spectrophotometer using DMSO- d_6 as a solvent at STIC, Kochi. The surface analysis of the PTMF copolymer was examined at different magnifications at STIC analysis centre, Kochi..

RESULTS AND DISCUSSION

Copolymer resin (4-MAPHF) sample was cream in colour, insoluble in commonly used organic solvents but was soluble in DMF, THF, DMSO and aq. NaOH. The resin was analyzed for carbon, hydrogen and nitrogen content. The resin synthesized do not show sharp melting point but undergo decomposition above 248 $^{\circ}\text{C}$. This resin was then purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value.

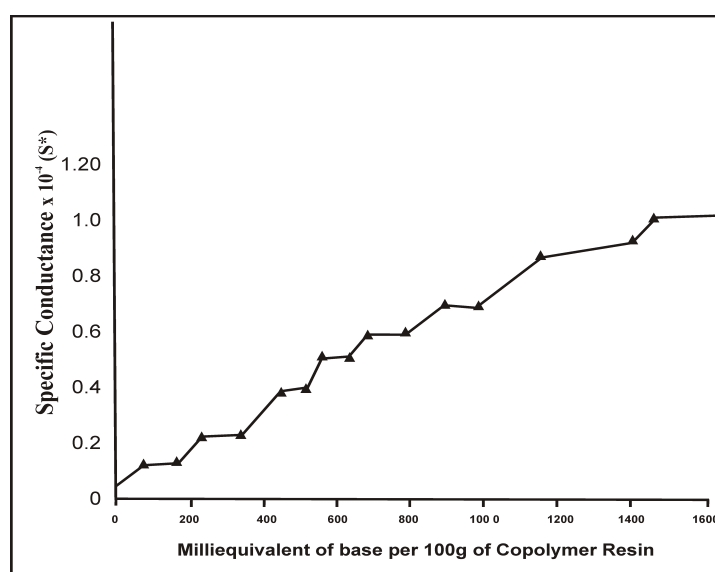
- Calculated for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$: C: 76.00 %; H: 6.70 %; N: 10.52 %., O: 6.01%,
- Found for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$: C: 76.06 %; H: 6.43 %; N: 10.17 % . O: 6.45%,

The molecular weight ($\overline{\text{Mn}}$) of the copolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in 50% (v/v) DMF/ alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of copolymers was made. Inspection of such a plot revealed that there are many breaks in plot. From this plot the first break and the last break were noted (Fig.2). The calculation of ($\overline{\text{Mn}}$) by this method is based on the following considerations [13].

(1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxy group of all repeating units are neutralized. On the basis of the average degree of polymerization ($\overline{\text{Dp}}$) is given by the following relation.

$$\overline{\text{Dp}} = \frac{\text{Total meq. of base required for complete neutralization i.e. last break}}{\text{Meq. of base required for smallest interval i.e. first break}}$$

The number average molecular weight ($\overline{\text{Mn}}$) could be obtained by multiplying the $\overline{\text{Dp}}$ by the formula weight of the repeating unit [13]. The results are incorporated in Table 1.



PTMF-I
Fig.2. Non-aqueous conductometric titration curve of 4-MAPHF copolymer

Viscometric measurements were carried out in DMF at 30°C. The resin showed normal behaviour. The intrinsic viscosity was determined by the Huggin [14] equation.

and Kraemers [21] equation :

$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 \cdot C$$

$$\ln \eta_{rel}/C = [\eta] - K_2 [\eta]^2 \cdot C$$

The viscometric plots are shown in Fig. 3. In accordance with the above relations, the plots of η_{sp} / C and η_{rel} / C against C were found to be linear giving as slopes K_1 and K_2 respectively. The intercept on the axis of viscosity function gave the $[\eta]$ value in both the plots. The calculated values of constants K_1 and K_2 [Table 1] in most of cases satisfy the relation. $K_1 + K_2 = 0.5$ favorably [14]. The values of $[\eta]$ obtained from equation (1) and equation (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of copolymer.

