Induction of Photodegradation of Poly(vinyl alcohol) Using a Cobalt Binary Mixed Ligand Complex

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ABSTRACT

ARTICLE INFO

Received: 10 / 07 /2023 Accepted: 21 / 08 / 2023 Available online: 18 / 12 / 2023

DOI: 10.37652/juaps.2023.141493.1097

Keywords:

optical segmentation, PVA, mixed ligands

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1. INTRODUCTION

PVA is produced commercially through the hydrolysis of polyvinyl acetate in a two-step process consisting of the polymerization of free radicals of the vinyl followed by hydrolysis[1,2] Therefore, the structural characteristics of PVA mainly depend on the molecular weight of the polymer and the degree of Hydrolysis, i.e. the percentage of vinyl alcohol in the polymer with increasing degree of hydrolysis of vinyl homogenate into vinyl alcohol, [3] The polymer structure becomes more crystalline, resulting in a heavyduty PVA structure, which becomes chemically inert. The degree of crystallization plays a role [4]Key in controlling the spread of hydrolytes PVA, which can be designed as either an array or tank for pallets[5] Medications .In general, due to its biocompatibility, compatibility with drugs, water solubility, film formation, properties .

mixing the complex [Aqua diphylcarbazide thiourea Cobalt (||)]chloride by weight (0.1% - 0.05%-0.025%-0.0125%-0.00625%) and polymer films dissolved in water and thickness (60±5) microns. The optical degradation of the prepared chips was followed up with the presence and absence of the added complex by violet-visible spectroscopy (U.V) using light with a maximum wavelength (356nm) and at different irradiation times (0,10,20,40,80) hours by calculating the constant rate of photolysis of the polymer additive. Using (FT. IR) by increasing the absorption coefficient of the hydroxyl group (I_{OH}). It was found that an increase in the concentration of the additive complex leads to an increase in the photolysis of polymer sheets compared to sheets without it, which in turn leads to an increase in the values of hydroxyl absorption coefficients. These results are consistent with the value of the speed constant of optical degradation the highest value of the dissociation constant (KD) and follow-up by changing the viscosity to weight ratio, degree of degradation and rate of chain

The present study included optical degradation of pure polyvinyl films and also when

Mechanical and good puffiness, PVA has been studied as a material for eye sutures, eye pain, nanoparticles, and microspheres (floating microspheres, mucous adhesives, transdermal patches, intramuscular drug delivery systems In addition to controlled drug delivery systems. The path of swelling in the colon, rectum, buccal, transdermal and degree[1,2,6] Acidity and temperature .due to its susceptibility to influence hydrogen bonding and excessive crystallization, PVA is very sensitive to moisture $\{2,7\}$ PVA hydrogens generally have distinctive mechanical properties, making them desirable for certain medical and pharmaceutical applications.

All types of polymers (natural, industrial and semisynthetic) suffer from photorefraction, especially when exposed to high beams Energy (UV), where the color turns yellow and its mechanical, physical and chemical properties decompose and change when exposed to the environment[8].

.polymer degradation processes are defined as processes that change physical, mechanical and chemical properties as a result of the effects of mechanical or external thermal, visible UV action and high-energy radiation or chemical exposure. These effects act individually or in combination, for example, oxygen, complexes, mineral salts, water, acids.[9]Rules, as well as air pollutants. Because photolysis is an important way to reduce the problem of environmental pollution caused by residues of materials polymer (plastic), great efforts are being made to increase the fragment ability of disposable polymer materials, using sunlight. The catalysts are in the form of [10]. The production of low molecular weight compounds, The catalysts are in the form of photoactive additives that absorb light in the area near the ultraviolet rays, or in the form of color-absorbing aggregates where[11] These additives are mixed with polymer saclyx or chemically structural of incorporated into the structure polymerization of the material.

