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Synthesis and characterization of Cu(II) containing PMMA co-polymer for optical applications

**Omar Rojas · Miguel Araya · Mavis L. Montero ·
Daniel E. Azofeifa · William E. Vargas**

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Abstract Homogenous, transparent, greenish blue Cu(II) containing PMMA co-polymer disks were prepared through the radical polymerization of the Cu(II) methacrylate, MMA and HMA using AIBN as an initiator. The dependence of the absorbance and transmittance spectra with the Cu(II) methacrylate concentration was investigated in the visible range (420–750 nm). From the transmittance measurements the refractive index and extinction coefficient spectral dependence were calculated by application of an inversion approach. To further characterize this co-polymer a thermogram was performed. The overall behavior of this material suggests its possible use as a standard solution for Spectroscopy Equipment Calibration and as a selective optical filter.

Introduction

The basic idea behind the development of inorganic-organic hybrid materials is the combination of inorganic and organic moieties on a molecular scale in order to achieve a synergetic combination of the properties typical of each of the constituents. There is an increasing interest in inorganic–organic co-polymers that are characterized by the covalent incorporation of structurally well-defined compounds [1]. Applications of hybrid materials in optical devices have been extensively reported, such as contact lenses, high refractive index materials, optical coatings, photochromic materials, nonlinear optical materials, etc [2–9]. Much interest has arisen on acrylic polymers, especially poly(methylmethacrylate) (PMMA), because of their well-known optical properties, process compatibility, flexibility in design and the ability for integration of optical functions [6–13].

The PMMA optical properties can be modified through the integration of inorganic compounds such as transition metal-complexes. In this paper, we present a simple synthetic approach to construct a series of Cu(II) containing co-polymers. The co-polymers were designed and synthesized through the reaction of $Cu_2(O_2CC(CH_3)CH_2)_4 \cdot 2\ HOCOC(CH_3)CH_2$ with methyl methacrylate (MMA) and methacrylic acid (HMA). The optical properties of Cu(II)-PMMA co-polymers obtained through these methods were investigated. The absorbance as well as the transmittance spectra were measured in the visible range as function of the Cu(II) methacrylate concentration. From the measured transmittance spectra, $T_{\exp}(\lambda)$, the corresponding index of refraction, $n(\lambda)$, and the extinction coefficient , $k(\lambda)$, are calculated using a numerical inversion method. Finally, the thermal behavior of the synthesized material is considered.

Experimental section

Measurements

FTIR spectra were recorded on a Perkin–Elmer spectrometer Spectrom-1000 by dispersing sample in KBr.

O. Rojas · M. L. Montero (✉)
Escuela de Química, Universidad de Costa Rica,
2060 San Jose, Costa Rica
e-mail: mmontero@equi.ucr.ac.cr

M. Araya · M. L. Montero · D. E. Azofeifa ·
W. E. Vargas
Centro de Investigación en Ciencia e Ingeniería
de Materiales, Universidad de Costa Rica,
2060 San Jose, Costa Rica

D. E. Azofeifa · W. E. Vargas
Escuela de Física, Universidad de Costa Rica,
2060 San Jose, Costa Rica

Thermogravimetric analysis (TGA) was carried out on a Universal V2.5H TA Instrument, under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Absorption spectra were recorded with a Shimadzu UV-60 spectrophotometer. Magnetic measurements were performed on a Johnson–Matthey MSB-1 balance. The co-polymer transmission and absorption spectra were obtained using a CVI spectrometer 3200 with range from 400 nm to 760 nm.

Materials

$CuCO_3Cu(OH)_2$ was purchased from Merk Co. Methyl methacrylate (Aldrich, 99%) and methacrylic acid (Aldrich, 99%) were purified by distillation.

