

Synthesis and studying the electrical conductivity and optical storage properties of some azo polymers

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Abstract

Seven azo polymers of different azo content and different intra-spacing linkage (aromatic or aliphatic esters and aromatic amide) are prepared by using interfacial polymerization process . The synthesized polymers were characterized by IR, ^1H NMR and ^{13}C NMR. The electrical conductivity and its activation energy were measured by using three probe cell. The optical absorbance measurement were carried out on the thin film of the prepared polymers through irradiation by 20 mW/ cm^2 green laser beam for appropriate time until saturation.

It was shown that there are many factors affecting on the electrical conductivity and the energy storage and release like chain flexibility and the type of spacing groups between the azo moieties.

The content of azo groups within the repeating unit showed an effect on the electrical conductivity but has no effect on the optical properties.

Keywords: azo polymer, photoisomerization, electrical conductivity, optical storage.

Introduction

Azo benzene is a chemical compound composed of two phenyl rings linked by N=N double bond. The azo compounds are considered as derivatives of diazene (dimide)⁽¹⁾. One of the most important properties of the azobenzene and its derivatives is the photoisomerization of trans isomer to cis one⁽²⁾. The two isomers can be switched with particular wavelength of light, UV light corresponds to the energy gap of $\pi \rightarrow \pi^*$ transition for trans - to - cis conversion whereas blue light is equal to that of the $n \rightarrow \pi^*$ transition for cis - to - trans transition⁽³⁾. For a variety of reasons the cis isomer is less stable than the trans, thus cis - azobenzene will thermally relax back to the trans isomer⁽⁴⁾. The trans isomer is more stable by approximately 50 KJ / mol. The growing interest in azobenzene - containing polymers is because of their potential utilities in many applications as in halographic storage and other optical and photonic applications^(5,6).

The influence of the polymer properties on the photochemical and thermal isomerization have been demonstrated by kinetics studies on different azo polymers. The rate of isomerization of the azo group attached covalently to the polymer chain depends on the structural properties of the matrix⁽⁷⁾.

The effect of azo contents on the photoinducing processes have been studied by many others⁽⁶⁾. It was shown that the dichroism and photoisomerization from trans to cis was decreased within the azo contents, while incorporation of biphenyl moieties in the backbone of the azo chain give place to increase of the order parameter and increase the photoisomerization processes⁽⁹⁾.

It was shown that bis azo polymers are promising for electro - optic applications⁽¹⁰⁾, since the azo moieties can enhance the conjugation of polymeric chain with their unsaturation contents. The high chromophore densities can lead to head - to - tail oriented chromophores which may increase the conductivity significantly⁽¹¹⁾. It was noticed that orientation of the azo chromophores change the charge carrier mobility and enhancing the ionic conductivity⁽¹²⁾.

Herein, we analyze the electrical conductivity and the photoisomerization properties of polymers with different azo moieties density. The influence of azo content and chain configuration of the prepared polymers are studied.

Experimental

Materials:

Chloroform, ethanol, methanol, acetone, dichloroethane and DMSO (Fluka) are dried before used with suitable drying agent. Aniline (Fluka) was purified by distillation under vacume before used. Hydrochloric acid (Fluka), sodium nitrite (B.D.H), phenol (Fluka) , sodium hydroxide (B.D.H), sebacoyl chloride (B.D.H). phthaloyl chloride (Fluka), p-phenylene diamine (Fluka), p-aminophenol (Fluka), 4,4'-methylene dianiline (B.D.H) were used as received.

Synthetic rout:

Monomers preparation:

Amino tetrazonium (II) was prepared by dissolving 0.25 g of 4,4'-methylene dianiline in 20 ml of concentrated hydrochloric acid. An aqueous solution of 0.3 g of sodium nitrite was added drop wise during 30 min. with stirring at -10°C . The stirring was continued for 30 min. at this temperature to the formed suspended solution, 4 ml of aniline was added to the this solution and stirred for 1.5 hr. The precipitated monomer was filtered, washed with chloroform and dried under vacuum.

The phenolic dizonium monomer (I) was prepared by dissolving 1.8 g of p-aminophenol in 4 ml of water and 4 ml of concentrated hydrochloric acid. The solution was cooled to 0°C . A solution of 1 g sodium nitrite in 2ml water was added drop wise in a period of 0.5 hr at 0°C , 12 ml of a solution of 1.2 g phenol dissolved in 12 ml of 10% NaOH was added to the cooled dizonium salt solution under cooling for a period of 0.5 hr. The precipitated monomer was filtered washed with chloroform and dried under vacuum.

