

STUDY ON PHOTODYNAMIC AND PHOTORESPONSIVE AZO POLYELECTROLYTES*

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Abstract Several kinds of novel azobenzene-containing polyelectrolytes with special molecular design have been developed from acryloyl chloride or epoxy based precursor polymers. The acryloyl chloride based precursor polymer, poly(acryloyl chloride), was prepared by free radical polymerization of acryloyl chloride. The azo polyelectrolytes were prepared by an esterification reaction between the precursor polymer and corresponding azo chromophores containing a reactive hydroxyl group, followed by hydrolysis of the unreacted acyl chloride groups. The epoxy based precursor polymer was prepared by the reaction between 1,4-cyclohexanedimethanol diglycidyl ether and aniline, and postfunctionalized by azo coupling reaction to form azo polymers containing chromophores with ionizable groups. The polyelectrolytes were characterized by elemental analysis, ¹H-NMR, IR and UV-Vis spectroscopy. The photodynamic and photoresponsive properties, as well as self-assembly of these azo polyelectrolytes are reported in this paper^[1].

Keywords Azo polyelectrolyte, Photodynamic, Photoresponsive, Self-assembly

INTRODUCTION

Azo chromophore functionalized polymers have attracted considerable attention in the last one or two decades for potential applications such as electro-optic modulation and information storage among others^[1-3]. Interesting properties with potential applications discovered in recent years include light-induced phase transition of LCP^[4], "command surfaces"^[5], light-induced birefringence and dichroism^[6], and light-induced surface relief gratings^[7, 8] etc.

The polyelectrolytes are well known for their solubility in aqueous media even in the presence of a hydrophobic polymer backbone^[9]. The conformation and solution properties of the polyelectrolytes are strongly dependent on the ionic strength or pH. The special interesting properties of azo polyelectrolytes stem both from the optical properties of azo chromophores and from the unique properties of polyelectrolytes. One of the fascinating properties of azo polyelectrolytes is the ability to form self-assembled multilayers through a layer-by-layer dipping process^[10]. Recently, it has been reported by several groups that the azo chromophores in the confined layer in multilayer films self-assemble into a noncentrosymmetric alignment and demonstrate second order optical nonlinearity^[11-13]. However, a thorough study of the photoisomerization of azo polyelectrolytes in the multilayer structure has not yet been reported^[14].

Recently, several kinds of novel azobenzene containing polyelectrolytes with special molecular design have

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been synthesized in our laboratory based on post functionalization of precursor polymers. In this paper, we report the synthesis, characterization, self-assembly and photofabrication of these azo polymers. Their structure-property relationship is discussed in some detail.

EXPERIMENTAL

Poly(acryloyl chloride) (PAC)^[15]

Acryloyl chloride was prepared from PCl_3 and acrylic acid. Acryloyl chloride (10 mL), anhydrous 1,4-dioxane (10 mL) and AIBN (0.334 g) were added into a flask under N_2 . The flask was sealed and then heated in an oil-bath (50°C) for 14 h. The polymer was precipitated by adding petroleum ether (40 mL) and washed twice with petroleum ether. The product was dried at 60°C under vacuum for 48 h.

Poly(4-(2-(acryloyloxy)ethoxy)-4'-nitroazobenzene-co-acrylic Acid)

PAC (0.3 g, 0.0033 mol), triethylamine (0.56 mL, 0.0040 mol) and 4-(2-(acryloyloxy)ethoxy)-4'-nitroazobenzene (whose amount is determined by the required degree of functionalization of the polymer) were dissolved in anhydrous DMF. The mixture was stirred at room temperature for 12 h under N_2 . Then a suitable amount of water was added into the mixture and stirred for 10 min. The product was precipitated into HCl solution (0.01 mol/L), filtered, washed several times with water and dried. The polymer was further purified by re-dissolving in THF and precipitating into petroleum ether twice and dried at 90°C under vacuum for 24 h.

Poly(4-(2-(acryloyloxy)ethoxy)-4'-ethoxyazobenzene-co-acrylic Acid)

A procedure similar to that described above for the synthesis of poly(4-(2-(acryloyloxy)ethoxy)-4'-nitroazobenzene-co-acrylic acid) was used.

Poly(4-(2-(acryloyloxy)ethoxy)-azobenzene-co-acrylic Acid)

A procedure similar to that described above for the synthesis of poly(4-(2-(acryloyloxy)ethoxy)-4'-nitroazobenzene-co-acrylic acid) was used.