Filiphic and aromatic complexes are used as additives to increase the rate of photooxidation of polyvinyl alcohol laminates.[12]

Study that these additives stimulate photooxidation in some polymers. Most transition element complexes are compounds Colorful, which means it is able to absorb energy in the UV region, visible area and infrared areas. The current research aims to find modern chemical and physical methods for the disintegration of single-use plastic materials without damage to the environment and maintained

2. MATERIALS AND METHODS

preparation complex [Aqua diphylcarbazide thiourea Cobalt (II)] chloride and its symbol Co – Y1

Use chemicals processed by Sigma company. The complex is prepared in a 250 ml jar placing 0.238 g of CoCl2.6H2O of absolute ethanol with quiet heating and complete dissolving process was added to it gradually with continuous stirring 0.242g of L1 dissolved in 20 ml ethanol and 0.076 g of L2 dissolved in 20 ml of ethanol leave the mixture in the process of sublimation Retrograde and for two hours, the precipitate was dark brown leaching the solution, so the percentage of the resulting complex after purification was 70%.[13] In the study, an infrared device belonging to a company was used Bruker And the ultraviolet-visible device belongs to the company Jenway . The results of the prepared complex showed that it takes the shape of a square planer.

Modeling

The samples were prepared in the form of flakes by dissolving polyvinyl alcohol in water and adding a

compound in the form of a catalyst and molded on glass panels with a thickness of (60±5 Maykrone), and the thickness was measured for the polymeric foils used in the search using the device (USA,company,panel. Q, Vtester.U.Q)(micrometer) then cut the models into Slices (1.5×3) cm according to the purpose for which the measurements were made.

Irradiation of models

The models prepared using a laboratorymanufactured irradiator were irradiated with a lamp equipped with a power of (18 watts) and a filter length 356 nm wave, for 80 hours and for several stages. The irradiated chips are placed in the device perpendicular and parallel to the lamp to ensure that UV rays fall perpendicular to the polymeric foils, the locations of the polymeric foils are changed periodically to ensure uniformity of the intensity of light incident on all polymer chips.

study spectral

Photodissociation of polymer sheets is used using device FTIR to determine the intensity of the absorbed beam before and after irradiation by measuring the amount of growth(I_{OH})as one guidesfell apart alcoholic polymer [14].

Calculation of the optical degradation speed constant of polyvinyl alcohol flakes with complex

Calculation of optical degradation rate constants for poly (vinyl alcohol) flakes with composites using UV spectrometer to calculate Absorption of prepared polymer plates in the wavelength range 400-800 cm-1. Optical oxidation of compounds prepared using the equation of the law of the first degree: [15]

 $Ln (a-x) = Ln a - k_dt \dots(1)$

Whereas:-

A : concentration of the complex before irradiation .

x : change in the concentration of the complex after time (t) of irradiation.

t : irradiation time (s).

If we consider that the absorption of the polymer wafer before the start of the irradiation process is (Ao) and the absorption after a period of irradiation is represented by t for the laminates itself with (At), so it is possible to consider($A\infty$) as the absorbance of the chips at the end. By linking absorption and concentration,

$$\mathbf{A} = \mathbf{A}\infty - \mathbf{A}\mathbf{o}$$

$$\mathbf{x} = \mathbf{A}\mathbf{t} - \mathbf{A}\mathbf{o}$$

 $A - x = A\infty - Ao - At + Ao = A\infty - At \dots(2)$

Substituting the values of (x-a,(a) into equations (1and 2) yields

 $\ln (A\infty - At) = \ln (A\infty - Ao) - Kdt \dots (3)$

When constructing the relationship between $(At\infty - Ao)$ ln and irradiation time (t) (seconds), we get a straight line with a slope of (-Kd)this it indicates that the degradation of additives is of the first class.

determination of the even rate of molecular weight by viscosity method the partial weight of the polymer wafer was calculated based on viscosity properties using the Houwink-Mark equation and from viscosity measurements the hash score (α) and the numerical average of the division of the series (S) were calculated using the following relationships: [16] The degree of fragmentation α) is calculated by the following relationship:

$$\alpha = \frac{1}{pt} - \frac{1}{po} \dots \dots \dots \dots \dots (4)$$

The numerical rate of cutting the series (S) is: S = α P0.....(5)

3. RESULTS AND DISCUSSION

Spectral study of the complex

It has been shown from the measurements of the molar electrical conductivity in the DMF solvent that it is consistent with the proposed structural formulation of the complexes, as it behaves electrolytic behavior consistent with what has been published from previous research, the molar electrical conductivity was $(133\Lambda_M \text{ cm2.ohm-1.mo}).[18]$

The magnetic sensitivity of the complex was also measured and its value (2.3) B.M, which showed that the proposed shape is tetrahedral and is consistent with research published in the same field.[17,18]

The ultraviolet spectrum was measured in a dimethylsulfoxide (DMSO) solvent using a cell with Diameter 1 cm and at room temperature, as can be seen from Figure (1) and Table (1)

Infrared technology was also used in this research to diagnose the prepared complexes through Comparison of the spectra of licandes with the spectra of the prepared complexes. Shows the most important elastic vibrations of important bonds.

