Synthesis and Photoconductivity Study of Azo Functional Polymers

XUEQIN ZHOU,^{1,2} HONGJUN REN,¹ HONGZHENG CHEN,^{1,2} MANG WANG^{1,2}

¹ Institute of Polymer Science and Materials, Zhejiang University, Hangzhou 310027, China

² State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: A new type of high photosensitive azo functional polymers was synthesized and characterized by viscometry, infrared (IR) spectroscopy and Raman spectroscopy. Xerographic properties were determined in bilayer devices. Results show that azo polymers have high photosensitivity resulting from the high electronic mobility (AP-1 and AP-3) and a high charge transfer (AP-4). The study of spectral responses indicates that these polymers exhibit good xerographic properties in visible region, and AP-1 also has high photosensitivity in the near-IR region. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1913–1920, 1999

Key words: photoconductivity; azo functional polymer; charge-transporting group; electronic mobility; charge-transfer

INTRODUCTION

Polymers containing azo groups^{1,2} are reported as early as 1951. A number of azo functional polymers have been prepared. Most of the azo polymers that have been reported in the literature may be broadly classified into the following three groups:

- 1. Polymers formed by modification of existing polymers;
- 2. addition polymers, which have azo structures appended to the polymer backbone and are obtained from azo compounds carrying olefinic groups;
- 3. polymers that have azo groups as an integral part of the main chain. Special polyesters and polyamides prepared by polycon-

densation of azobenzene derivatives have received much attention.

Some of the interest in this type of polymer is due to their possible use as high-grade pigments of good fastness to light and also as materials that exhibit photochromism, photocontraction, photodegradation, thermal degradation, and biodegradation. But little attention was put on the photosensitivity because of poor photoconductivity of previous azo polymers. However, based on the study of azo compounds, especially the photogeneration mechanism study of Umeda et al.3 and our studies on bisazos containing hydrazone groups,⁴ we wondered whether the photosensitivity of those azo polymers, which had intergrated the charge transporting groups into the macromolecules, could be improved, and even may be higher than those of common azo compounds.

With this in mind, we synthesized four azo polymers containing charge-transporting groups (hydrazone group or charge-transporting amine group). The structures are shown in Figure 1. The xerographic properties were studied in bilayer de-

Correspondence to: M. Wang.

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Figure 1 Structures of the azo functional polymers.

vices. Results show that this type of azo polymers has good photosensitivity, and even some could be applied to photoreceptors.

EXPERIMENTAL

Materials and Equipment

1,3-Benzenodiamine, 1,4-benzenodiamine, benzidine 3-hydroxy-2-naphthalene carboxylic acid, and *p*-nitrobenzaldehyde were purchased in analytical grade. 3-Nitrophenylhydrazine was obtained from 3-nitrophenylamine by the method of Fischer.^{5,6} All inorganic compounds used are of analytical grade. Elemental analyses were performed by a Perkin-Elmer 240C Elemental Analyzer. Infrared (IR) spectra were determined on NIC-5DX Fourier transform infrared (FTIR) and Raman spectra were obtained on NUCLET 950. Absorption spectra were recorded on DU-50 Spectrophotometer. Viscosities were determined by Ubbelohde dilution viscosimeter in concentrated solphonic. Xerographic measurements were performed on a GTD-II model photoconductivity measuring device.

Synthesis of *p*-Nitrobenzaldehyde-3-aminophenyl hydrazone

As shown in Scheme 1, 0.1 mol of 3-nitrophenylhydrazine was dissolved in alcohol, and quantitative acetic acid was added. Under room temperature, to the solution, 0.1 mol of *p*-nitro-phenylaldehyde solved in alcohol was added, and the reaction was kept for 5 h. After filtration, the crude *p*-nitro-phenylaldehyde-3-nitrophenylhydrazone [Scheme 1(a)] was recrystallized from alcohol. orange 3-nitrophenylhydrazone The [Scheme 1(a)], 230 g of stannic chloride, and 800 mL of hydrochloric acid were refluxed at room temperature for 24 h. After filtration, the red filtrate was alkalified using hydroxy natriate solution, and the precipitate was separated. The amine containing 3-nitrophenylhydrazone groups [Scheme 1(b)] was recrystallized from alcohol in yellow crystal.

Synthesis of 4,4'-Bis(1"-azo-2"-hydroxy-3"chlorocarbonyl naphthalene) biphenyl

19 G of 4,4'-biamino biphenyl was dissolved in 80 mL of 36% hydrochloric acid and approximately 900 mL of water in a three-necked reaction flask. After being cooled to 2°C, 50 mL of the nitrous natriate solution (15 g of nitrous natriate and 50 mL of water) was dropped in. At lower than 5°C, the reaction was kept for another 1 h, then the



Scheme 1 Reaction scheme of *p*-nitrobenzaldehyde-3-aminophenyl hydrazone.