Epoxy Based Precursor Polymer CH-AN

The precursor polymer was synthesized by the reaction between 1,4-cyclohexanedimethanol diglycidyl ether and aniline (AN). The 1,4-cyclohexanedimethanol diglycidyl ether (CH) was purchased from Aldrich and used without further purification. The precursor polymers were prepared by mixing equimolar quantities of the epoxide monomer and aniline under gradual heating and polymerized at 110°C for 48 h. The products were fractionated to remove low molecular weight oligomers before the next reaction step.

Epoxy Based Azo Polyelectrolytes

All of epoxy based azo polyelectrolytes studied in this work were synthesized by post azo coupling reaction on the precursor polymers CH-AN. The preparation of diazonium salts for the reaction was reported elsewhere^[11, 16]. The reaction was carried out in a DMF solution at 0°C for 12 h. The products were obtained by precipitation of the above solution in water and washed with plenty of water until a neutral stage was achieved. The polymers were further purified by solvent extraction and dried under vacuum at least for 24 h.

Measurement of Photochromic Effect

The solutions of azo polyelectrolytes (0.05 g/L) were prepared by dissolving the polymers in an aqueous solution of NaOH (0.001 mol/L). The polymeric films were prepared by spin-coating the solution of azo polymers in DMF (40 g/L) on clean quartz slides. A Cole-Parmer E-97600-15 UV lamp was used as the light source. Upon irradiation, the dependence of UV-Vis spectra of the samples on the irradiation time was measured by an HP-8452A UV-Vis spectrometer.

Surface Relief Grating Formation

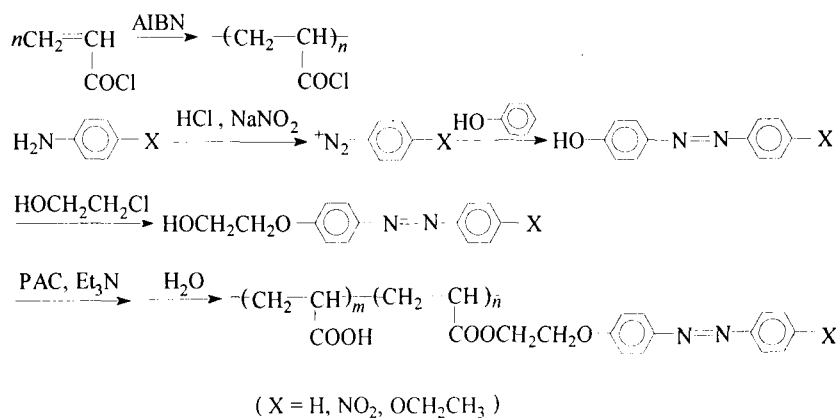
A linearly polarized laser beam at 488 nm from an Ar^+ laser was used as the recording source. The polarized laser beam passes through a halfwave plate, and is then expanded and collimated. Half of the collimated beam is incident upon the film directly. The other half of the beam is reflected onto the film from a mirror. The

polarization condition of the recording beam can be adjusted by rotating the halfwave plate. The angle α that is defined as the angle between the polarization with respect to *s*-polarization, was selected to be 45° for optimal recording. The intensity of the recording beams ranged from 50 to 100 mW/cm^2 . The incident angle θ of the recording beam was adjusted to control the grating space. The diffraction efficiency of the first order diffracted beam from the gratings in transmission mode was probed with an unpolarized low power He-Ne laser beam at 633 nm.

RESULTS AND DISCUSSION

Polymer Synthesis

The poly(acrylic acid) based azo polyelectrolytes were synthesized by chemical modification of poly(acryloyl chloride), a very reactive polymer prepared by free radical polymerization of the monomer. Poly(acryloyl chloride) was reacted with different aromatic azo compounds containing a hydroxyl group through esterification. The corresponding azo polyelectrolytes were formed by the hydrolysis of the unreacted acyl chloride groups (Scheme 1). Selecting suitable feed ratio in the post functionalization could control the degree of functionalization of the polyelectrolytes synthesized. The graft rate is linearly dependent on the feed ratio. The solubility of the polyelectrolytes in aqueous solution deteriorates when the degree of functionalization is over 50%.



Scheme 1 Synthetic route of poly(acrylic acid) based azo polyelectrolytes

The epoxy based precursor polymer was synthesized by the reaction of 1,4-cyclohexanedimethanol diglycidyl ether with aniline. The precursor polymer was postfunctionalized by an azo-coupling reaction to form polymers tethered with donor-acceptor type chromophores containing ionizable groups (Fig. 1)^[4, 5].