In the prepared licandes and complexes, the following group stretch vibrations were emphasized :[18,19]

1- Group stretch vibrations (C=O)

2- Group stretch vibrations (C=S)

- 3- Group stretch vibrations (N-H)
- 4- Group stretch vibrations (M-X)

This package can be seen in the complexes prepared in this paper.

1-Group stretch vibrations (C=O):

Group stretch vibrations (C=O) appeared in the licandes at Range (cm 1618-1620), and the decrease in the values of this group is observed in the case of complexe, as it is shown in the table(2), this decrease in the elasticity (C=O) indicates the bond of the metal to the oxygen atom. Affiliated to the group (C=O).

2-Group stretch vibrations (C=S):[20]

Group stretch vibrations (C=S) appeared in the licandes at the value of (728cm) This value has been shifted towards lower frequencies in all complexes, as shown in the table(2) and figure(2), which indicates the bonding of the metal to the sulfur atom belonging to the sum of (C=S).

3- Group stretch vibrations (N-H):

Group stretch vibrations (N-H) appeared in the licandes atrange (3360-3330cm⁻¹), it was observed that the values of this group in the complexes are constant or close to Its values are in the spectrum of the prepared licandes, as shown in Table (2), which indicates that the set of (N-H) did not share consistency with metal .

4-Group stretch vibrations (M -X): We find that group stretch vibrations (M-X) where the M-N beams appearM-O and M-S beams are in the prepared complex (443,513,420) respectively, while these types of beams do not appear in lycands.

Follow-up of optical degradation of poly phenyl alcoholic flakes in the presence of different concentrations of complex (Co-Y1) in ultraviolet-visible spectroscopy.

Irradiation of pure polyvinyl alcohol with highenergy UV rays with a wavelength of 356 nm leads to clear changes in the radiation spectra under the heat of the ultraviolet rays Increased absorbency at wavelengths above 280 nm, indicates bond absorption [14]

Multiple doubles that propagate to longer wavelengths in the visible spectra of ultraviolet rays (Table 4) illustrates this, and shows the ray spectrum ultraviolet-visible of alcoholic poly phenylic catalyzed by the addition of complex (CO-Y1), concentrations

P- ISSN 1991-8941 E-ISSN 2706-6703 2023,(17), (2):115 – 125

(0.1%,0.05%,0.025) high acting on Increasing the degradation speed by photooxidation of poly phenyl alcohol flakes, and this can be observed through an increase in the value of absorbency (shape 11,12and 13) where the beams of the poly phenyl alcohol added to the complex appear higher than the packets of the poly phenyl alcohol free of addition, where it works the complex added as a catalyst for dissociation, while the spectra of polyvinyl alcoholic flakes added to low concentrations (0.00625)%.0.0125%) give low absorption packs (Figure 9,10), which in turn are higher than additive-free PVA absorbers (Fig. 8).

Follow-up optical segmentation of multiple chips vinyl alcohol In the presence of concentrations different from complex(Co-Y1) by infrared spectroscopy.

appears (Fig3,4) changes in infrared additivefree polyvinyl alcohol (PVA)(60 ± 5) microns, ftheirr adiation time (80) Hours, as the package appears petition with in range (3200-3600) cm-1, which is increasing ad Irradiation time, due to the formation of hydroxyl groups and polymeric hydro peroxide [21]Which is one of the types formed from the dissociation process of poly(vinyl alcohol), bearing in mind that this absorption band is present at a very low value before the start of the chips irradiation process as a result of thermal oxidation during the polymer manufacturing process. .Infrared spectroscopy provides evidence for increased photodissociation of alcoholic, as shown in (Table3) and (form6). count hydroxyl absorption coefficient (I_{OH}) using the baseline method (Band Index) [22], where a straight line is drawn between the two shoulders of the beam to extract the baseline for calculating the difference between the growth of peaks and the increase in their intensity with the increase in irradiation time and its relationship with focus the added accelerator .The changes in the carbonyl group were not monitored due to the difficulty of measuring them because they were very slight.

