Chem. Mater. **2006,** *18,* 1261−1267

Structural and Photoisomerization Cross Studies of Polar Photochromic Monomeric Glasses Forming Surface Relief Gratings

Eléna Ishow,* Bertrand Lebon, Yaning He,† Xiaogong Wang,† Laurent Bouteiller,‡
Laurent Galmiche, and Keitaro Nakatani

ENS Cachan, PPSM UMR CNRS 8531, 61 Av. Pdt Wilson, 94 235 Cachan Cedex, France, Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China, and Laboratoire de Chimie des Polymères, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

Received September 28, 2005. Revised Manuscript Received November 28, 2005

A novel class of photochromic materials based on polar azo derivatives containing functionalized biphenyl substituents has been synthesized. Once melt and cooled, these compounds formed amorphous transparent monomeric materials whose glass transition temperatures depend mainly on the bulkiness of the biphenyl substituent; by contrast, a change in polarity, evidenced by absorption spectroscopy and DFT calculations, exerts insignificant influence. Photoisomerization of the azo groups occurred both in solution and thin films; the rate constants of the thermal back-relaxation in both media increase with compound polarity. Photoconversion yields display smaller values in solid state than in solution, due to more packed surroundings; surprisingly, they increase substantially with the monomer bulkiness, despite raising T_gs. Comparative dynamic surface relief grating writings and AFM surface modulation measurements of irradiated thin films showed that the efficiency of the writing process improves dramatically for glasses consisting of more hindered and less polar compounds with a 4- and 2-fold increase in the diffraction efficiency and peak-to-trough amplitude, respectively. Such results highly contrast with those obtained in polymer matrices, where competitive polymer chain reorganization occurs. Free volume enhancement upon back-and-forth photoisomerization of bulky photochromes, facilitating the azo photoisomerization, has been put forward to explain these results.

Introduction

The simultaneous discovery by two independent research groups of macrosopic photoinduced mass transport into azopolymer matrices[1] has stimulated for a decade tremendous studies on various systems, including polymers,[2] liquid crystals,[3] Langmuir−Blodgett films,[4] electrostatically self-assembled layer-by-layer films,[5] and more recently single crystals[6] as valuable holographic data storage materials. This mass transport has been proved to stem from the diffusion of azo moieties when exposed to an optical field gradient issued from two interfering polarized coherent beams at a wavelength close to their absorption maxima.[7] Repetitive photoisomerization $E-Z$ cycles conduct to a fast birefringence process where photochromes orient perpendicularly to the impinging light polarization plane. Such a fast process is followed by slower migration of the photochromes from the lighted to the dark regions to form time-stable surface relief gratings (SRG). Yet the actual mechanism is still debated.[2a−b,8] The high efficiency of the writing process determined by the measurements of the first-order diffraction intensity of a weak energy probe beam and the peak-to-

---

* To whom correspondence should be addressed. Tel: +33-1-47407660. Fax: +33-1-47402454. E-mail: ishow@ppsm.ens-cachan.fr.

† Tsinghua University.

‡ Université Pierre et Marie Curie.

(1) (a) Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. *Appl. Phys. Lett.* **1995**, *66*, 136−138. (b) Kim, D. Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 8835−8839.

(2) (a) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139−4175. (b) Oliveira, O. N.; Li, L.; Kumar, J.; Tripathy, S. K. In *Photoreactive Organic Thin Films*; Sekkat, Z., Knoll, K., Eds.; Academic Press: San Diego, CA, 2002; pp 429−486. (b) He, Y.; Wang, H.; Tuo, X.; Wang, X. *Opt. Mater.* **2004**, *26*, 89−93. (c) Börger, V.; Kuliskovska, O.; G.-Hubmann, K.; Stumpe, J.; Huber, M.; Menzel, H. *Macromol. Chem. Phys.* **2005**, *206*, 1488−1496. (d) Loppinet, B.; Somma, E.; Vainos, N.; Fytas, G. *J. Am. Chem. Soc.* **125**, *127*, 9678−9679.

(3) (a) Stracke, A.; Wendorff, J. H.; Goldmann, D.; Janietz, D.; Stiller, B. *Adv. Mater.* **2000**, *12*, 282−285. (b) Ubukata, T.; Seki, T.; Ichimura, K. *Adv. Mater.* **2000**, *12*, 1675−1678. (c) Yamamoto, T.; Hasegawa, M.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Mater. Chem.* **2000**, *10*, 337−342. (d) Kim, J. Y.; Kim, T. H.; Kimura, T.; Fukuda, T.; Matsuda, H. *Opt. Mater.* **2002**, *21*, 627−631. (e) Ramanujam, P. S.; Holme, N. C.; Hvilsted, S. *Appl. Phys. Lett.* **1996**, *68*, 1329−1331.

(4) Mendoca, C. R.; Dhanabalan, R.; Balogh, D. T.; Misoguti, L.; dos Santos, D. S.; Pereira-da-Silva, M. A.; Giacometti, J. A.; Zilio, S. C.; Oliveira, O. N. *Macromolecules* **1999**, *32*, 1493−1499.

(5) (a) He, J.-A.; Bian, S.; Li, L.; Kumar, J.; Tripathy, S. K.; Samuelson, L. A. *J. Phys. Chem. B* **2000**, *104*, 10513−10521. (b) Goldenberg, L. M.; Kulikovska, O.; Stumpe, J. *Langmuir* **2005**, *21*, 4794−4796. (c) He, Y.; Wang, H.; Tuo, X.; Deng, W.; Wang, X. *Opt. Mater.* **2004**, *26*, 89−93.