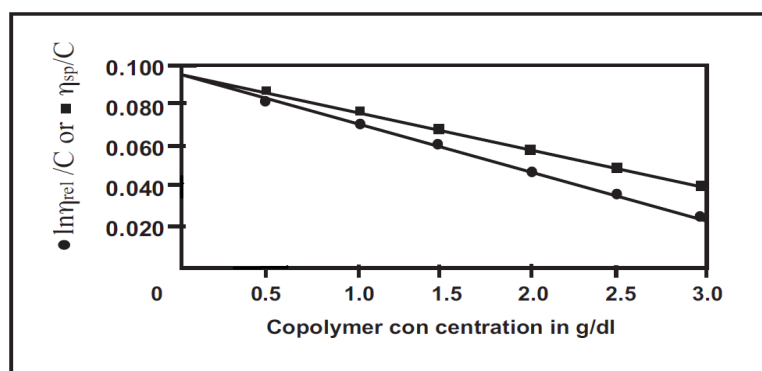


Fig.3. Viscometric plots of 4-MAPHF copolymer

The electronic spectra of the 4-MAPHF copolymer resin are depicted in Fig.4. The spectra of the copolymer exhibit two absorption maxima in the region 260 to 290 nm and 320 to 330 nm. The intense band at 280 nm is due to ($\pi - \pi^*$) allowed transition of 4-methylacetophenone moiety which readily attains coplanarity and the shoulders merging (loss of fine structure) band at 324 nm may be due to ($n - \pi^*$) forbidden transition in saturated aliphatic carbonyl compounds [15]. The bathochromic shift from the basic values viz. 260 nm and 270 nm respectively may be due to combined effect of conjugation and phenolic hydroxy group (auxochrome) [15].

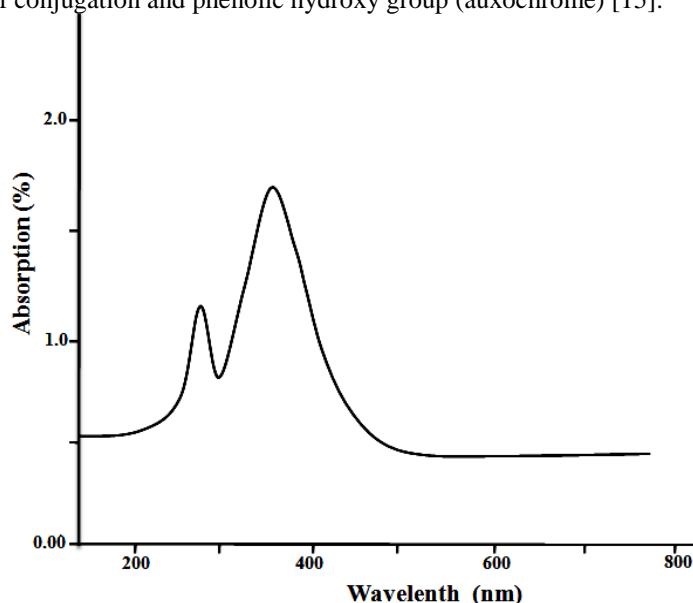


Fig.4. Electronic spectra of 4-MAPHF copolymer

The IR spectra of copolymer resin is presented in Fig. 5. The IR spectra revealed that the resin give rise to a broad band appearing in the region 3400-3800 cm^{-1} may be assigned to the stretching vibration of COCH_3 groups [16]. The band at 2900 cm^{-1} assignable to $-\text{NH}-$ stretching, bending and deformation out of plane vibrations of phenyl

hydrazine moiety in copolymers respectively. The band at 1502 cm^{-1} may be ascribed to aromatic skeletal ring [16]. The presence of methylene bridges ($-\text{CH}_2-$) in the polymeric chain may be assigned due to presence of band at $1460-1470\text{ cm}^{-1}$, $1375-1360\text{ cm}^{-1}$ and $788-753\text{ cm}^{-1}$ [$-\text{CH}_2-$ rocking] [16].