Computational methods

Transmittance spectra of PMMA co-polymer disks normally illuminated, with different thicknesses and containing Cu(II) at increasing concentrations, were measured to obtain from them the corresponding optical constants: $n(\lambda)$, the refractive index and $k(\lambda)$, the extinction coefficient. The spectral dependence of the refractive index gives information about the dispersion of the light when traveling through the medium, while the extinction coefficient determines the degree of light absorption. From the knowledge of the $n(\lambda)$ and $k(\lambda)$ spectral dependence one is able to predict the performance of a material as an element of a structured optical device. From a theoretical point of view the transmission of the disk, considered as an unsupported thick slab, depends on $n(\lambda)$ and $k(\lambda)$, as well as on its thickness h and the wavelength λ of the incident radiation. There is an explicit expression giving a transmittance value $T_{\text{calc}}(\lambda)$ in terms of the optical constants and the slab thickness [14]. However it is not possible to invert analytically this expression to evaluate $n(\lambda)$ and $k(\lambda)$ from $T_{\text{calc}}(\lambda)$, h and λ Thus, numerical approaches are required to carry out the inversion. We have chosen a conjugate-gradient method (CGM) which is very suitable to treat this optimization problem [15] as described below. To accomplish the task from the measured transmittance spectrum, $T_{\text{exp}}(\lambda)$, the cost or objective function F is defined according to:

$$F = \sum_{i=1}^{M} \left| \, T_{\text{exp}}(\lambda_i) - T_{\text{calc}}[n_i, k_i, h, \lambda_i] \, \right|^2 \tag{1}$$

where $n_i = n(\lambda_i)$, $k_i = k(\lambda_i)$ and M is the number of measured spectral points. In order to apply the CGM, F is considered a function of the vector $\mathbf{Z}$ whose $2M$ components are given by $Z_i = n_i$ (i=1,2,...M), k_i ($i = M$+1,...2M). Our purpose is to calculate this vector in such way that $F(Z) \cong \varepsilon_1$ with ε_1 as small as possible for $\| \mathbf{g}(\mathbf{Z}) \| \leq \varepsilon_2$, where $\mathbf{g}(\mathbf{Z})$ is the vector gradient of the function $F(\mathbf{Z})$, and where ε_2 is a previously defined numerical tolerance. The condition $\| \mathbf{g}(\mathbf{Z}) \| \leq \varepsilon_2$ (the norm of each gradient component must be very close to zero) is the numerical approach of the analytical condition $\partial F / \partial Z_i = 0$ with i=1,2, ..., 2M, which defines a system of 2M equations with 2M unknown parameters. In our computations we have used $\varepsilon_2 = 10^{-5}$. In these CGM the desired vector $\mathbf{Z}$ is approached from an initial value $\mathbf{Z}^{(0)}$ according to the formula: $\mathbf{Z}^{(m+1)} = \mathbf{Z}^{(m)} - \alpha_m \, \mathbf{g}(\mathbf{Z}^{(m)})$ where $\mathbf{g}(\mathbf{Z}^{(m)}) = \mathbf{g}_m$ is the gradient of the function F, and m=0,1,2... until the numerical tolerance criterion is satisfied, or until some maximum number of iterations is reached. Several conjugate-gradient approaches have been devised depending on the method followed to compute the steplength α_m in a recursive way. In particular we apply the spectral projected gradient method (SPGM) as devised by Raydan [16], who combines the approach of Barzilai and Borwein to compute the steplength [17] and the nonmonotone line search devised by Grippo et al. [18]: the current approximation of $\mathbf{Z}$ is accepted if $F(\mathbf{Z}^{(m+1)}) \leq F(\mathbf{Z}^{(m-j)}) + \gamma \, [\mathbf{g}(\mathbf{Z}^{(m)})]^t \cdot [\mathbf{Z}^{(m+1)} - \mathbf{Z}^{(m)}]$ with j = 0,1,2,... L where L is a positive integer and where γ is a small positive number. Otherwise the α_m value is recalculated by using two safeguarding parameters, σ_1 and σ_2 with $0 < \sigma_1 < \sigma_2 < 1$, and quadratic interpolation to generate a new α_m value contained between $\sigma_1\alpha_m$ and $\sigma_2\alpha_m$. A typical value of L is 10 and of γ is 10^{-4}. The values of σ_1 and σ_2 were set to 0.1 and 0.9 respectively. Typical values of the optimized object function are of the order of 10^{-15}. The computational efficiency of this approach has recently been compared with that of other standard methods [19]. Several applications of SPGMs have been reported recently in the literature [20–23].