(6) Nakano, H.; Tanino, T.; Shirota, Y. *Appl. Phys. Lett.* **2005**, *87*, 061910−061912.

(7) (a) Dumont, M.; Osman, A. E. *Chem. Phys.* **1999**, *245*, 447−442. (b) Ivanov, M.; Todorov, T.; Nikolova, L.; Yomova, N.; Dragostinova, V. *Appl. Phys. Lett.* **1995**, *66*, 2174−2176. (d) Schönhoff, M.; Mertesdorf, M.; Lösche, M. *J. Phys. Chem.* **1996**, *100*, 7558−7565. (e) Buffeteau, T.; Natansohn, A.; Rochon, P.; Pezolet, M. *Macromolecules* **1996**, *29*, 946−952.

(8) (a) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. *J. Phys. Chem.* **1996**, *100*, 8836−8842. (b) Viswanathan, N. K.; Balasubaramanian, S.; Li, L.; Kumar, J.; Tripathy, S. K. *J. Phys. Chem. B* **1998**, *102*, 6064−6070. (d) Pietsch, U.; Rochon, P. *J. Appl. Phys.* **2003**, *94*, 963−967. (e) Lagugné-Labarthet, F.; Brunel, J. L.; Buffeteau, T.; Sourisseau, C. *J. Phys. Chem. B* **2004**, *108*, 6949−6960. (e) Fiorini, C.; Prudhomme, N.; de Veyrac, G.; Maurin, I.; Raimond, P.; Nunzi, J.-M. *Synth. Met.* **2000**, *115*, 121−125.

10.1021/cm052176b CCC: $33.50

trough depth modulation still represents a major challenge, since many parameters like polarity, molecular weight, glass transition temperature, and viscosity come into play and make the writing optimization rather complex. More recently a novel family of photochromic glassy materials made of small bulky organic molecules, hence called “monomeric” or “molecular” glasses,[9] has deserved attention for SRG studies. Indeed, the structural identity and composition of their molecular components are perfectly controlled in regard to those of the polymeric systems.[10,11] Since the sterically hindered moieties impede considerably tight molecular aggregations, thin films obtained by using the common spin-coating technique show an excellent surface quality with no deleterious scattering effects. In addition, no matrix dilution is required during the deposition process from concentrate solutions; hence, tiny changes of the monomer structure exert deep impact onto the bulk properties.

Following these lines, starburst amorphous molecular materials containing weakly polar aminophenylazo photoisomerizable units have been elaborated and their SRG behaviors compared with those of the corresponding grafted polymers. Studies have revealed noticeable differences between both classes of materials, with molecular glasses responding faster to the writing process and yielding smaller birefringence.[10b−11] Yet comparative experiments reported so far dealt with matrices presenting distinct glass transition temperatures (T_gs) and/or containing different classes of photochromes (Disperse Red 1 (DR1) functionalized polymers vs aminophenylazo-based molecular glasses), which does not bring straightforward conclusions. Surprisingly, whereas numerous SRG experiments have been carried out on polymers functionalized with push−pull azo moieties such as DR1, no studies have dealt yet with monomeric glasses based on strongly polar bulky azo units and tried to evidence SRG formation. Moreover, concomitant photoisomerization in the solid state and SRG writing studies are rarely discussed, although the latter process is mainly driven by the ability of azo derivatives to orient and migrate within the films through multiple photoisomerization cycles. To gain insight into the structural features and molecular interactions ruling the efficiency of the SRG writing process, we want here to report the synthesis of one novel class of asymmetric azobenzene compounds. Their polarity and bulkiness have been systematically varied and their photochromic properties investigated in solution and thin films before undertaking comparative SRG formation studies.

2. Experimental Section

Chemicals and solvents were purchased from Acros or Aldrich and used as received. Spectroscopic grade solvents were utilized for preparing solutions used for spin-casting thin films and photoisomerization experiments. Compounds **4a**,[12] **4b**,[12] and 4-[di-(biphenyl-4-yl)amino]azobenzene (DBAB)[12,13] were synthesized following literature procedures.

Thermal measurements were performed on a Netzsch DSC 204 Phoenix F1 or Universal V2.5H TA Instrument at a 10 K·min^{-1} heating gradient in a dynamic nitrogen atmosphere. Solutions (2 and 8 wt %) of compounds in a 3:2 chloroform:1,1,2,2-tetrachloroethane mixture were prepared for photoisomerization and SRG studies, respectively. Thin films were spin-cast from solutions previously filtered through 0.45 μm pore size Millex membranes (Millipore) onto precleaned 1-mm-thick glass substrate at a 300 rpm rate for 45 s. After drying in vacuo at room temperature for 24 h, the film thickness was measured by utilizing a Dektak 3.0 profilometer and found to be around 0.2 and 0.8 μm for both types of samples.