Phenolic tetrazonium monomers (II) was also prepared by the same method through the azotisation

of 0.25 g of p-phenylene diamine by sodium nitrite and concentrated hydrochloric acid under cooling at (-10°C), the tetrazonium salt was reacted with solution of phenol in sodium hydroxide solution.

The phenolic tetrazonium monomers (III) and (IV) were prepared by azotisation of 4,4'-methylene dianiline and amino tetrazonium monomer I respectively. The disodium salts were reacted with phenol to obtain the indicated monomers.

Polymer synthesis:

Polymer I was prepared by dissolving 0.428 g of phenolic diazonium monomer I in 5 ml of 1N NaOH (aqueous). Another solution contain 0.288 ml of phthaloyl chloride in 5 ml DCE was poured on the first solution, and mixed well at room temperature. The separated polymer was filtered, washed with chloroform and dried under vacuum.

All the investigated polymers in this work were prepared by the same method as shown in table (1). The prepared monomers and polymers have been characterized by using FTIR spectrophotometer, biotech. engineering management CO. LTD, UK, ¹HNMR and ¹³CNMR Bruker (300MHZ).

Electrical conductivity measurements:

Films of 2 cm diameter and about 0.5 mm thickness from the pure polymers are prepared under 3-4 ton / cm². Electrical volume conductivity measurements are performed using the standard 3-probe D.C technique according to the ASTM method⁽¹³⁾.

Optical measurements:

Thin films of the synthesized polymers have been accomplished on a pre – cleaned glass substrate using spin coating technique from DMSO solution 10% at 4000 r/m rotation. The specimens were kept in dark and dried atmosphere until conducting the optical measurements. The specimens were irradiated with a green laser beam of 20 mW/cm². The maximum absorption was measured during irradiation until saturation. The laser then turned off and the absorption was followed until a constant absorption values was reached.

Results and discussion

Synthetic routs:

Schem 1 illustrate the synthetic route for the preparation of dizonium monomers. The monomers were characterized by IR spectroscopy . The frequency of the bands belong to the different functional groups of the synthesized monomers are shown in table 1.

Seven different azo polymers have been prepared by using interfacial polymerization process. Polymers I-VI are polyesters of different moieties within the repeating unit. Polymers I and II are aromatic polyesters of repeating units containing one and two azo groups respectively. Polymers III and IV are respected to polymers I and II with long aliphatic group within the chain. Polymers V and VI are aromatic polyesters with methylene groups separate two azo moieties. Polymer VIII is consort of polymer

V except it was a polyamide type. Table (2) shows the chemical structures of the prepared polymers.

The IR spectrums of the polymers show a new characteristic bands which are belong to the functional groups formed through polymerization processes. Polymer I spectrum shows a band at 1743 cm⁻¹ and two bands at 1200 cm⁻¹ are belong to the carbonyl and C-O ester groups respectively. The C=O band of polymer II was appeared at 1813 cm⁻¹. The spectrum of polymer III shows a new band at 1302 cm⁻¹ which is related to the aliphatic segment. In spectrum of polymer V there is a band appeared at 2925 cm⁻¹ belong to methylene group.

Tables (3) and (4) indicates the chemical shifts appeared in ¹H NMR and ¹³C NMR of the investigated polymers respectively.

Electrical conductivity measurements:

Effect of chemical structure:

Table (5) shows the volume electrical conductivity of the pure prepared polymers under different electrical fields.

The results indicate that the electrical conductivity increased with increasing the applied voltage, except that in polymers I and II. This may be explained by that the applied voltage effects on the polarization of the azo moieties and increased its dipole moment and make the charge transferred more easy.

It is clearly noticed that the chemical structures of the investigated polymers are very important in effecting the measured conductivity. Azo group can be considered as a rigid rod, increasing its ratio in the main chain result a decrease in the flexibility and decrease the conductivity, this can be observed on going from polymer I to II. This effect was neglected when the comparison is between polymer III with IV, where the chain conjugation was interrupted by aliphatic moiety, which led to increasing flexibility by a large magnitude and increase the conductivity.