The problem of inversion is degenerate due to the existence of several groups of values of n and k that satisfy the equations within the chosen tolerance. In this sense, a solution given by the SPGM must be analyzed in terms of the previous knowledge one has about the materials being considered, as well as the nature of the expected variations of the optical constants owing to specific physical effects, before it is considered as an acceptable solution. Within this background, the Spectral Projected Gradient Methods are a valuable tool to solve the problem of inverting transmission spectra of thin films, coatings, and thick slabs.

In the following this method is applied to optimize the optical constants of thick semitransparent systems as a function of wavelength. The components n_0 and k_0 of the initial vector Z^0 are not known a priori but for a single wavelength of the undoped material thus, the initial values of n were extrapolated by using a Sellmeier's dispersion [24] approximation:

$$n_0(\lambda) = 1.46 + \frac{4.0}{\lambda - 401.0} \tag{2}$$

(where λ is measured in nanometers) and the parameters in the formula were adjusted in such a way that n_0 corresponds to a particular measurement of the refraction index (namely, 1.49 for $\lambda = 534$ nm). The initial values for the extinction coefficient were calculated using the Beer–Lambert formula

$$k_0 = -\frac{\lambda}{4\pi h} Log(T). \tag{3}$$

This approximation is appropriate when h is relatively large compared to λ as is the case in this work. For samples with higher concentration of Cu(II) methacrylate the values of n and k obtained for previous concentrations were used as initial values.

Synthesis of copper(II) methacrylate, $Cu_2(O_2CC(CH_3)CH_2)_4 \cdot 2HO_2CC(CH_3)CH_2$

A mixture of $CuCO_3Cu(OH)_2$ (0.50 g, 0.78 mmol) in 50.0×10^{-6} m^3 of toluene, and 5.0×10^{-6} m^3 (58.6 mmol) of methacrylic acid was refluxed for 6 h. Right after, 20×10^{-6} m^3 of hexane were added to the reaction mixture and the precipitate was collected, filtered off and washed out with hexane. Greenish blue crystals were obtained. Yield ca. 70%. Mp (240 °C)dc. FTIR (KBr, cm^{-1}): 2967(w), 1680(m), 1646(m), 1594(s), 1414(s), 951(m). UV–Vis (acetone, λ_{max}: 679 nm), ε: 477. μ_{eff}: 1.60. Anal. Calcd. for $Cu_2C_{24}O_{12}H_{32}$: C, 56.2; H, 5.0; Cu, 19.9. Found: C, 52.3; H, 5.10; Cu, 19.7.

Synthesis of copper(II) containing co-polymer

Homogeneous solutions of 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 1.27% mass/volume, Cu(II) methacrylate in a 4:1 mixture MMA : HMA were prepared. Each solution was added into a glass polymerization tube together with the initiator AIBN. The mix was degassed with N_2 and heated at 75 °C per 1 h. Concentrations larger than 2% require longer polymerization times and the final product does not acquire the solid state.

Homogenous, transparent, greenish blue blocks were cut and polished in disks with thickness of 0.70, 1.00, and 1.30 mm respectively. Fig.1 shows the greenish blue appearance of the thick disk. Optical absorbance spectra were collected for different concentrations and thicknesses. Optical transmittance spectra were also measured for the 1.00 and 1.30 mm thick samples, and from these measurements $n(\lambda)$ and $k(\lambda)$ were obtained according to the inversion approach previously described.

Results and discussion

The Cu(II) methacrylate X-ray structure was elucidated in 1986 by Foxman et al. [25]. This complex has the familiar tetracarboxylatedimetal structure adopted by a large number of $M_2(O_2CR)_4L_2$ compounds [26]. Crystals of this material were found to be unreactive upon exposure to X- and γ-irradiation, as well as heating up to 200 °C. We have found, that this compound is reactive in a co-polymerization process. The Cu(II) containing PMMA co-polymer were prepared by the radical polymerization of the Cu(II) methacrylate, MMA and HMA using AIBN as an initiator. Figure 1 shows different Cu(II) co-polymer sample disks with different Cu(II) methacrylate concentrations. The greenish-blue color typical of copper compounds, increases with concentration. From the absorbance measurements it was found that the maximum absorptance occurs at a wavelength equal to 689 nm, which is close to the Cu(II) methacrylate compound maximum absorbance that occurs at 679 nm. This similarity indicates that the Cu(II) methacrylate has not lost its chemical configuration inside the polymer matrix. Furthermore, the absorptance shows a linear behavior as a function of Cu(II) methacrylate concentrations (Fig. 2) for the thicknesses studied, that is, it follows the Beer–Lambert law. This linearity suggests a possible use for this material as standard solution for spectroscopy equipment calibration.