Photoisomerization kinetics were recorded on two various setups: investigations in stirred 5×10^{-5} mol·L^{-1} toluene solution required use of a continuous wave (cw) argon ion laser working at 488 nm (30 mW·cm^{-2}) as a pump source, while simultaneous probing was performed with a continuous Xe lamp (450 W) and a CCD camera coupled with a spectrometer (Princeton Instruments). Photoisomerization in thin films previously irradiated by a Hamamatsu UV spot light source Xe−Hg lamp equipped with a 460 nm bandpass filter (30 mW·cm^{-2}) and an optical fiber was followed on a Varian Cary 5E spectrophotometer.

Holographic inscriptions were carried out on 0.8-μm thin films using two interfering beams of equal intensity obtained by division by means of a Lloyd mirror of a cw 150 mW·cm^{-2} linearly polarized argon ion laser emitting at 488 nm. Interference gratings of a 0.76 μm spatial period were obtained. First-order diffraction intensity was monitored in real time by means of a low-power He−Ne probe beam operating at 633 nm. Surface-relief amplitudes were evidenced by atomic force microscopy (AFM; Digital Instruments Nanoscope) operating in the tapping mode. Erasure of the written SRGs was performed by means of a 100 mW·cm^{-2} circularly polarized circular Ar$^+$ laser beam.

Full geometry optimization and single-point energy calculations were conducted using density functional theory (DFT) with the correlation functional of Lee, Yang, and Parr (B3LYP)[14] and a 6-31G(d) basis set as implemented in the GAUSSIAN 03W[15] package. Illustrations were obtained with GaussView 3.0.

3. Results and Discussion

Synthesis. Design of the compounds reported below was motivated by the elaboration of polar amorphous monomeric

---

(9) (a) Shirota, Y. *J. Mater. Chem.* **2005**, *15*, 75−93. (b) Kim, M. S.; Maruyama, H.; Kawai, T.; Irie, M. *Chem. Mater.* **2003**, *15*, 4539−4543.

(10) (a) Nakano, H.; Takahashi, T.; Kadota, T.; Shirota, Y. *Adv. Mater.* **2002**, *14*, 1157−1160. (b) Ando, H.; Takahashi, T.; Nakano, H.; Shirota, Y. *Chem. Lett.* **2003**, *32*, 710−711. (c) Ueda, H.; Tanino, T.; Ando, H.; Nakano, H.; Shirota Y. *Chem. Lett.* **2004**, *33*, 1152−1153.

(11) Kim, M.-J.; Seo, E.-M.; Vak, D.; Kim, D.-Y. *Chem. Mater.* **2003**, *15*, 4021−4027.

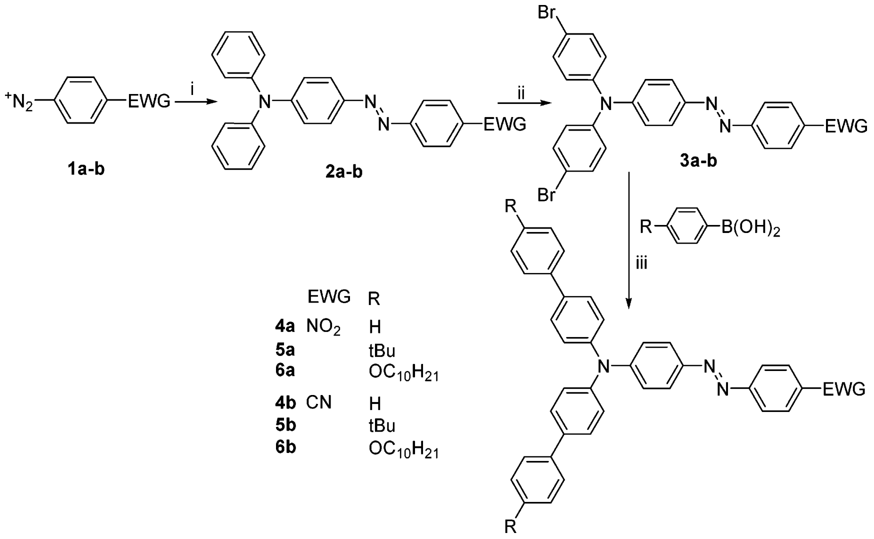
(12) Ishow, E.; Bellaïche, C.; Bouteiller, L.; Delaire, J.; Nakatani, K. *J. Am. Chem. Soc.* **2003**, *125*, 15744−15745.

(13) Shirota, Y.; Morikawi, K.; Yoshikawa, S.; Ujike, T.; Nakano, H. *J. Mater. Chem.* **1998**, *8*, 2579−2581.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.04; Gaussian, Inc., Wallingford CT, 2004.

Scheme 1. General Synthesis of Glass-Forming Asymmetric Azo Derivatives[a]



[a] (i) Triphenylamine, NaDBS, CH_2Cl_2/H_2O, rt, 18 h. (ii) NBS, $CHCl_3$ reflux, 4 h. (iii) $Pd(PPh_3)_4$, 2 mol L^{-1} Na_2CO_3, toluene, MeOH, 70 °C, 24 h.

materials, which entails both the introduction of bulky groups and the creation of strong electronic charge transfer across the N═N bond (Scheme 1). Nitro and cyano units, commonly used in azo-functionalized polymers, were targeted as electron-withdrawing groups. As for the electron-donating and glassy properties, we retained a triphenylamino core functionalized with various electron-donors. All six compounds have been synthesized by reacting the nitro- or cyano-substituted 4-[*N*-bis(4-bromophenyl)amino]-4′-azobenzene compounds with adequate arylboronic acids following a Suzuki cross-coupling reaction with $Pd(PPh_3)_4$ as catalyst.[12] After purification by column chromatography and further recrystallization, compounds were obtained as shiny deep red to violet crystals in 30−80% yield. Electron impact mass spectrometry analyses have highlighted the remarkable stability for all these compounds possessing a fully π-conjugated backbone; only very few fragmentation peaks were actually detected along with the parent molecular peak presenting an unusually high intensity.