On the other hand the conductivity was decreased on going from polymer I to III, where the chain was interrupted by long aliphatic group which weaken the conjugation in the main chain. The flexibility effect on conductivity is dominate when the chain was interrupted by only methylene groups as shown in comparison between polymer I and IV.

Temperature effect:

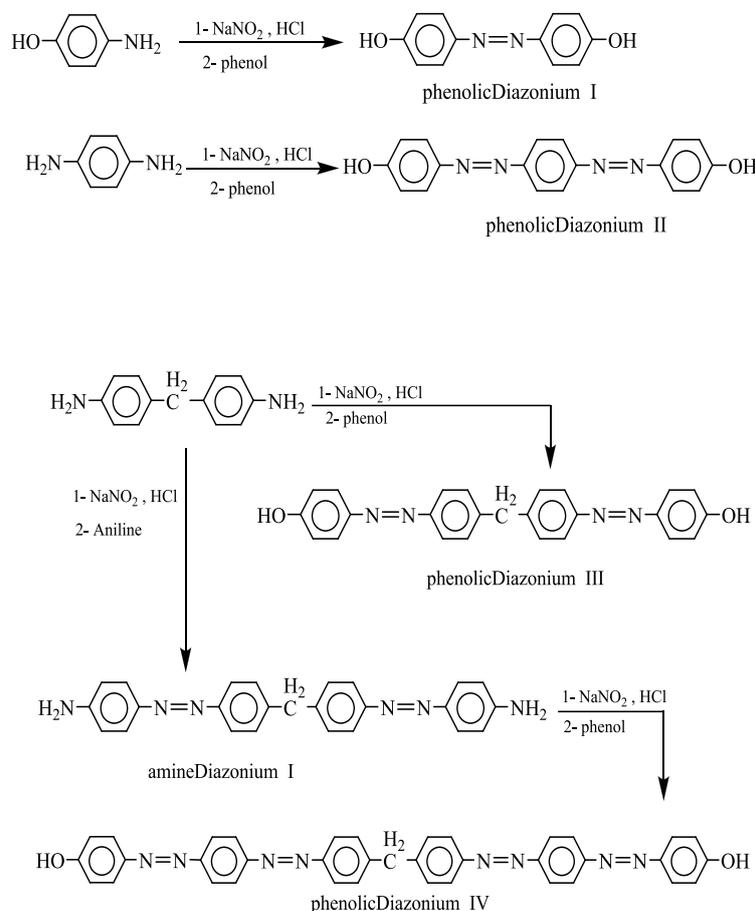
Table (6) shows the electrical conductivity of the prepared polymers at different temperature. There are a systematic increase of the electrical conductivity with the temperature. The calculated activation energy derived from the relation between log electrical conductivity vs. the inverse absolute temperature was shown in Table (7). The increasing in the conductivity with temperature elevation can be attributed to two kinds of hypothesis, the first one is due to increasing the distribution of electrons from HOMO to LUMO levels by increasing temperature, this need an activation energy lay in 0.1-0.15 eV⁽¹⁵⁾, the second hypothesis is belong to increase the segmental motion by temperature elevation under T_g,

this need higher activation energy than the first one⁽¹⁶⁾. The results in table (7) proved that the second hypothesis is dominate.

Optical measurements:

The cis-trans isomerization in the azo group can be estimated as an optical energy storage processes. This behavior of the prepared chromophores are investigated at room temperature by means of photolysis. The polymers film are irradiated with a linear polarized beam of a green laser light with 20 mW/cm². Before irradiation, the azo chromophores can exist only in the energetically favored trans forms. Since the laser beam turned on, photoisomerization is induced and photostationary state of both trans and cis isomer is reached. This causes a sharp decrease in the absorbance and hence an increase in the light intensity passing through the sample. Once the beam is turned off, thermal cis-trans isomerization spontaneously follows and put the system back into the more stable isomer⁽¹⁷⁾. Table (8) shows the results of irradiation the samples. As we can postulate that the time of irradiation until reaching the saturation is the time needs to storage the sufficient energy within the sample, whereby the time after the laser is turned off until the absorbance reaches the original absorbance can be represented as the time needs to loss the stored energy. On the other hand, the difference between the absorbance before