The transmittance spectra, $T_{exp}(\lambda)$, was measured on samples with different Cu(II) methacrylate concentrations, 0 to 1.27 mass %, in the visible range. Figure 3 depicts the results for the 1.0 mm thick disks. Samples with other thicknesses show similar behavior. In contrast with the pure polymer's transmittance spectrum which has almost no structure between 400 nm and 760 nm, the Cu(II) methacrylate containing samples show an attenuation centered at 690 nm, attenuation that gets stronger as concentration increases. In fact for the highest concentration studied, the values of T near the minimum are below the sensitivity of our spectrometer. From $T_{exp}(\lambda)$, the thickness of the sample and using the computational method described above, n and k as functions of wavelength are calculated. These results are shown in Fig. 4(a) and (b) for a few characteristic concentrations. For the doped samples $n(\lambda)$ shows similar behavior as the pure polymer, i.e. $n(\lambda)$ is almost constant with an increase for wavelengths shorter than 450 nm (see Fig. 4a). Figure 5 depicts the calculated values of $n(\lambda)$ for different concentrations at a few given wavelengths. As concentration increases $n(\lambda)$ increases slightly, reaching a change of 3%, with respect to the undoped sample. Most of this change occurs between 0.5 and 0.7 mass % concentrations. The small variation of the refractive index with the Cu(II) methacrylate concentration indicates that the polarization of the polymer matrix

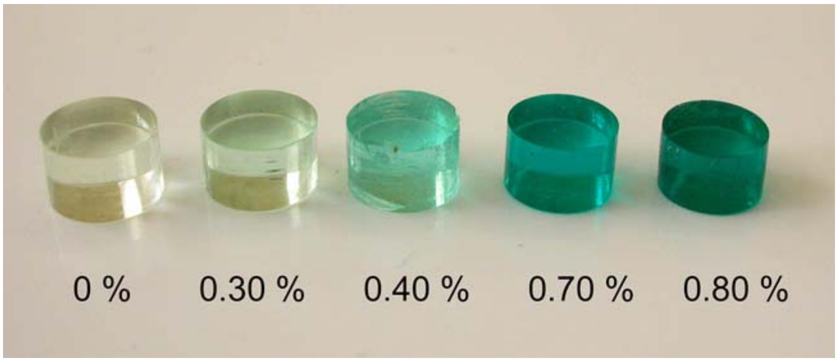

Fig. 1 Picture of disks of the polymer doped with different Cu(II) methacrylate concentrations. Concentrations (m/V) are typical of the samples analyzed in this work

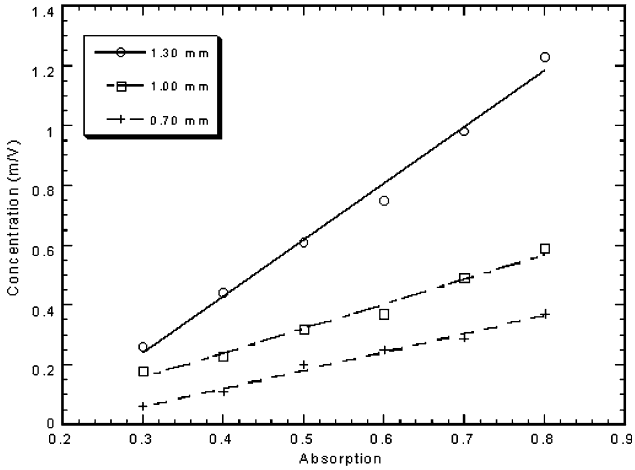

Fig. 2 Measured absorbance for three different thicknesses samples as function of Cu(II) methacrylate concentrations. Each one of them shows a clear linear behavior as expected from the Beer–Lambert Law

surrounding the metal ions does not change significantly when concentrations increases. The $k(\lambda)$ (Fig. 4b) curves show the maximum absorption centered at approximately 695 nm. The values of k allow to calculate the absorption coefficient, $\alpha = {}^{4\pi k}/_{\lambda}$ (see Fig. 6). This calculated absorption has a maximum at 693 nm a value consistent with the measured absorption maximum in the disks and the maximum obtained from the absorbance measurements of the Cu(II) methacrylate. The small magnitude of the absorption coefficient indicates that the composite material is low absorbing, even in the wavelengths of maximum absorption. However the applied inversion technique was able to discriminate the increasing absorption as the Cu(II) methacrylate concentration increases.