Thermal Properties. Thermal gravimetry analyses (TGA) of all compounds show no decomposition up to 270 °C. This noteworthy thermal stability originates from the structural stiffness of the π-conjugated backbone and the thermally robust triphenylamino core.[16] Differential scanning calorimetry analyses evidence the formation of stable glassy phases for the compounds **4** and **5** once melted but not for **6**. Further heating−cooling cycles performed on compounds **4** and **5** induce the appearance of weak endothermic transitions around 76−118 °C, whereas the melting peaks were no longer observed (Table 1). As reported earlier, T_gs increase notably when bulky *tert*-butyl groups are introduced.[13] Contrary to our expectations, grafting flexible decyloxy chains, such as for **6a** and **6b**, did not induce higher disorder; greater chain interactions led instead to melt recrystallization after a few hours. As evidenced in Table 1, the thermal properties of compounds containing the same bulky groups are similar whatever the electron-accepting extremity. This is particularly true for the family of compounds containing only H atoms as substituents, whose glass transition temperatures change from 74 °C (against 68 °C measured by other groups)[13] for the “apolar” compound DBAB to 76 and 85 °C for the nitro **4a** and cyano **4b** derivatives, respectively. We can thus conclude on the absence of strong dipole−dipole interactions in the solid state and dismiss their influence on the photoisomerization process as discussed later. From the dramatic T_g modifications, we can infer that the peripheral biphenyl substituent clearly rules the glassy properties of this class of monomeric materials.

Table 1. Thermal and UV−Vis Absorption Data of Compounds 4 and 5

compd	λ^{max}_{abs} (nm) toluene	λ^{max}_{abs} (nm) film	T_g (°C)	T_m (°C)	μ_{th} (D)
4a	493, 331	509, 334	76	227	9.59
5a	499, 331	509, 333	118	>350	10.43
6a	503, 333	550, 359	29[a]	125	12.49
4b	475, 328	483, 329	85	239	8.77
5b	478, 329	483, 328	117	>350	9.53
6b	482, 330	513, 350	20[a]	112	11.71
DBAB	435, 335	448, 344	74	225	1.75

[a] Thermally unstable.

Films **4**, **5**, and **6** were prepared by spin-coating under the same conditions and their thickness adjusted to 200 nm and 800 nm for photoisomerization and SRG writing experiments, respectively. The use of weakly absorbing thin films ensures uniform excitation throughout the films and permits relevant comparisons with photoisomerization studies performed in toluene solution whose absorbance was similarly adjusted to less than 1. While amorphous films **4** and **5** remain perfectly homogeneous and transparent, films **6** provide opaque and scattering structure within 1 day.

UV−Vis Absorption Characterizations. The absorption spectra of all compounds in toluene solution exhibit two intense bands located in the UV and visible range (Figure 1). The first band appearing around 330 nm undergoes very little change whatever the substituents and has been assigned to a biphenyl-centered $\pi-\pi^*$ transition on photoinduced

---

(16) Prime, R. B.; Chiou, G. Y.; Twieg, R. J. *J. Therm. Anal.* **1996**, *46*, 1133.

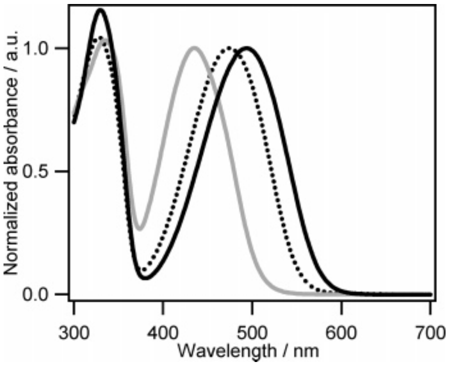


Figure 1. Normalized UV−vis absorption spectra of compounds **4a** (black line), **4b** (dotted line), and DBAB (gray line) in toluene solution.

linear dichroism experimental basis. The second band in the visible corresponds to a $\pi-\pi^*$ azo-based charge transfer transition. Its absorption maximum is dramatically red-shifted according to an increase in the charge transfer from the electron-donating biphenyl substituents to the electron-withdrawing moieties (from 478 nm for DBAB to 503 nm for **6a**), as revealed also by DFT computations of the dipole moment ($OC_{10}H_{21}$ > tBu > H) (Table 1). Identity of the charge transfer has been confirmed by DFT computations: the HOMO electronic density is mainly spread over the triphenylamino core and the biphenyl substituents, while the LUMO one is located on the electron-withdrawing nitro or cyano groups with contribution from the N═N bridge (Figure 2). A 10-nm red shift of the charge transfer energy occurs systematically for the spin-cast films **4a,b** and **5a,b**, which lies in slightly more polar molecular environments in the solid state and not in aggregation effects. By contrast, crystallized thin films made of **6a** and **6b** display a more pronounced bathochromic shift of their absorption maximum; following previous studies on polar azo-based liquid crystalline polymers, the formation of J-aggregates owing to strong head-to-tail intermolecular stacking has been suggested.[17]

Photoisomerization Studies in Solution and Thin Films. Photoisomerization studies were carried out by irradiating solutions or thin films in their charge transfer band, namely at 488 and 462 nm, while identical excitation intensities were kept. The course of the reaction during and after stopping illumination was followed while evolution of the maximal absorbance was recorded as a function of time.

