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Influence of extrinsic and intrinsic parameters onto the formation of surface relief gratings in polar azo molecular glasses

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ABSTRACT

Polar azo derivatives exhibiting stable glass-forming properties displayed efficient migration properties as thin films when subjected to interferential illumination, and formed time-stable and rewritable surface relief gratings as high as the initial film thickness. Intrinsic (film thickness, structure bulkiness) as well as extrinsic (laser fluence and polarization) parameters dramatically influenced the rate of the relief growth as well as the maximum relief amplitude. The superimposition of +45°/−45°-polarized beams unexpectedly conducted to a diffraction efficiency ten times as high as the combination of two p/p (parallel to the incident plane) polarized beams. The introduction of bulky anthryl Diels–Alder substituents showed net increase in the modulation amplitude due to the creation of large free volume around each azo unit, facilitating the azo migration within the less densely packed material.

1. Introduction

Azo compounds, known for their strong one-photon absorption cross-section, have been used for long as dyes for textile dyes [1] and non-rewritable optical data storage [2]. In the late 80's, their photochromic properties involving a reversible *E*–*Z* photoisomerization around the N═N double bond initiated an entire field of new investigations related to their startling photomechanical capabilities [3–5]. The latter have been illustrated in photonics for the fabrication of electro-optical modulators [6], the translation of micrometric-sized objects such as liquid droplets [7,8] or polystyrene microspheres [9], and the stretching and bending of azo-functionalized liquid crystalline polymers along the direction of the impinging polarized light [10,11]. Another phenomenon whose mechanism is still highly debated relates to the bulk migration of azo moieties when subjected to interferential illumination [12,13]. It is beyond the scope of the present manuscript to describe them in detail but three main models based on asymmetric diffusion [14], mean-field theory [15,16], and isomerization pressure [17], have been proposed to explain the formation of surface relief gratings. All of them relate to the photoisomerization reaction of azo polymers whereas a new class of organic materials, involving glass-forming small molecules [18,19], could offer simpler models to assess the critical structural and electronic parameters coming into play. No chain entanglement needs to be considered while kinetic and thermodynamic characteristics linked to the independent microscopic properties of each molecule (such as the molecular volume, dipole moment, energy levels of the *E* and *Z* isomers) can be more precisely defined than for polymeric systems. Although there is a growing interest in amorphous molecular azo materials [20–23], their structure often resembles that of aminoazobenzene-like derivatives following Rau's classification [1], which makes direct comparison more delicate with the usual push–pull structure of the azo polymerized units referred as to pseudo-stilbene-like. We report herein detailed investigations of the influence of intrinsic (molecular bulkiness, film thickness) and extrinsic (light fluence and polarization) parameters onto the migration efficiency of polar azo molecules leading to perfectly time-stable and optically rewritable surface relief gratings at room temperature.

2. Materials and methods

2.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer and chemical shifts were reported in ppm relative

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to TMS or referenced to the residual solvent. High resolution mass spectra were obtained by MALDI-TOF (Voyager DE-STR, Applied Biosystems). Glass transition temperatures T_g were measured by using differential scanning calorimetry (Perkin Elmer Pyris Diamond) in aluminum caps under a nitrogen flow at a scan rate of 20 °C min^{-1} over the temperature range [30 °C–250 °C].

2.2. Commercial chemicals and compounds

All chemical reagents and solvents were purchased from commercial sources (Aldrich, Acros, SDS) and used as received. Spectroscopic grade toluene was used for spectroscopic measurements. All air-sensitive reactions were performed under argon using a vacuum line. Analytical thin layer chromatography was performed on Kieselgel F-254 precoated plates. Flash chromatography was carried out with silica gel from SDS. The compounds 4-nitrosobenzoic acid [24], methyl 4-nitrosobenzoate [24], bis(4′-tert-butylbiphenyl-4-yl)-4-aminophenylamine **1** [25], and 2,6-dihydroxy-9,10-dihydro-11,12-dicarbomethoxy-ethenoanthracene **4** [26] were synthesized according to literature procedures. Thin films were obtained by spin-casting chloroform solutions at various azo wt.% (1 wt.% and 2 wt.%) on pre-cleaned glass substrates at a speed comprised between 500 and 2000 rpm, and dried further under vacuum for 24 h. All solutions were systematically filtered before spin-coating with 0.45 μm porous Millex membranes purchased from Waters.