The structures and purity of all the polymers were confirmed by various spectroscopic methods.

Photochromic and Photoresponsive Effect

Upon irradiation with ultraviolet light of 365 nm, aqueous solutions and spin coating films of poly(4-(2-(acryloyloxy)ethoxy)-azobenzene-*co*-acrylic acid) or poly(4-(2-(acryloyloxy)ethoxy)-4'-ethoxyazobenzene-*co*-acrylic acid) containing azobenzene or 4-ethoxy-azobenzene chromophores, respectively show significant photochromic effect. When the irradiation time increases, a high-intensity absorbance corresponding to $\pi \rightarrow \pi^*$ transition gradually decreases and a low-intensity $n \rightarrow \pi^*$ band increases slightly, both due to the *trans-cis* isomerization (Fig. 2). When the samples were kept in the dark, *cis* isomer slowly relaxed to the lower energy *trans* isomer, the UV-vis spectrum returned to its original form (Fig. 3). For poly(4-(2-(acryloyloxy)ethoxy)-4'-nitroazobenzene-*co*-acrylic acid) and all epoxy based polyelectrolytes given in Fig. 1, no significant photochromic effect could be observed. The reason for this is that the fast thermal back-isomerization of the *cis* isomer results both from the strong electron-withdrawing nitro substituent in the former and from the amino donor in the

latter. It is obvious from the comparison that the *cis-trans* isomerization rate of the azo polyelectrolytes is governed by the chromophore structure.

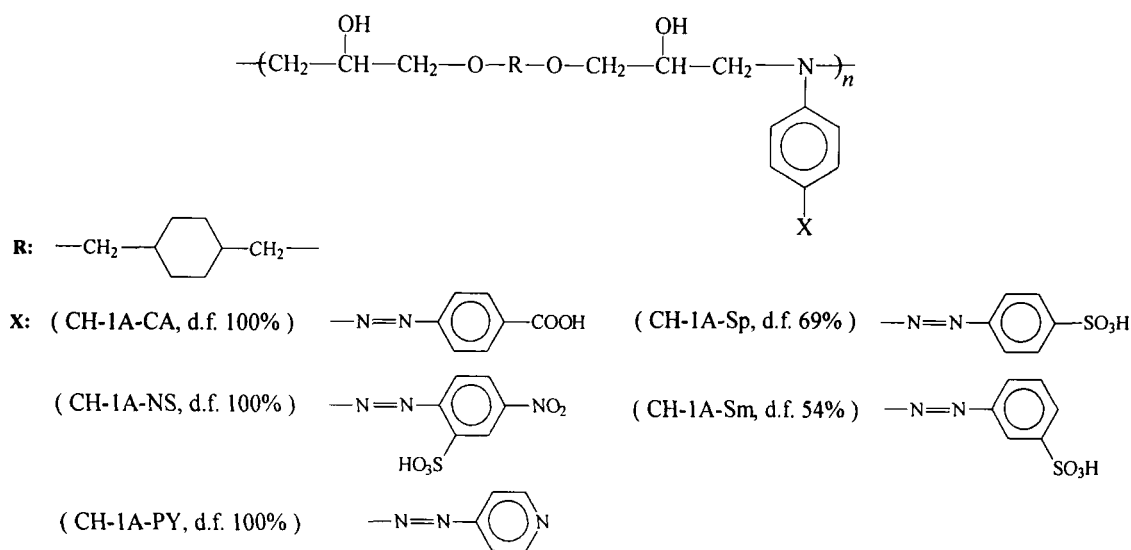


Fig. 1 Chemical structure of epoxy based polyelectrolytes synthesized in this work

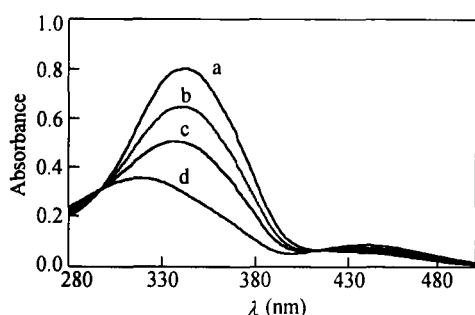


Fig. 2 Variation of UV-Vis spectra of poly(4-(2-(acryloyloxy)-ethoxy)-azobenzene-co-acrylic acid) with irradiation time under 365 nm