The results of multiple irradiation came Vinyl alcohol using concentrations different it has an effect Clearhin spectra the rays are underred FTIR, as it appears high concentrations((0.1,0.05%0.025))wide package with in the range((3150-3650) cm⁻¹, which he explained that it is due to the hydroxyl groups and the polymeric hydro peroxide formed during irradiation, While the value of the hydroxyl coefficient (I_{OH})At low

concentrations(%0.0125%, 0.00625) (afor schedule 3) And It showed through drop the intensity of the bundle and its appearance as bundles is weaker than that of bundles Concentrations aliyah and this in turn Higher than the multi-absorbency packet alcoholic phenyl additive-free (Fig3).

These results are consistent with the values of the dissociation constant calculated from the slope of the straight line in (Figs14-18)Where the percentage of the addition of the complex (0.1) to the flakes gave the highest percentage of the dissociation constant, while the addition percentage (0.00625%) gave a say value for the dissociation constant (Table4).

Follow up the optical degradation of the polymeric chips with the presence and absence of a concentration (0.1%) of the complex by viscosity method.

Viscometry shows that the viscous partial weight rate decreases with increasing irradiation time due to fragmentation of the polymer chains (Table6,7), and (Fig 19) A decrease in the viscous partial weight in the presence of pain additive complexes, and the figure shows a rapid decrease in the partial weight at the beginning of the irradiation, then a slow downa, attributed alow quick to break ties at weak links[23],And(the shape20) appears that speed alow the average viscous molecular weight is proportional to the square of the weight viscosity at the time [24], indicating a random distribution of ligands along the polymer chain, as indicated by the linear relationship between the chain breaking rate and the degree of fragmentation in(shapes21,22,)respectively [25], they give another indication of the efficacy of complexes promoting photolysis. So can be used complexes under consideration in high proportionsinthe production of plastic materials, agricultural containers, shopping bags, or disposable items to accelerate degradation in order to prevent environmental pollution with plastic materials, and the results of the empirical research are consistent with the data of references in this area.

Conclusions

It was concluded from this current study and the results that were reached that the dissociation of poly phenyl alcohol increases with the addition of the prepared complex, and it was found that the highest concentration for the 0.1% complex, it gave better

results than other concentrations of the additive and polymer without the additive

In a previous study, PVA decomposition was found to be good for preparing 25 nm nanooxide by the Sol - gel method, and was used to prepare compounds, with polyvinyl alcohol PVA by various weight, exposing PVA films to ultraviolet (UV) for 96 hours. The films have shown secondary compounds with lower thermal stability than the pure PVA film, and the price data indicate the interaction between polyphenyl alcohol (PVA) and zinc nanooxide in the compact film by directly relying on the secondary zinc oxide concentration. The original structure of the secondary zinc oxide remains unchanged in the PVA matrix and is distributed uniformly on the film surface. The roughness of PVA film was not modified after the addition of zinc nanooxide; however, it increased after 96 hours of ultraviolet (UV) irradiation, and films showed absorption at 370nm and wide emissions in the visible ultraviolet region.[26]

A comparison of this study with that of the study found that the effect of addition of polymer oxide for photosynthesis has more effect than complex addition. This research, however, has studied photolysis of polymer in order to find new ways of disintegrating polymer to achieve a less polluting environment in a large number of ways.

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Table (1) : the electronic spectra of the

	0	
Complex and ligand	(nm)	Electronic transition type
т 1	282	$\pi \rightarrow \pi^*$
LI	470	n→π*
1.2	242	$\pi { ightarrow} \pi^*$
L2	401	n→π*
	270	$\pi { ightarrow} \pi^*$
Co-Y1	538	$^{2}A_{1}g^{2}E_{1}g$
	252	$n \rightarrow \pi^*$

Table (2) : Values and frequencies of infrared spectra in cm units of the levands under study M-S, M-O, M-N, C=S C=O N-H complexes

Complexes	N-H v	C=O	C=S	M-N	M-0	M-S			
L1	3337	1652							
L2	3364		728						
Co-Y1	3331	1595	706	443	516	423			



the shape(3): The infrared spectrum of a poly(vinyl alcohol) additive-free film with a thickness of (5 ± 60) microns before irradiation.



the shape(4): The infrared spectrum of a poly (vinyl alcohol) film without additives, with a thickness of (60 ± 5) microns, and an irradiation time of (80) hours.