Kinetics of the thermal *Z*−*E* back-photoisomerization for all compounds in solution after reaching the photostationary state was successfully modeled by a monoexponential law, $a\ \exp(-kt)$, in agreement with reactions occurring in constraint-free and isotropic media (the terms a and k are related to the minimum photoconversion yield and rate constant of the reaction, respectively). Unlike DBAB, which reverts thermally to its *E* form with a rate constant around 3.2×10^{-5} s^{-1}, all the photoirradiated compounds **4**−**6** relax much faster with rate constants ranging from 10^{-4} to 10^{-3} s^{-1} (Table 2). Rate constants were found to be invariably larger for the nitro compounds **4a**−**6a** than for the cyano ones **4b**−**6b**. This trend perfectly agrees with the well-documented polarity effects causing a speeding up of the thermal back-relaxation when azo compounds exhibit strong internal charge transfer or are placed in polar media.[18]

Table 2. Kinetics Data of the Thermal *Z*−*E* Back-Relaxation of 4a−c and 5a−c in Toluene Solution and Thin Films

	solution^{a,c}		thin film^{b,d}				
compd	k (10^{-3} s^{-1})^{c}	ρ_{min} (%)	k_1 (10^{-3} s^{-1})^{d}	f_1	k_2 (10^{-4} s^{-1})^{d}	f_2	ρ_{min} (%)
4a	0.76	40	1.4	0.5	1.2	0.5	6
5a	1.53	40	2.2	0.5	1.8	0.5	8
6a	1.89	37	−	−	−	−	−
4b	0.24	46	0.45	0.2	0.66	0.8	18
5b	0.30	43	0.62	0.3	0.95	0.7	23
6b	0.40	49	−	−	−	−	−
DBAB	0.037	54	0.08	0.33	0.16	0.66	31

[a] 5×10^{-5} mol·L^{-1} solution. [b] 200-nm-thick films. [c] First-order kinetics of the thermal *Z*−*E* back-relaxation from the photostationary state generated by irradiation at 488 nm. [d] First-order kinetics of the thermal *Z*−*E* back-relaxation from the photostationary state generated by irradiation at 460 nm.

When extended to photoirradiated thin films, the fit of the experimental thermal back-photoisomerization process requires use of a double exponential model to account for inhomogeneous free volume distribution, as already reported for polymer and monomeric matrices.[19] We found no additional improvement when applying the Kohlrausch−William−Watt stretched exponential law. Except for the decyloxy-substituted azo derivatives **6a** and **6b**, whose film crystallization precludes any accurate kinetics studies, rate constants of the fast and slow components for all compounds **4** and **5** were found to be around 10^{-3} and 10^{-4} s^{-1} in a ratio close to unity. Again, both relaxation rates were found to be larger for nitro thin films **4a** and **5a** with regard to the cyano ones **4b** and **5b**. Surprisingly, the fast process for all compounds occurs around twice as fast as in solution. Whereas strained conformations of Z-isomers trapped upon irradiation are usually put forward to interpret this fast component,[17,19] the influence of polar surroundings in the solid state, known to accelerate the thermal *Z*→*E* relaxation, could also be involved. Yet this latter argument has to be ruled out, since we observed no real enhancement of the rate constants for the nitro compounds relative to those of the cyano compounds when going from apolar toluene solution to polar monomeric glasses. Steric constraints in the solid state seem then mainly responsible for the fast relaxation process.

As for the compound photoconversion quantum yields, their accurate determination would require strenuous calculations because of strongly overlapping absorption spectra of both the *E* and *Z* photoisomers. Thus, a rough estimation of the minimum photoconversion yield (ρ_{min}) consists of assuming no absorption from the *Z* photogenerated isomers at the *E* form absorption maximum and measuring the absorbance depletion of this maximum once the photostationary state is reached. If we are looking into the evolution of the ρ_{min} as a function of glass polarity and rigidity, three main features can be stressed:

---

(17) Zebger, I.; Rutloh, M.; Hoffmann, U.; Stumpe, J.; Siesler, H. W.; Hvilsted, S. *J. Phys. Chem. A* **2002**, *106*, 3454−3462.

(18) Wildes, P. D.; Pacifici, J. G.; Irick, G.; Whitten, G. G., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 2004−2008.

(19) (a) Mita, I.; Horie, K.; Hirao, K. *Macromolecules* **1989**, *22*, 558−563. (b) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729−1736.