a) 0 s, b) 1 s, c) 10 s, d) 50 s

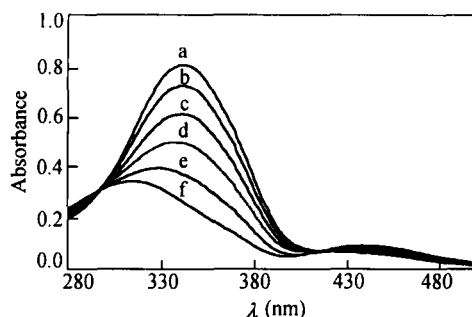


Fig. 3 Variation of UV-Vis spectra of poly(4-(2-(acryloyloxy)-ethoxy)-azobenzene-co-acrylic acid) with time in dark after UV irradiation

a) 262 h, b) 142 h, c) 70 h, d) 22 h, e) 4 h, f) 0 h

The contact angle of water on the surface of the spin coated films prepared from the polyelectrolytes evidently changes upon UV irradiation. The contact angle exhibits a critical point at the degree of functionalization of about 36% for polyelectrolytes containing 4-ethoxyazobenzene chromophores both before and after UV irradiation.

SELF-ASSEMBLED MULTILAYERS

The acrylic acid based azo polyelectrolytes synthesized in this work were assembled with some commercially available polyelectrolytes such as poly(diallyldimethylammonium chloride) by an alternating polyelectrolyte deposition (APD) method. The UV-Vis spectra of the films with increasing number of bilayers of a representative system are shown in Fig. 4. A linear increase of absorbance can be seen as the number of bilayers increases. The linear relationship was observed for other polyelectrolytes synthesized in this work too. The thickness of the 20-bilayer film was measured to be 120 nm by atomic force microscopy (AFM).

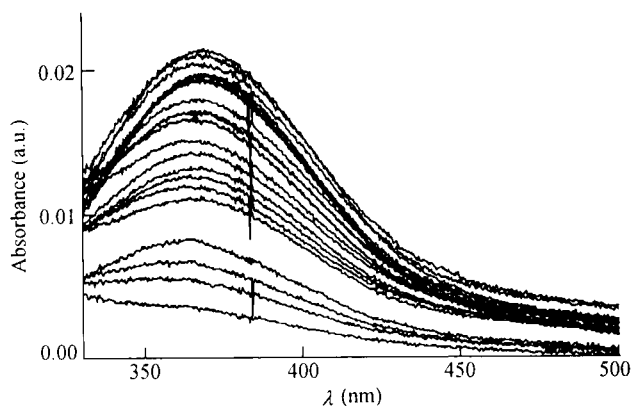


Fig. 4 UV-Vis spectra of poly(4-(2-(acryloyloxy)ethoxy)-4'-nitroazobenzene-co-acrylic acid) films with increasing number of bilayers

SURFACE RELIEF GRATING

Holographic surface relief gratings (SRG) with large surface modulation could be formed on the epoxy based polyelectrolyte CH-1A-CA films. Large surface modulation (> 600 nm) and high diffraction efficiency ($> 40\%$)

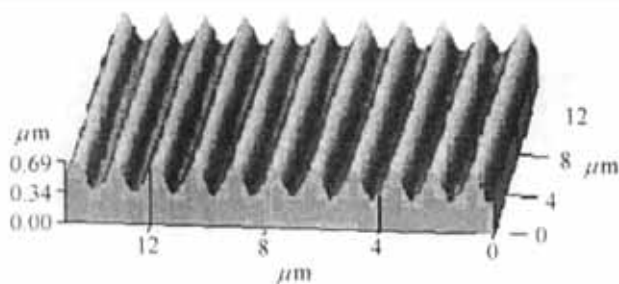


Fig. 5 Atomic force microscopy image of surface relief grating on CH-1A-CA polymer film

were obtained under optimal recording conditions. The atomic force microscopic image of a surface relief grating on a CH-1A-CA film is given in Fig. 5. However, for the other epoxy based polyelectrolytes given in Fig. 1 and poly(acrylic acid) based polyelectrolytes given in Scheme 1, only very low surface modulation (< 10 nm) and diffraction efficiency ($< 1\%$) could be observed. It can be seen from this experiment that the formation of the surface relief grating is very sensitive to the chromophore structures. The amino donor seems to be necessary for forming SRG with high surface modulation. In the case of an amino donor, the type of electron withdrawing groups also plays an important role in the modulation efficiency.

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