2.2.1. Synthesis of methyl 4-{4′-[bis(4′-tert-butylbiphenyl-4-yl)amino]phenylazo}benzoate ***2 AzoMe***

Methyl 4-nitrosobenzoate (80 mg, 0.48 mmol) was dissolved in glacial acetic acid (3.5 mL) under argon. Bis(4′-tert-butylbiphenyl-4-yl)-4-aminophenylamine **1** (210 mg, 0.4 mmol) was added portionwise; meanwhile the pale yellow solution turned deep brown red. After stirring at room temperature for 48 h, a fine orange product precipitated, corresponding to the pure compound **2** which was filtered off and washed thoroughly with water (95%, 250 mg). T_g 68 °C; λ_{max} (nm) [ε (mol^{-1}.L.cm^{-1})]: 465 [17900], 330 [29600]; ^{1}H NMR (400 MHz, CDCl$_3$, TMS): (ppm) = 8.16 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.90 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 7.86 (d, ^{3}J(H,H) = 8.2 Hz, 4H), 7.56 (d, ^{3}J(H,H) = 8.2 Hz, 4H), 7.54 (d, ^{3}J(H,H) = 8.2 Hz, 4H), 7.46 (d, ^{3}J(H,H) = 8.7 Hz, 4H), 7.27 (d, ^{3}J(H,H) = 8.7 Hz, 4H), 7.21 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 3.95 (s, 3H, $-CO_2CH_3$), 1.37 (s, 18H, −tBu); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): (ppm) = 166.8, 159.8, 155.7, 150.3, 147.3, 145.7, 137.6, 137.2, 131.1, 130.7, 128.2, 126.6, 125.95, 125.92, 124.9, 122.4, 121.6, 52.4, 34.7, 31.5; HRMS (MALDI-TOF), *m/z* [M$^+$]: for $C_{46}H_{45}N_3O_2$ calculated 671.3512; found 671.35063.

2.2.2. Synthesis of 4-{4′-[bis(4′-tert-butylbiphenyl-4-yl)amino]phenylazo}benzoic acid ***3***

4-Nitrosobenzoic acid (570 mg, 3.82 mmol) was dissolved in a 1:1 DMSO:glacial acetic acid (52 mL) mixture under argon. Bis(4′-tert-butylbiphenyl-4-yl)-4-aminophenylamine **1** (1.0 g, 1.91 mmol) was added portionwise; meanwhile the pale yellow solution turned deep brown red. After stirring at room temperature for 48 h, a fine red product precipitated, corresponding to the pure acid **3** which was filtered off and washed thoroughly with water (95%, 1.2 g). T_m = 108 °C; ^{1}H NMR (400 MHz, CDCl$_3$, TMS): (ppm) = 8.22 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 7.93 (d, ^{3}J(H,H) = 8.2 Hz, 2H), 7.88 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 7.56 (d, ^{3}J(H,H) = 8.2 Hz, 4H), 7.55 (d, ^{3}J(H,H) = 8.7 Hz, 4H), 7.47 (d, ^{3}J(H,H) = 8.2 Hz, 4H), 7.27 (d, ^{3}J(H,H) = 8.7 Hz, 4H), 7.21 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 1.37 (s, 18H, −tBu); HRMS (MALDI-TOF), *m/z* [M+] for $C_{45}H_{43}N_3O_2$ calculated 657.3355; found 657.3349.