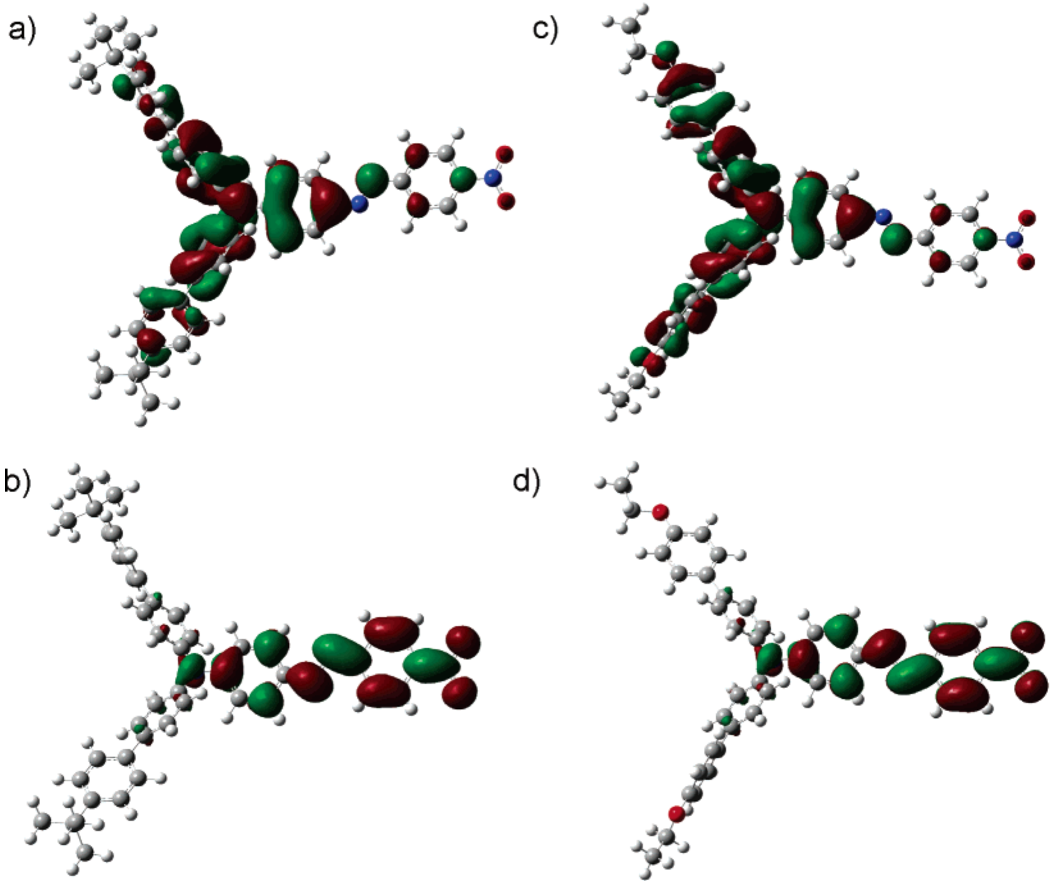


Figure 2. DFT-computed molecular frontiers orbitals: (a) HOMO and (b) LUMO of **5a** and (c) HOMO and (d) LUMO of the diethyloxy analogue of **6a** as a model compound.

(1) Photoirradiation of thin films provides lower photoconversion (6−31%) than in solution (37−54%), which agrees with the greater steric constraints encountered in the solid state as emphasized previously.

(2) The $\rho_{\min}$ values show strong dependence on polarity, the more polar compounds **4a**, **5a**, and **6a** leading to the lesser $\rho_{\min}$ in thin films and solution. This result contrasts with what has been reported for polymer matrices containing polar azo compounds. Indeed, when donor−acceptor azobenzenes, referred to "pseudostilbenes" following Rau's classification for their strongly overlapping weak n−π* and intense π−π* transitions,[20] are subjected to visible irradiation, both the *E*−*Z* and *Z*−*E* photoconversions are activated. The dyes undergo numerous photoisomerization cycles, which allow the whole photoisomerization process in polymer films to work more efficiently and at higher speed. Polar azo monomeric glasses react clearly in the opposite way: their polar azo constituents do not accumulate in the *Z* state and revert back efficiently not only photochemically but also thermally during the pumping process. The thermal *Z*−*E* back-relaxation, whose rate has been found to increase with polarity, appears then to compete notably with the *E*−*Z* photoisomerization.

(3) Finally, thin films **5**, exhibiting higher T_g, present significantly enhanced $\rho_{\min}$ values compared with films of lower T_g made of H-substituted **4**. It has been long known that the higher the T_g of polymer matrices, namely the higher the viscosity, the lower the photoisomerization efficiency. This is even truer as soon as the process requires significant changes in the photochrome geometry. Free volume around the chromophores is then sorely needed for the photoisomerization process to take place. In compounds **5**, the presence of bulky *tert*-butyl moieties creates a large free volume around each photochrome. During the multiple back-and-forth pumping cycles, the more compact *Z* forms of **5** may induce a substantial increase in free volume, which would plasticize progressively the whole irradiated glass and allow molecules to photoisomerize to a larger extent. Such matrix softening and free volume increase following photoirradiation of push−pull azo-based polymers have been recently highlighted through mechanical and refractive index change measurements.[21] Here again, photochromic monomeric glasses behave differently from photoactive polymers, which is likely due to the absence of competitive entangled chain reorganization. Such an assumption has to be related to recent studies performed on self-assembled azo-functionalized self-assembled monolayers reporting considerable enhancement of the photoisomerization reactions when bulky carboranes, creating substantial free volume, were grafted to the monolayers.[22]

---

(20) (a) Rau, H. In *Photoreactive Organic Thin Films*; Sekkat, Z., Knoll, K., Eds.; Academic Press: San Diego, CA, 2002; pp 3−38. (b) Dürr, H.; Bouas-Laurent, H. In *Photochromism, Molecules and Systems*; Elsevier: Amsterdam, 1990.