P- ISSN 1991-8941 E-ISSN 2706-6703 2023,(17), (2):115-125



the shape (5): Infrared spectrum of a poly(vinyl alcohol) film with a thickness of (60±5) microns containing complex (Co-Y1) at a concentration of (0.1%).and irradiation time (80) h.

Table 3: Hydroxyl group adsorption coefficient values (I_{OH}) with the irradiation time of poly(vinyl alcohol) containing different concentrations of complex (Co-Y1).

I _{OH}					irradiation time (hour)		
80	40	20	10	0	percentage for additivesw%		
2,856	2,066	1,779	1,706	1,545	PVA		
3,206	2,404	2,122	2,012	1,778	PVA+ 0.00626% Co-Y1		
3,508	2,844	2,403	2,172	2,007	PVA+ 0.0125% Co-Y1		
3,889	3,234	2,711	2,467	2,291	PVA+ 0.025% Co- Y1		
4,233	3,601	3,003	2,678	2,483	PVA+ 0.05% Co- Y1		
4,660	4,027	3,408	2,967	2,689	PVA+ 0.1% Co-Y1		







Figure (7) Change in hydroxyl adsorption coefficient with complex concentration (Co-Y1) for poly(vinyl alcohol) chips with a time of (80) hours



Figure (8): Variation in UV-Visible spectrum of additive-free poly(vinyl alcohol) films with thickness(60 \pm 5) microns at the irradiation times.





it's complicated(Co-Y1) has a thickness of $60 \pm 5 \,\mu\text{m}$ at the irradiation times











Figure 12: Variation in the ultraviolet-visible spectrum of poly(vinyl alcohol) films containing a concentration of 0.05% it's complicated(Co-Y1) with a thickness of (60 \pm 5) microns at the time of irradiation



Figure 13: Variation in the ultraviolet-visible spectrum of poly(vinyl alcohol) films containing a concentration of 0.1% of the complex (Co-Y1) with a thickness of (60 \pm 5) microns at the time of irradiation.

Schedule(4) Absorbance values of poly (vinyl alcohol) films with a thickness of (60 ± 5) microns pure, as well as containing different concentrations of the complex (Co-Y1), calculated at wavelength 280 nm from UV-Visible spectroscopy measurements.

	a	Irradiation			
80	40	20	10	0.0	chips type
0.305	0.220	0.174	0.131	0.119	PVA
0.359	0.271	0.217	0.162	0.129	PVA + 0.00625% Co- Y1
0.404	0.351	0.287	0.199	0.130	PVA + 0.0125% Co- Y1
0.503	0.433	0.357	0.269	0.132	PVA + 0.025% Co-Y1
0.571	0.490	0.429	0.307	0.133	PVA + 0.05% Co-Y1
0.632	0.554	0.475	0.358	0.135	PVA + 0.1% Co-Y1



Figure 14: The relationship between the natural logarithm of the complex absorbance (Co-Y1) at a concentration of 0.0626% in poly(vinyl alcohol) films

with a thickness of (60 \pm 5) microns with an irradiation



Figure (15): The relationship between the natural logarithm of the complex absorbance (Co-Y1) at a concentration of 0.0125% in poly(vinyl alcohol) films with a thickness of (60 ± 5) microns with an irradiation



Figure (16): the relationship between the natural logarithm of the complex absorptivity (Co-Y1) at a concentration of 0.025% in poly(vinyl alcohol) films with a thickness of (60 ± 5) microns with an irradiation



Figure (17): the relationship between the natural logarithm of the complex absorptivity (Co-Y1) at a concentration of 0.05% in poly(vinyl alcohol) films with a thickness of (60 ± 5) microns with an irradiation time



Figure (18): The relationship between the natural logarithm of the complex absorbance (Co-Y1) at a concentration of 0.1% in poly(vinyl alcohol) films with a thickness of (60 ± 5) microns with an irradiation time

Schedule (5) The values of the dissociation velocity constants Kd for the complex (Co-Y1) in poly(vinyl alcohol) films

alconor) mins.					
dissociation velocity constantKd (Sec.)-1x10-5	the focus %Co-Y1				
0.357	0.00625				
0.454	0.0125				
0.537	0.025				
0.550	0.05				
0.581	0.1				