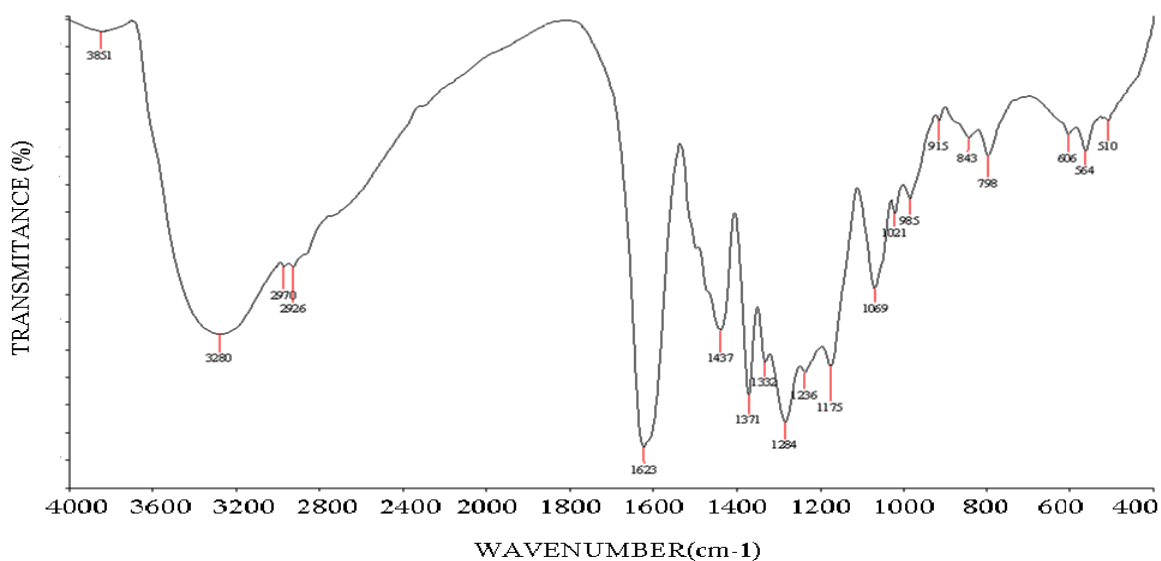


Fig. 5. Infrared spectra of 4-MAPHF copolymer

Proton NMR spectra of copolymer resin is presented in Fig.6. Proton NMR spectra of copolymer resin show the intense signal arising in the region $7.80(\delta)$ ppm which may occur on account of hydroxyl proton of $-\text{COCH}_3$ group [16]. The sharp intense peak at $6.80(\delta)$ ppm may be assigned to aromatic proton. A weak signal made its appearance at $3.90(\delta)$ ppm which may be due to amido protons of $-\text{NH}$ bridge in the chain[17]. An intense signal appearing at $2.60(\delta)$ ppm may be due to methylene proton ($-\text{CH}_2-$). Copolymer show signal around $3.62(\delta)$ ppm suggesting the presence of methylene bridges of $\text{Ar}-\text{CH}_2-\text{N}$ linkage[17].