(21) Mechau, N.; Saphiannikova, M.; Neher, D. *Macromolecules* **2005**, *38*, 3894−3902.

(22) Ito, M.; Wei, T. X.; Chen, P.-L.; Akiyama, H.; Matsumoto, M.; Tamada, K.; Yamamoto, Y. *J. Chem. Mater.* **2005**, *15*, 478−483.

Table 3. SRG Characteristics of Illuminated Thin Films

thin film[a]	modulation of height (nm)	diffraction efficiency η (%)
4a	42	0.9
5a	95	3.1
4b	53	2.4
5b	174	10.8

[a] 0.8-μm-thick films.

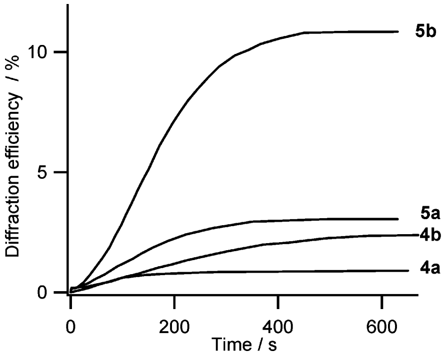


Figure 3. Diffraction efficiency for the SRG writing with a 0.76-μm period on 0.8-μm-thick films of **4a,b** and **5a,b**.

In conclusion, these photochemical studies point out the considerable influence of the free volume and thermal relaxation on the photoisomerization reaction efficiency and help us better understand the results obtained from comparative SRG writing experiments performed on films **4** and **5**.

Surface Relief Gratings Experiments. Exposure of films **4** and **5** to a light pattern generated by two interfering linearly p-polarized Ar^+ beams gave time-stable relief structures. Peak-to-trough modulation has been characterized by atomic force microscopy (AFM), while SRG formation kinetics has been monitored by measuring the first-order diffracted light of a low-energy He−Ne probe laser. The height amplitude was seen to depend significantly on the investigated compound and could reach 174 nm for **5b**. When s-polarized beams were used instead, it hardly reached 2.6 nm for the same compound. Diffraction efficiency (η), defined as I/I_0 (where I and I_0 are the intensity scattered along the first scattering maximum and the primary beam intensity, respectively), saturated after 10 min only. It is worth noting that neither a drop nor a jump of η has been observed right after having stopped irradiation, contrary to prior studies carried out on aminophenylazo-based monomeric glasses.[10a,23] From the η and surface modulation depth measurements gathered in Table 3, we have detected two distinct trends that can be related again to the polarity and bulkiness of the molecular compounds. As a matter of fact, cyano films **4b** and **5b** react more efficiently to the SRG writing process than their nitro analogues **4a** and **5a** (Figure 3); furthermore, compared to films **4**, SRG inscribed on *tert*-butyl-functionalized films **5** display a 4- and 2-fold increase in η and surface modulation depth, respectively (Table 3 and Figure 4). These comparative studies illustrate once more the peculiar role played by the *tert*-butyl groups, whose bulkiness and related induced free volume are seemingly responsible for such an efficient SRG formation despite a 30−40 °C increase in the glass transition temperature. Shirota et al. have already noticed that constricted "apolar" azo molecules such as 4-[bis(9,9-dimethylfluorenyl)amino]azobenzene, which form amorphous molecular materials with T_g around 97 °C, could generate SRGs with larger height modulation and diffraction efficiency than those obtained with less hindered DBAB characterized by lower T_g.[23] All these results highly contrast with most of the studies dealing with azo-functionalized polymers, which have reported that high T_gs inhibit efficient SRG formation.[24] Monomeric glasses react in a very specific way, since photoinduced motions (rotation and translation) of the dyes no longer entail the polymeric chain traction by the dye diffusing throughout the matrix. Indeed, when compared to polymers containing similar side-chain chromophores, monomeric glasses have been shown to react faster to illumination, with saturation of the diffraction efficiency reached within 20 min under similar illumination conditions.[11] The large excitation probability permitted by a high chromophore density along with the large free volume created during the multiple back-and-forth $Z-E$ photoisomerization cycles, may explain the fairly fast writing process: molecules can move across the film and "pile up" in dark regions without competing with the entangled polymer chain relaxation.[25]

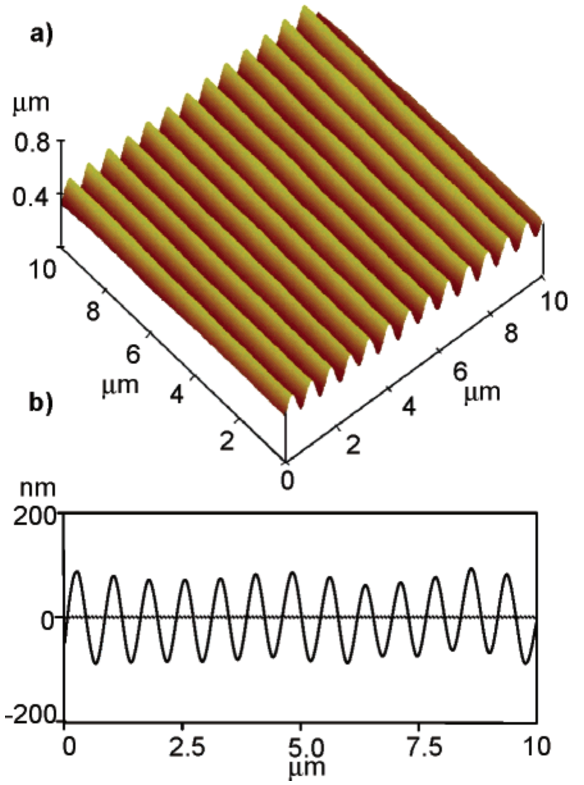


Figure 4. AFM surface imaging of SRG written in a 0.8-μm-thick amorphous thin film of **5b** with p-polarized Ar^+ interfering beams: (a) 3D topography and (b) amplitude modulation profile.