Scheme 2 Reaction scheme of azo polymers containing charge-transporting groups.

solution was filtered. Under room temperature, the filtrate was added to the 3-hydroxy-2-naphthalenecarboxylic acid solution (500 mL of water, 40 g of 3-hydroxy-2-naphthalenecarboxylic acid, 34 g of hydroxy natriate, and 30 mL of acetic acid). The whole solution was stirred for 1 h and then kept over night. Purplish red azo [Scheme 2(c)] was filtered out, washed with 500 mL of water, 1000 mL of alcohol, and a great deal of water and then dried in 80°C. The dried azo [Scheme 2(c)], 500 mL of chlorobenzene, 80 mL of dichloro sulfone, and some N,N'-dimethyl formamide (DMF) were placed in a flask and heated to reflux for 1 h. After filtration, azo [Scheme 2(d)] was washed with tetrachloromethane and dried in 110°C.

Preparation of Azo Polymers Containing Charge-Transporting Groups

4,4'-Bis(1''-azo-2''-hydroxy-3''-chlorocarbonylnaphthalene)biphenyl, 500 mL of chlorobenzene, some pyridine, and propriate amine were placed in a flask equipped with a reflux condenser. The reaction mixture was then heated to 130°C for over 2 h, after which the mixture was cooled to about 60°C, and the product was separated by filtration. The blue–violet solid was washed with alcohol, water, and DMF successively and then dried.

Preparation of Bilayer Devices and Photoconductivity Measurement

Bilayer devices [Fig. 2(a)] were prepared by coating an interface layer (IFL) of a kind of polyamine, the charge generation layer (CGL) of product azo polymer with the PVB as coherent, and the charge transporting layer (CTL) of N,N'-diethyl-*p*-phenyl aldehyde biphenyl hydrazone (DEH) dispersed in PC successively onto aluminium substrates.

A GDT-II model photoconductivity measuring device was used with a 5-W, 24-V incandescent lamp as a light source. In the measurement, the surface of the bilayer device was negatively charged in the dark. As soon as the lamp was lit, charge carriers were generated in the CGL and



Figure 2 (a) Cross section of a bilayer xerographic device. (b) Schematics of the photoinduced discharge curve.

injected into CTL. During the exposure, the surface potential decreased, and the photoinduced discharge curve (PIDC) of the device was recorded.⁷ From PIDC [Fig. 2(b)], we obtained $\Delta V_1 \%$ (the percentage of potential discharge after 1 sec of exposure), $t_{1/2}$ (the time from the original potential to half under exposure), and $E_{1/2}$ (the product of $t_{1/2}$ multiplied by I, (the intensity of light). $E_{1/2}$ can indicate photosensitivity. The smaller the $E_{1/2}$, the higher the photosensitivity.

RESULTS AND DISCUSSION

Synthesis and Physical Properties of Polyazos

The reaction scheme of these azo polymers is noted in Scheme 2. AP-1 was synthesized containing 1,4-benzenodiamine groups, AP-2 was prepared containing 1,4-benzenodiamine groups, and AP-3 was obtained with benzidine groups, while AP-4 contained p-nitrobenzaldehyde-3aminophenyl hydrazone groups. Except for the reddish-violet AP-1, other three azo polymers are blue-violet. IR spectra (Fig. 3) and elemental analyses (Table I) confirmed the structures of Figure 3(c) and (d). The structures of azo polymers were characterized by IR spectra (Fig. 3) and Raman spectra (Fig. 4).



Figure 3 IR spectra of (c), (d), and azo polymers.

As shown in Figure 3, spectrum (d) exhibits a strong absorption band at 1740 cm^{-1} , which is caused by carbonyl C=O of chlorocarbonyl groups. However, in the spectrum of azo polymers, besides this band, there exists another strong absorption band of C=O at $\sim 1680 \text{ cm}^{-1}$. This information can be attributed to the presence of amide groups (-CONH-). The structures of azo polymers were further confirmed by Raman spectra. The Raman spectra of Figure 4(c) and (d) are similar with those of azo polymers. All spectra exhibit strong Raman intensity of N=N at $\sim 1590 \text{ cm}^{-1}$ and Raman intensities of aromatic rings at 1170, 1288, 1365, and 1494 cm⁻¹. Because they had similar structures, we infer that the Raman band of N=N is not sensitive to the various charge-transporting groups. Further study of these spectra revealed another important feature that the ratios of N=N Raman intensity to aromatic ring Raman intensity were different. In the Raman spectra of Figure 4(c) and (d), the ratios of N=N Raman intensity to aromatic Raman intensity at 1170 cm^{-1} were about 3 to 1, while those values of all azo polymers were about 2 to 1. We also took Raman spectra of similar bisazos, and the results show a ratio of about 3 to 1. The reason may be that in azo polymers, more aromatic rings were introduced into by the charge-transporting groups, which results in the lower N=N concentration in a repeated unit. It is clear that structures of product azo polymers are those we had expected.