The combined behavior of k and n suggest a possible application for this material as a selective optical filter which cuts significantly light with wavelengths larger than 600 nm without significantly dispersing the transmitted light.

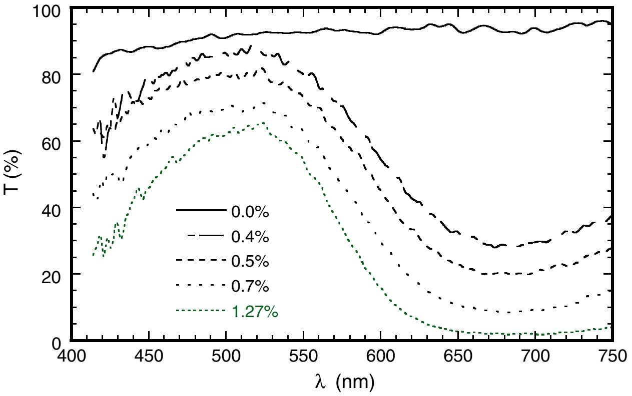

Fig. 3 Optical transmission spectra measured on disks (1.0 mm thick) of different Cu(II) methacrylate concentrations

To study the thermal stability of the Cu(II) co-polymer a comparison between the thermograms of the polymer without Cu(II) and the co-polymer containing this metal was perform (Fig. 7). The Cu(II) co-polymer thermogram exhibits a weight loss at 237, 311 and 422 °C. It is clear, that the first and second peaks correspond to the decomposition of the Cu(II) methacrylate contained and the last peak corresponds to the PMMA matrix decomposition. The study shows that the thermal stability of the Cu(II) co-polymer is lower than the polymer without the metal, which is an indicator that a hybrid material synthesized with a covalent interaction between de Cu(II) species and the polymer matrix.

Conclusions

A series of Cu(II)-containing co-polymer disk was synthesized by direct co-polymerization of Cu(II) methacrylate with methyl methacrylate and methacrylic acid. The Cu(II) methacrylate conserves its chemical and structural composition inside the polymer matrix as strongly suggested by the proximity of the λ values of the maxima in

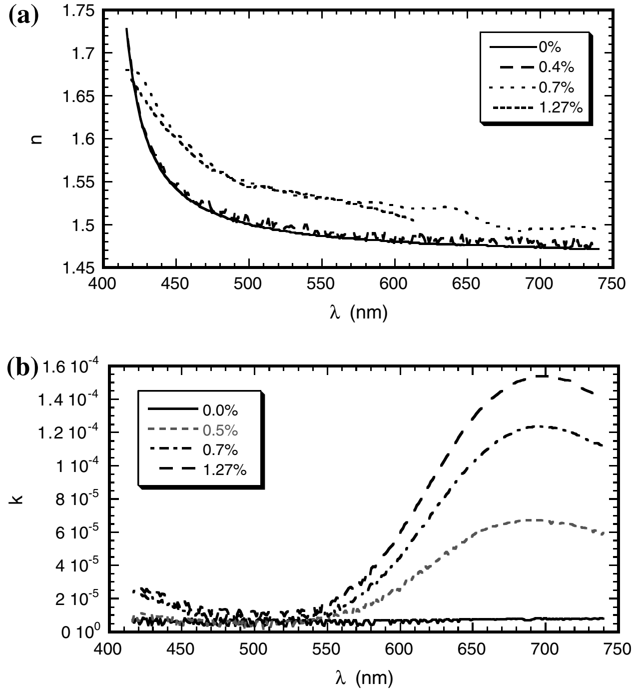

Fig. 4 Calculated values of the refraction index (**a**) and the extinction coefficient (**b**) obtained from $T_{\mathrm{exp}}(\lambda)$ by the SPGM for different concentrations as function of wavelength