As for the decrease in SRG writing efficiency with monomer polarity, which has already been reported in epoxy-based polymer matrix,[26] thermal spatial diffusion of the Z

---

[23] Shirota, Y.; Utsumi, H.; Ujike, T.; Yokishawa, S.; Morikawi, K.; Nagaham, D.; Nakano, H. *Opt. Mater.* **2002**, *21*, 249−254.

[24] Srikhirin, T.; Latschitsch, A.; Neher, D.; Johannsmann, D. *Appl. Phys. Lett.* **2000**, *77*, 963−965.

[25] Fritz, A.; Schönhals, A.; Sapich, B.; Stumpe, J. *Macromol. Chem. Phys.* **1999**, *200*, 2213−2220.

[26] He, Y.; Wang, X.; Zhou, Q. *Polymer* **2002**, *43*, 7325−7333.

photoisomers seems necessary for the grating to be formed efficiently. In our systems, quick back-and-forth photoinduced isomerization appears to impede time-demanding cooperative molecular rearrangements, since displacement of one molecule entails that of the neighboring ones. Long-living *Z* isomers may then favor such molecular reorganization. Moreover Dumont and al. have reported that strong push−pull azo compounds such as DR1, **4a**, **5a**, or **6a**, undergoing high photocycling between their *E* and *Z* forms, achieve a high photoalignment perpendicularly to the polarization direction of the optical field.[27] Such perpendicular photoorientation. known as the Weigert effect. freezes the molecular dipole moments in a configuration where no absorption is further enabled. Hence azo molecules cannot migrate further under light excitation, reducing the SRG writing efficiency, which requires large bulk mass transport. It appears then that large molecular photoorientation permitted by more polar structures such as **4a** and **5a** disfavors the azo migration needed for SRG formation.

Finally, surface generation and the rewriting process have been successfully tested on SRG formed from films **5b**. Irradiation of the modulated surface by means of a circularly polarized Ar^+ beam for about 10 min led to the complete erasure of the SRG, which has been rewritten further with the same efficiency and amplitude modulation by projecting again the same initial interfering light pattern.[28]

In summary, a series of polar photochromic azo derivatives containing bulky groups has been easily elaborated following a building-block synthetic strategy. They provide transparent monomeric glasses whose T_gs, varying from 74 to 118 °C, were mainly ruled by the peripheral bulky groups with no influence from the compound polarity. All compounds underwent photoisomerization reaction in solution and thin films as well, to a lesser extent though in the solid state because of a more constrained environment. Thermal *Z*−*E* back-relaxation in solution and thin films obeys monoexponential and biexponential kinetics, respectively, with rate constants increasing dramatically with polarity. Photoconversion in solid state was found to be larger for monomeric glasses made of less polar and bulkier compounds, albeit presenting higher T_gs. Accordingly, surface relief gratings were more successfully written in this kind of glasses. Such striking results have been explained through the large free volume induced by the presence of *tert*-butyl groups and the slow thermal back-relaxation of less polar azo compounds, leading in turn to a high photoconversion yield and consequently high SRG writing efficiency. The combined photoisomerization and SRG studies performed on photochromic monomeric glasses clearly point out the insufficiency of comparative descriptions based only on macroscopic properties such as T_g when intending to design more efficient SRG-forming materials. This work tries to highlight that SRG formation is essentially driven by the presence of a large free volume surrounding the azo moieties, which can be easily created by grafting peripheral bulky groups in vicinity of the azobenzene core. SRG thermal treatments as well as the elaboration and study of composite monomeric matrices where the load of azo photochromes is systematically varied by adding inactive glass-forming molecules of distinct T_gs are currently under investigations to draw guidelines in terms of polarity and bulkiness for the engineering of efficient SRG-forming materials.

Acknowledgment. Rebecca Martin is thanked for the preliminary photophysical experiments performed in the framework of the American student exchange REU program. K. Leblanc and F. Perez running the mass spectrometry facilities at ICMO-Paris Sud University (France) and Netszch expertise laboratory (Selb/Germany) are gratefully thanked for providing mass spectrometry and thermal analyses (DSC 204 Phoenix F1), respectively.

Supporting Information Available: Experimental procedures for compounds **4a,b**, **5a,b**, and **6a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

CM052176B

---

(27) Sekkat, Z.; Dumont, M. *Appl. Phys. B* **1992**, *54*, 486−489. (b) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817−1845.

(28) Lagugné-Labarthet, F.; Buffeteau, T.; Sourisseau, C. *Phys. Chem. Chem. Phys.* **2004**, *4*, 4020−4029.