Schedule (6): Values calculated from viscous molecular weight measurements of pure poly(vinyl alcohol) chips

1 average to cut Series (S)	م 0.0	0.18 7	0.42 5	0.74 0	1,07 4
Degree hash ax10-3	0.0	0.189	0.428	0.745	1,081
$\frac{1}{P}x10^{-4}$	10,061	11,952	14,347	17,514	20,872
degree of Jymerization P	993,886	836,636	696,977	570,954	479,090
$\frac{dM_v}{dt} = \frac{dt}{M_{v0} - M_{vt}}$	00	0.192	0.181	0.129	0.078
$(M_v)^2 x 10^9$	1,912	1,355	0.940	0.631	0.444
$(M_v)x10^3$	43,731	36,812	30,667	25,122	21,080
time :adiation (hour)	≓. 0	10	20	40	80

Schedule (7): Values calculated from viscous molecular weight measurements of poly(vinyl alcohol) chips containing 0.1% concentration of complex (Co-Y1)



0	43,731	1,912	x	993,886	10,061	0.0	0.0
10	34,098	1,162	0.267	774,954	12,903	0.284	0.282
20	27,002	0.729	0.232	613,681	16,295	0.623	0.619
40	21,567	0.465	0.153	490,159	20,401	1,034	1,027
80	18,089	0.327	0.089	411,113	24,324	1,426	1,417



Figure (19) The relationship of the average viscous molecular weight with the irradiation time of poly(vinyl alcohol) chips in the presence and absence of concentration0.1% of complex (Co-Y1)



Figure (20) The relationship between the speed of decrease in the rate of molecular weightdMv/dt) and the square of the average viscous molecular weight of a

poly(vinyl alcohol) flake in the presence and absence of a concentration of 0.1% of complex (Co-Y1)



the shape(21) The relationship of the numerical rate of chain cutting with the irradiation time for a poly (vinyl alcohol) foil with a thickness of (5 ± 60) in the presence and absence of a concentration of 0.1% of the complex (Co-Y1)



the shape(22) The relationship of the degree of fragmentation with the irradiation time for polyvinyl alcohol films with a thickness of (5 ± 60) microns in the presence and absence of a concentration of 0.1% of the complex (Co-Y1)

حث التحلل الضوئي للبولي (كحول فينيل) باستخدام معقد الكوبالت الثنائي مختلط الليكاندات

یاسمین مثنی یاسین 1 ، حمید خالد علی 2 ، عمر حمد شهاب 3

^{2،1} قسم الكيمياء ، كلية التربية للعلوم الصرفة ، جامعة الانبار ، العراق ³قسم الكيمياء ، كلية العلوم ، جامعة الانبار ، الرمادي ، العراق

الخلاصة:

اشتملت الدراسة الحالية على التفكك الضوئي لأغشية البولي فينيل الكحولي النقية وأيضًا عند خلط المعقد [أكوا ديفيل كاربازيد ثيوريا كوبالت (II)] كلوريد بالتراكيز (0.1% 0.025-0.025-0.025-0.02%) وأغشية بوليمر مذابة في الماء وسمك (60 ± 5) ميكرون . تمت متابعة التفكك الضوئي للرقائق المحضرة بوجود وغياب المعقد المضاف بواسطة التحليل الطيفي المرئي البنفسجي (UV) باستخدام ضوء بطول موجي أقصى (356 نانومتر) وفي أوقات تشعيع مختلفة (0،0،10،20،40 ، 80) ساعة عن طريق حساب المعدل الثابت للتحلل الضوئي لمادة البوليمر المضافة. استخدام (IT) عن طريق زيادة معامل الامتصاص لمجموعة الهيدروكسيل (IOH). وجد أن زيادة تركيز المركب المضاف يؤدي إلى زيادة البوليمر المضافة. بالصفائح بدونها مما يؤدي بدوره إلى زيادة قيم معاملات امتصاص الهيدروكسيل. تتوافق هذه النتائج مع قيمة ثابت السرعة للتدهور البصري وأعلى قيمة لثابت التفكك (KD) والمتابعة عن طريق تغيير نسبة اللزوجة إلى الوزن ودرجة التدهور ومعدل قطع السلسلة.

الكلمات المفتاحية: التجزئة الضوئية ، pva، مختلط الليكاندات