Viscosities of solutions of these azo polymers in 98% sulfuric acid (Table II) are also obtained by a Ubbelohde dilution viscosimeter. Under the same conditions, solutions of azo polymers showed longer flux times and higher inherent viscosities than those of bisazo compounds. This can further confirm the structures of products. But as the

Table I Elemental Data of (a), (b), (c), and (d)

		Ele	Elemental Data			
Compound		С	Н	Ν		
(a)	Cald:	54.55	3.52	19.57		
	Found:	54.31	3.28	19.43		
(b)	Cald:	69.00	6.24	24.76		
	Found:	68.79	6.04	23.97		
(c)	Cald:	70.10	3.81	9.62		
	Found:	69.98	3.78	9.54		
(d)	Cald:	65.92	3.25	9.04		
	Found:	64.88	3.30	8.76		



Figure 4 Raman spectra of (c), (d), and azo polymers.

inherent viscosities showed, because of the low solubility of dichlorocarbonyl bisazo compound, the degree of polymerization of product azo polymers could not attain a high value.

The solubility of these azo polymers in organic solvents are very poor, while they are soluble in 98% sulfuric acid. So the inherent viscosity was obtained in 98% sulfuric acid. Figure 5, which depicts typical absorption spectra of these azo functional polymers in $CHCl_3$ (10^{-5} g/L), shows that the absorption covers most of the visible region (450–650 nm), with a maximum at about 560 nm. It is important to point out that the maximum is not sensitive to the various charge-

Sample	Flux Time (t)	Relative Viscosity $(\eta_{\rm r})$	Inherent Viscosity $[\eta]$	Molecular Weight
AP-1	14'1"2	1.025	1.542	_
AP-2	13'58"9	1.022	1.371	_
AP-3	13'59"3	1.023	1.401	
AP-4	14'0"8	1.025	1.512	_
(a)	13'42''5	1.002	0.137	583
Bisazo 1	13'48"1	1.009	0.561	781
Bisazo 2	13'48"9	1.010	0.621	871

Table II Inherent Viscosity of Azo Polymers

The solvent is 98% sulfuric acid, and its flux time (t_0) is 13'40"7. The concentration of the solutions (c) is 0.016 g/l. Calculated equation: $\eta_r = t/t_0$; $[\eta] = \eta_r/(c \cdot \eta_r^{1/2})$.

transporting amine groups. Very similar results have been obtained for bisazos containing hydrazone groups⁴ and common photosensitive bisazos without hydrazone groups.^{8,9}

Xerographic Properties and Structure–Photosensitivity Relation

The xerographic properties of azo polymers were examined in bilayer xerographic devices consisting of CGLs of various azo polymers and a common CTL onto IFL (Fig. 2). The IFL is a ~ 0.2 -



Figure 5 Absorption spectra of azo polymers in CHCl_3 .

 μ m-thick film of PMMA. The CTL is $\sim 23 \ \mu$ m in thickness and contains 50% by weight of a holetransporting material, DEH, in polycarbonate matrix, while the CGL is $\sim 0.7 \ \mu m$, and the concentration of azo polymer in the CGL is 50% by weight. Thus, the geometry of all xerographic devices examined is held to be the same, enabling the xerographic properties of various azo polymers to be compared. The data, which were obtained on GTD-II, are shown in Table III. The results indicate that three azo polymers (AP-1, AP-3, and AP-4) exhibit good photosensitivity (low $t_{1/2}$ and $E_{1/2}$, as well as low dark-decaying values). Under the same fabrication and evaluation conditions, a severe charging problem was experienced with AP-2, and its xerographic properties could not be evaluated.

These four azo polymers were synthesized containing charge-transporting groups (1,3-Benzenodiamine, 1,4-benzenodiamine, benzidine, and p-nitrobenzaldehyde-3-aminophenyl hydrazone). It was reported that hole-transporting molecules actually penetrate into the CGL during the CTL overcoating step and that the sites for the photogeneration of e-h pairs are at the boundaries of excitons that are residing on the surfaces of pigment particles in the CGL.³ In other words, e-h pairs are actually generated in the bulk of the CGL between the exciton of the pigment and the hole-transporting molecule. These azo polymers have intergrated charge-transporting groups in the macromolecular. As our studies⁴ of bisazos containing the hydrazone groups indicated, they should have high photosensitivity, and the experimental results show that they do have high photosensitivity, except for AP-3.