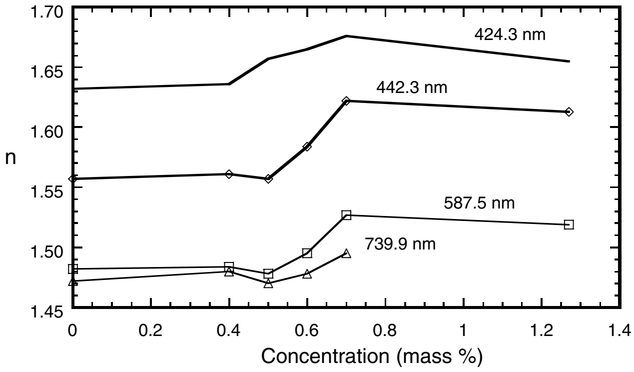

Fig. 5 Calculated values of n for some particular wavelengths as a function of concentration. The maximum change amounts to 3% and most of this change occurs between the concentrations 0.4 and 0.7 m/V with a saturation thereafter

the co-polymer absorptance and extinction coefficient spectra and the λ_{max} in the Cu(II) methacrylate compound absorptance spectra. The absorptance as a function of different Cu(II) methacrylate concentrations in the co-polymer is linear, as expected according to the Beer–Lambert law. The behavior of $\alpha(\lambda)$ as concentration increases clearly shows a selective absorption of light due to the Cu(II) methacrylate. Thermal stability of the Cu(II) co-polymer was lower than the polymer without the metal, indicating the possibility of a covalent interaction between Cu(II) species and the polymer matrix.

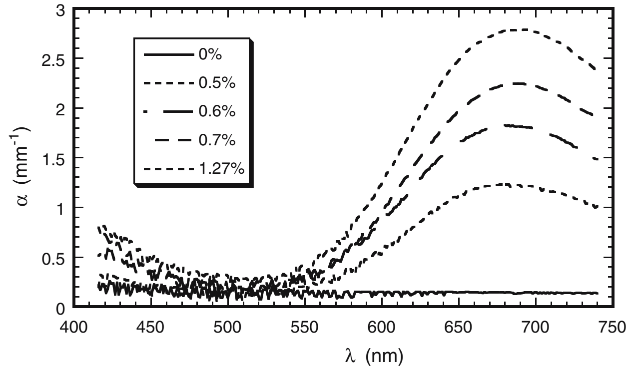

Fig. 6 Calculated absorption coefficient for different concentrations as function of wavelength. The attenuating effect for wavelengths larger than 600 nm is clear as concentration increases while the effect for shorter wavelengths is much smaller

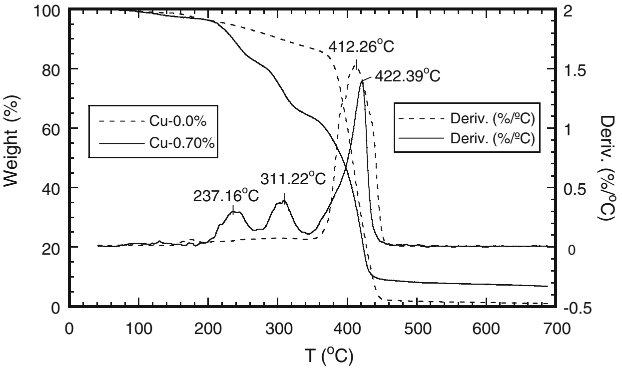

Fig. 7 Thermogram comparison between the polymer without Cu(II) and the co-polymer with Cu(II) methacrylate. The peaks on the derivative of the second sample clearly indicate the Cu(II) methacrylate decomposition

This work also allowed us to show that the SPGM used is an alternative inexpensive approach to study the effects of the doping on the optical parameters of otherwise transparent material. This numerical approach allowed to invert the transmittance spectra to obtain consistent results for $n(\lambda)$ and $k(\lambda)$ as long as appropriate initial values are found and the samples thickness are precisely known. To obtain similar results with other techniques, like ellipsometry, require more specialized and expensive equipment.

Finally, we conclude that the optical characterization this material suggests its possible use as standard solution for spectroscopy equipment calibration as well as selective optical filter.

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