and after irradiation represent the amount of energy stored in the sample film. The results in table (8) revealed that the chemical structure and the of azo content in the repeating unit plays the important role affecting on these processes. The long flexible spacers within the polymer chain between the azo groups assists to store energy by reducing the time to reach the saturation and the time to loss the stored energy but reduced the amount of the stored energy. This effect can be explained by that the flexible spacer (that can enhanced the formation of an amorphous phases) produce an anisotropy optical properties, as shown in comparison between polymer I with III or II with IV. It can be noticed that the presence of methylene group between the two phenyl groups substituted with the azo groups have the same effect of the long spacers as shown in polymers V and VI. Comparison between polymer V with VII, the chemical structure difference is in the type of the linkage moieties(ester in polymer V and amide in polymer VII) indicate that the ester group is more efficient in taken and holding the energy than the amide group, while the amount of energy was reduced to about half. It was necessary to observed that increasing the amount of azo contents within the repeating unit have no noticeable effects on these optical properties.



Scheme 1 : Synthetic route of monomers preparation

Table 1 : FTIR band frequencies of the monomers

Monomer	-OH	NH ₂ -	C=C aromatic	N=N	-CH Aliphatic
Phenolic(I)	3979	-----	1506	-----	-----
Phenolic(II)	3481	-----	1516,1489	1628	-----
Phenolic(III)	3350	-----	1417,1361	1624	Bending 1190
phenolic IV	3309	-----	1568,1520 1471,1404	1653	2947 def
Amine (I)	-----	3240	1558,1508	1616	2925 def

Table(2): Chemical formula of prepared polymer

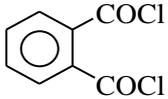
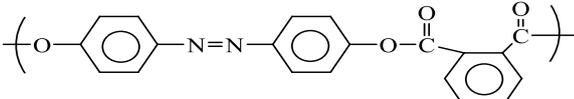
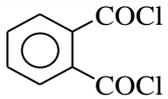
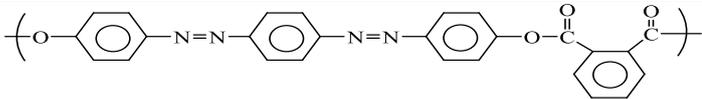
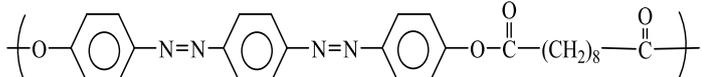
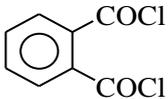
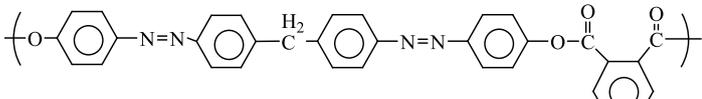
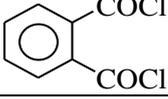
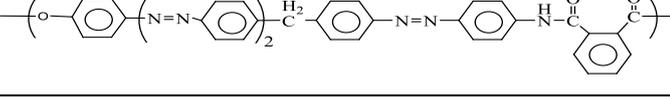
no of pol	First monomer	Sec. monomer	Pol. structure
I	I		
II	II		
III	I	ClCO(CH ₂) ₈ COCl	
IV	II	ClCO(CH ₂) ₈ COCl	
V	III		
VI	IV		

Table 3: ¹H NMR bands of the prepared polymers

Polymer	(aromatic) H	(aliphatic) H
I	7.593 7.696 7.634	-----
II	7.990 – 6.551 Multiple	-----
III	-----	1.474 – 1.241
V	8.088 – 6.046	2.499
VII	9.37 – 10.3	CH ₂ – 2.506 And at 12.6 for NH group

Table 4: ^{13}C NMR bands of the prepared polymer

Polymer	Frequency	Structure
I	a-(169.053) b-(133.425) c-(131.738) d-(131.459) e-(131.183) f-(129.033) g-(129.637)	
II	a-(131)	
III	a(175.041) b(24.994) (28.799) (35.504)	
V	a-(150.860) b-(146.821) c-(128.278) d-(127.907) e-(127.399)	
VII	a-(142-323)	

Table 5 : electrical conductivity of the pure polymer under different applied voltages