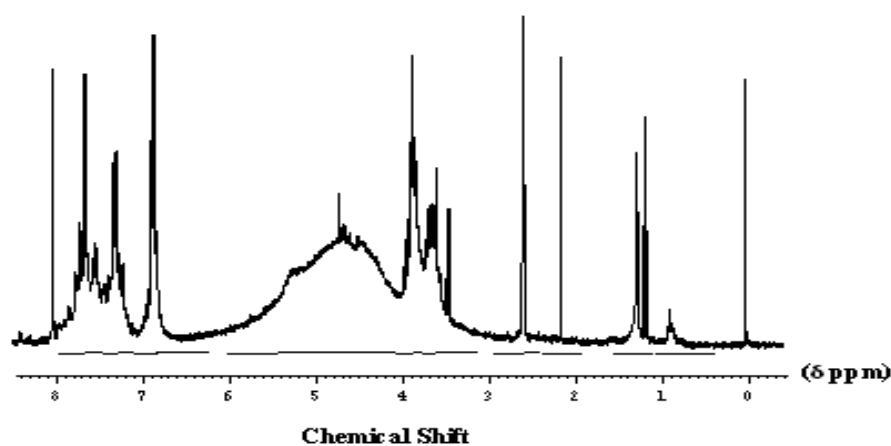


Fig.6. Proton NMR spectra of 4-MAPHF copolymer

The SEM photographs obtained in different magnifications for the 4-MAPHF copolymer resin are shown in Fig.7. It indicates that the 4-MAPHF copolymer has a net-like appearance and the surface features of the copolymer shows a fringed, scattered, and miscellaneous model of the crystalline-amorphous structure. Scanning electron microscopy of copolymer was carried out to understand the inner morphology and pore structure. The morphology of fracture surfaces of the copolymer is quite different from that of polymer-metal complexes. It is clear from SEM that the copolymer is porous in nature. The morphology of the copolymer shows a fringed model of the semi crystalline nature. The fringes represent the transition between the crystalline and the amorphous phases. The copolymer exhibits a more amorphous character with a close-packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix. The presence of few holes and cracks are noted which may be due to air voids [17]. On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, NMR spectra and molecular weight, the most probable structures have been proposed for copolymer resin.

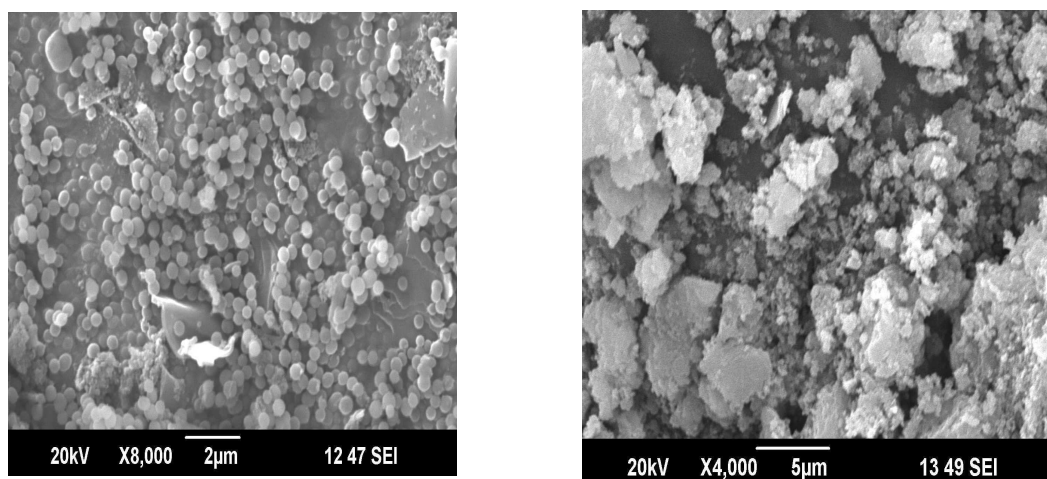


Fig. 7. SEM Image of 4-MAPHF copolymer resin

Table 1. Molecular Weight Determination and Viscometric Data of copolymer

Copolymer	Empirical formula of repeating unit	Empirical formula weight	\overline{Dp}	\overline{Mn}	Intrinsic viscosity $dl\ g^{-1}$	Huggin's constant (K_1)	Kraemer constant (K_2)	K_1+K_2
4-MAPHF	$C_{17}H_{18}N_2O$	266	14.30	5204	0.148	-0.321	0.2423	0.58

CONCLUSION

A copolymer resin 4-MAPHF based on polycondensation reaction of 4-methylacetophenone and phenyl hydrazine with formaldehyde in the presence of acid catalyst has been prepared. On the basis of elemental analysis, UV-Visible spectra, FTIR, NMR spectra and conductometric titration in non-aqueous medium, the structure for the copolymer resin has been suggested. The copolymer resin can be used as ion-exchanger and can also be used for the preparation of polychelates with transition metal ions.

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