2.2.3. Synthesis of 4-[bis(4′-tert-butylbiphenyl-4-yl)amino]-4′-([(6-hydroxy-9,10-dihydro-11,12-dicarbomethoxy-etheno)anthracene-2-yl]oxycarbonyl)azobenzene ***5 AzoDA*** *[27]*

To a solution of 2,6-dihydroxy-9,10-dihydro-11,12-dicarbomethoxy-ethenoanthracene **4** (200 mg, 0.56 mmol) in anhydrous dichloromethane (200 mL) was slowly added a solution of acid **3** (184 mg, 0.28 mmol), dimethylaminopyridinium *p*-toluenesulfonate (DPTS) (26 mg, 0.08 mmol) and diisopropylcarbodiimide (DIPC) (53 mg, 0.42 mmol) dissolved in anhydrous dichloromethane (100 mL). The reaction mixture was allowed to stir at reflux overnight. Concentration under vacuum followed by silica gel column chromatography using petroleum ether/ethyl acetate 7/3 as an eluent, afforded **5** as a deep red solid (65%, 180 mg). T_g 123 °C; UV–vis (toluene), λ_{max} (nm) [ε (mol^{-1} L cm^{-1})]: 474 [22800], 328 [29600]; ^{1}H NMR (400 MHz, CDCl$_3$, TMS): (ppm) = 8.27 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 7.94 (d, ^{3}J(H,H) = 8.7 Hz, 2H), 7.88 (d, ^{3}J(H,H) = 9.1 Hz, 2H), 7.56 (d, ^{3}J(H,H) = 8.2 Hz, 4H), 7.28–7.19 (m, 8H), 6.92 (d, ^{4}J(H,H) = 2.3 Hz, 1H), 6.88 (dd, ^{4}J(H,H) = 2.3 Hz, ^{3}J(H,H) = 7.7 Hz, 1H), 6.45 (dd, ^{4}J(H,H) = 2.3 Hz, ^{3}J(H,H) = 7.7 Hz, 1H), 5.40 (s, 1H), 3.80 (s, 3H, $-CO_2CH_3$), 3.79 (s, 3H, $-CO_2CH_3$), 1.37 (s, 18H; −tBu); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): (ppm) = 166.06, 165.99, 164.97, 156.03, 153.75, 151.19, 150.21, 148.27, 147.52, 147.10, 146.75, 145.95, 145.46, 145.24, 141.28, 137.40, 137.14, 134.92, 131.19, 129.98, 128.03, 126.45, 125.84, 125.77, 124.88, 124.55, 125.35, 122.48, 121.36, 117.98, 117.59, 112.18, 111.30, 52.54, 51.85, 51.56, 34.53, 31.35; HRMS (MALDI-TOF), *m/z* [M$^+$+H]: for $C_{65}H_{57}N_3O_7H$ calculated 992.4275; found 992.4269.

2.3. Experimental techniques

All comparative photoisomerization and holographic photomigration experiments involving **AzoMe** and **AzoDA** were performed on isoabsorbing solutions or thin films to avoid artifact interpretations.

2.3.1. Absorption spectroscopy and kinetic studies

UV–vis absorption spectra in solution and thin films were measured with a Varian spectrophotometer (model Cary 500).

The *E–Z* photoisomerization reaction was induced in toluene solution by means of a continuous white light Hg–Xe source (Hamamatsu, Model LC8) equipped with a quartz optical guide and a narrow bandpass filter at 485 nm, and in thins films by means of a continuous wave argon ion laser working at 488 nm as a pump source. Kinetics of the *Z–E* back thermal relaxation was recorded on samples in the photostationary state, by following the absorbance change at specific wavelengths. Rate constants k_i were determined by modeling the back thermal reaction in fluid solution and thin films with a monoexponential fit $a \times \exp(-kt)$ and a biexponential fit $a_1 \times \exp(-k_1 t) + a_2 \times \exp(-k_2 t)$ respectively.

2.3.2. Holographic setup and refractive index measurements

Holographic inscriptions were carried out on spin-coated thin films by means of a two-arm interferometer setup splitting an Ar$^+$ laser beam working at 488 nm into two coherent beams of equal intensity. Polarization and fluence were varied with regard to the experiments to be performed. Interference gratings were obtained with a spatial period Λ = 1.40 μm in accord with the bissecting incident angle $\theta = 10°$ between both interfering beams following Bragg's diffraction law $\wedge = \lambda/2\sin(\theta)$. Surface relief grating (SRG) height measurements were carried out by using a Veeco Explorer atomic force microscope working in a tapping mode. Formation of SRGs was followed *in situ* by recording the first diffracted order of a low-power He–Ne laser (1.9 mW) working at 632.8 nm by means of a photodiode detector (Ophir – PD300 and PD300 UV heads) (Fig. 1).