Polymer	v/volt	$\sigma/\Omega^{-1} \cdot \text{cm}^{-1}$
I	1000	$1.0069 \cdot 10^{-9}$
	1500	$9.270 \cdot 10^{-10}$
	2000	$4.555 \cdot 10^{-10}$
II	1000	$1.8023 \cdot 10^{-10}$
	1500	$1.8063 \cdot 10^{-10}$
	2000	$1.8073 \cdot 10^{-10}$
III	1500	$2.545 \cdot 10^{-10}$
	2000	$6.786 \cdot 10^{-10}$
	2500	$1.0810 \cdot 10^{-9}$
VI	1000	$3.135 \cdot 10^{-10}$
	1500	$7.3155 \cdot 10^{-10}$
	2000	$1.0973 \cdot 10^{-9}$
V	2000	$1.663 \cdot 10^{-9}$
	2500	$1.1493 \cdot 10^{-9}$
VII	1000	$1.438 \cdot 10^{-10}$
	1500	$2.876 \cdot 10^{-10}$
	2000	$4.0745 \cdot 10^{-10}$

Table 6 : electrical conductivity of the polymer under different Temperatures

Polymer	T/C ^o	$\sigma / \Omega^{-1} \cdot \text{cm}^{-1}$
I	100	$2.581 \cdot 10^{-9}$
	85	$1.475 \cdot 10^{-9}$
	74	$5.532 \cdot 10^{-10}$
	65	$2.766 \cdot 10^{-10}$
II	100	$3.590 \cdot 10^{-9}$
	80	$1.632 \cdot 10^{-9}$
	70	$5.440 \cdot 10^{-10}$
III	76	$4.647 \cdot 10^{-9}$
	58	$1.991 \cdot 10^{-9}$
	30	$2.45 \cdot 10^{-10}$
IV	101	$4.327 \cdot 10^{-9}$
	90	$3.2503 \cdot 10^{-9}$
	80	$1.622 \cdot 10^{-10}$
	70	$8.114 \cdot 10^{-10}$
	55	$1.947 \cdot 10^{-10}$
VI	30	$8.358 \cdot 10^{-9}$
	52	$1.424 \cdot 10^{-8}$
	74	$1.8045 \cdot 10^{-8}$
VII	62	$9.497 \cdot 10^{-8}$
	74	$1.1397 \cdot 10^{-7}$

Table 7 :Activation energy of the electrical conductivity process

Polymer	$\Delta E(\text{e.v})$
I	0.793387
II	0.6645421
III	0.445025
IV	0.52698
V	0.1593378
VII	0.1507938

Table 8 : Optical properties , view irradiation with green laser light of 20m W/cm²

Pol	λ / nm	Before irradiant A	Irradiant time / min	After irradiant A	amount of energy gained	relaxation time/min
I	230	2.37	22	2.1	0.2	8
II	240	2.41	20	1.9	0.51	6.5
III	240	2.05	17	1.8	0.25	1
IV	240	2.20	17	1.9	0.1	2
V	240	2.37	19	1.9	0.47	10 sec
VI	250	2.28	21	1.7	0.58	50 sec
VII	260	2.37	28	2.12	0.25	16

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تحضير ودراسة خواص التوصيلية الكهربائية والخصائص الضوئية لبعض بوليمرات الآزو

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الملخص

في هذه الدراسة حضرت سبعة بوليمرات تحتوي على كميات مختلفة من مجاميع الآزو ومختلفة بنوع المجاميع الرابطة بينها وباستخدام البلورة بين السطوح .

شخصت البوليمرات المحضرة باستخدام طيف الأشعة تحت الحمراء واطياف $^1\text{H-NMR}$ و $^{13}\text{C-NMR}$. تم قياس التوصيلية الكهربائية للنماذج البوليمرية النقية وحسبت طاقة التنشيط لها باستخدام خلية ثلاثية الأقطاب . درس الامتصاص البصري وقابلية البوليمرات على تخزين الطاقة والإحتفاظ بها من خلال تشعيع الأغشية الرقيقة للبوليمرات بواسطة ضوء الليزر الأخضر بقوة 20 mW/cm^2 حتى الوصول الى حالة الاشباع.

أوضحت النتائج ان هناك عدة عوامل تؤثر على قيم التوصيلية الكهربائية وقابلية البوليمر على تخزين الطاقة وفقدانها مثل مرونة السلسلة ونوع المجاميع الرابطة بين مجاميع الآزو بينما لم تؤثر كمية مجاميع الآزو ضمن السلسلة الرئيسية على هذه الخواص.