These azo polymers were prepared with common highly photosensitive bisazo groups, 4,4'-

Wavelength (nm)	Surface Potential (v)	Dark Decaying (v/s)	V_{R} (v)	$\Delta V \%$	$t_{1/2}$ (s)	$\frac{E_{1/2}}{(\text{lux s})}$
(a) AP-1:						
570	781	74.8	125	70.17	0.25	7.500
605	785	84.8	125	69.53	0.25	7.500
679	835	68.0	117	79.10	0.19	5.625
762	816	9.6	144	72.96	0.31	9.375
772	800	34.0	113	58.32	0.81	24.375
(b) AP-3:						
570	822	38.0	93	77.19	0.38	11.250
605	867	33.2	85	77.34	0.38	11.250
679	840	28.0	93	71.87	0.44	13.125
762	853	28.0	132	57.30	0.75	22.500
772	857	20.0	117	26.75	1.81	54.375
(c) AP-4:						
570	1237	64.0	187	77.86	0.31	9.375
605	1070	43.2	156	78.88	0.31	9.375
679	1031	35.1	156	77.04	0.38	11.250
762	1304	52.8	218	66.91	0.50	15.000
772	1031	13.6	164	15.36	2.94	88.125

Table III Xerographic Properties of Azo Polymers

^a Due to the low charge acceptance of this device, its xerographic properties could not be evaluated.

bis(1"-azo-2"-hydroxy-3"-amide naphthalene) biphenyl. Through polymerization, the photosensitivity could be enhanced by improving the electronic mobility and by strengthening the degree of charge-transfer. AP-1 and AP-3 enhance the electronic mobility in the whole macromolecules, which leads to high photosensitivity of these azo polymers. Investigation of the structure of AP-2, which reacted from 4,4'-bis(1"-azo-2"-hydroxy-3"-chlorocarbonyl naphthalene) biphenyl and 1,3-benzenodiamine, shows that the mobility of electrons in AP-2 is poor in the 1,3-benzenodiamine; and the middle azo groups becames charge trap in the devices. The result is that AP-2 has low charge acceptance. However, 4,4'-bis(1''-azo-2"-hydroxy-3"-chlorocarbonyl naphthalene) biphenyl (charge-releasing group) of AP-4 is linked by hydrazone groups, which has charge acceptance. The result is that the degree of charge transfer enhanced, and the photosensitivity is good. This is also the reason that AP-4 has higher xerographic properties than AP-2 when both of them have poor electronic mobility in amine groups.

Spectral Responses

The spectral responses were obtained by analyzing the xerographic data at various wavelengths. Plots of the spectral sensitivity and the CGM absorption spectra in solid film on quartz (PVB as binder) are given in Figure 6. Data of AP-3 and AP-4 indicate that the spectral responses of these two azo polymers in bilayer devices are parallel to their absorption spectra and are panchromatic in the visible region from 450 to 760 nm. Hence, AP-1 exhibits a particular spectral responses that the best photosensitivity is observed at about 690 nm, but the maximum of the spectral absorption is recorded at ~ 570 nm, though absorption at 690 nm is exhibited. That is to say that the highest photogeneration efficience is not obtained at the maximum of absorption spectra, which may also be found in bisazos containing hydrazone groups. Moreover, AP-1 also shows good photosensitivity in the near-IR region (772 nm; see Fig. 7). We ascribe this to the best electronic mobility in the whole macromolecule of AP-1.

CONCLUSIONS

In this work, four azo polymers were synthesized by polymerization of 4,4'-bis(1"-azo-2"-hydroxy-3"-chlorocarbonyl naphthalene)biphenyl with various diamines. They were characterized by inherent viscosity, IR spectra, and Raman spectra. The absorption spectra of these azo polymers exhibit a red shift as compared with bisazo compounds. Photosensitivity studies show that azo polymers containing charge-transporting groups have high photoconductivity. Xerographic data indicate that azo polymers, which can improve the electronic mobility or which can enhance the charge-transferring degree, have high photosensitivity. AP-2 and AP-4 exhibit panchromatic responses in the visible region, while AP-1 is found the best photosensitivity at about 690 nm, and the maximum of absorption spectra is recorded at ~ 570 nm. Xerographic data also indicate that a potential application in photogenerating pigments in photoreceptors in copies exists for these azo polymers. Another important result obtained



Figure 6 Absorption spectra of azo polymers in solid film.



Figure 7 Plots of $E_{1/2}$ against wavelength.

was that some polymers also have good xerographic properties in the near-IR region and may be applied to photoreceptors in printers.

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